

IMPACT OF HARMONICS ON COMMUNICATIONS SYSTEMS AND CIRCUITS

O.D. Osunde

*Department of Electrical/Electronics Engineering, University of Lagos, Akoka, Yaba, Lagos.
osundave2@yahoo.com, dosunde@unilag.edu.ng*

ABSTRACT

Harmonics is an unwanted frequency signal that distorts supply waveforms of current and voltages thereby causing interference of connected systems. The impact of the harmonics produced by the asymmetrical drive connected to Communications circuits and Traction systems is presented. The drive was characterized into four distinct intervals of operations and explicit expressions of input current supply to the drive were obtained for the various intervals using the piece – wise linear (PWL) analysis approximation method. Fourier intergral analysis was carried out on the ac currents to derive the harmonics spectrum for the different firing angles of the drive. The composite spectrum demonstrates the range of frequency that has significant harmonics level that can interfere with the performance of communications systems and circuits.

***Keywords:** Harmonics, Drive, Traction Systems, PWL, Fourier Analysis*

INTRODUCTION

Most equipment connected to an electricity distribution network usually may need controlled power conversion equipment which produces a non - sinusoidal line current due to the nonlinear load. With such loads as RLC, the switching action of the devices makes the system non- linear. Also, with the steadily increasing use of such equipment, line current harmonics have become a significant problem. Their adverse effects on the power system are well recognized. Harmonics are unwanted frequency components, which arise from the use of semi-conductor controllers. Modern industries and applications which include the steel plants, traction systems, industrial drives, furnaces etc generate voltage and current harmonics which have adverse effects on the supply lines and equipment connected to such lines. The harmonics generated according to Okoro [1] and Redl[2] result in distortion of line voltages, degradation of power factor of electrical equipment thereby increasing the reactive power consumption and also overall running cost of equipment. The overall effects are reduced efficiency, increased heating effect and lead to Poor Power Factor on the AC inputs of the industrial drives. Also, voltage distortion produces such effects as motor prematurely burning out due to overheating, increased losses and lower efficiency.

It is to be noted that the presence of harmonics in the supply waveforms has other wide-ranging effects on the supply system. These include:

- Communication system interference.
- Degradation of equipment performance and effective life
- Sudden equipment failure
- Protective system mal-operation
- Increased power transmission losses
- Overheating in transformer, shunt capacitor, power cables, AC machines and switchgear leading to pre-mature ageing

Harmonics result in distortion of line voltages and currents, degradation of power factor of electrical equipment thereby increasing the reactive power consumption and also overall running cost of equipment

The major concern in this work is the effects of harmonics on communication systems interference operating within a certain range of frequency [5]. To demonstrate this, a study of the single phase AC – DC drive has been conducted [3 - 5]

METHODS

A complete characterization of the Single – Phase AC – DC drive carried out by Osunde [4–5] examines four different modes of operations of the drive presented in Fig. 1. Explicit expressions of the ac input current were obtained by analyzing the half cycle equivalent circuit of the drive of Fig. 1 for the different intervals [5] by assuming that the terminal condition of one interval are the initial condition of the next interval.

Analytical Results

Results of the analysis of the ac input current obtained in [3-5] is as stated;

In the conduction interval, $\alpha < \omega t < \alpha + \mu$

With initial condition $i = 0$ at $\omega t = 0$, the current in this interval is given by:

$$I_{ao} = K_1 \left\{ \sin(\omega t + \alpha - \theta_1) + \sin(\theta_1 - \alpha) \exp\left(\frac{-u}{\omega \tau_1}\right) \right\} \quad (1)$$

The conduction interval ($\alpha + \mu < \omega t < \pi$) current flows in the path shown in Fig. 1 and the ac input current in this interval is;

$$i(t) = k_2 [\cos \theta_2 \sin(\omega t + \alpha + \mu - \theta_2) - P] + [k_2 (\cos \theta_2 \sin(\theta_2 - \alpha - \mu) + P) + I_{ao}] e^{-\frac{t}{\tau}} \quad (2)$$

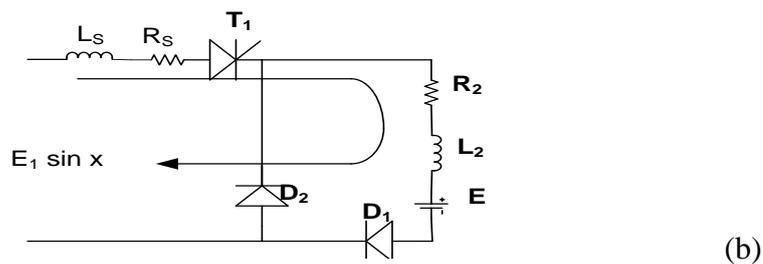
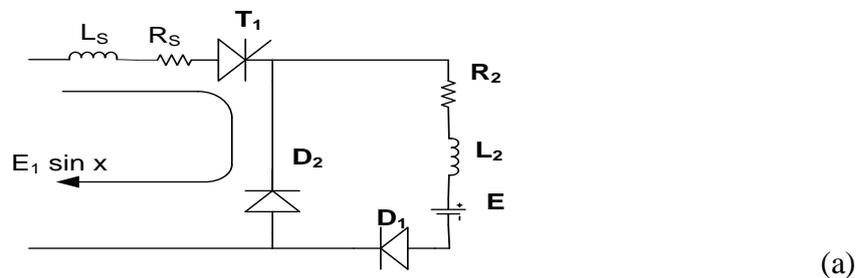
Next is the free wheeling interval $\pi < \omega t < \alpha$

The current expression is given as;

$$I_1 = k_2 [\cos \theta_2 \sin \theta_2 - p] + [k_2 (\cos \theta_2 \sin(\theta_2 - \alpha) + p) + I_{ao}] e^{-\frac{(\pi - \alpha - \mu)}{\omega \tau}} \quad (3)$$

At the end of the extinction interval, $\pi + \beta < x < \pi + \beta + x_s$

$$i(t) = -\frac{E_s}{z} \sin(\omega t + \beta - \theta_1) - \left[\frac{E_s}{z} \sin(\theta_1 - \beta) - I_\beta \right] e^{-\frac{t}{z}} \quad (4)$$



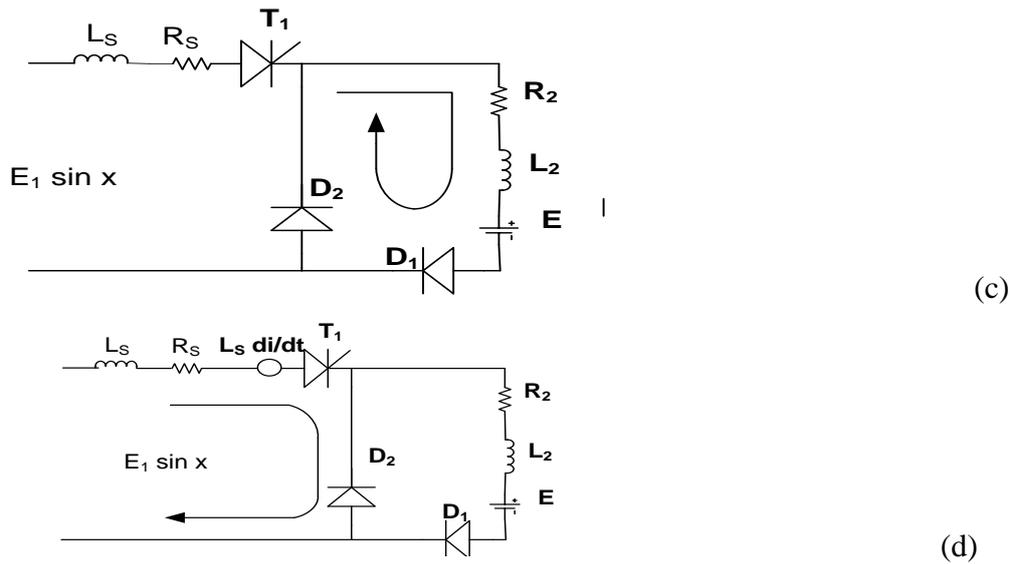


Fig. 1: Bridge Converter with half Cycle Equivalent Circuits showing path of current during different intervals

- (a) Forward Commutation Interval, $\alpha < x < \alpha + \mu$
- (b) Thyristor Conduction Interval $\alpha + \mu < x < \pi$
- (c) Freewheeling Interval $0 < x < \alpha$
- (d) Reverse Commutation Interval or Extinction Interval $\pi + \beta < x < \pi + \beta + x_s$

The equations of currents for the different intervals equations 1 - 4 put together give the total ac input current to the drive.

Analysis of the Harmonics produced by the controller

The harmonic spectrum of the motor input current is obtained from Fourier analysis of the explicit expressions for the armature current over a period of the waveform such that;

$$i(x) = \sum_{n=2}^{\infty} (A_n \cos nx + B_n \sin nx) \tag{5}$$

The coefficients A_n and B_n are obtained as

$$A_n = \frac{1}{T} \int_0^T i(x) \cos nx dx \tag{6}$$

$$B_n = \frac{1}{T} \int_0^T i(x) \sin nx dx \tag{7}$$

T is the period.

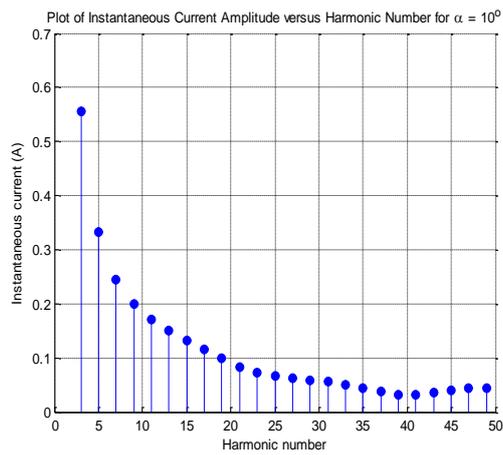
Where A_n and B_m are the harmonic components. Harmonic components as derived in [5] for the different interval of operation is;

$$A_n = \frac{1}{\pi} \left[\begin{aligned} & \frac{k_3}{n+1} [\cos((n+1)(\alpha+u)-\theta_2) - (-1)^{n+1} \cos \theta_2] \\ & - \frac{k_3}{n-1} [\cos((n-1)(\alpha+u)+\theta_2) - (-1)^{n-1} \cos \theta_2] \\ & + 2 \left(\frac{A_6 \sin n(\alpha+u) - A_5 \sin n\alpha}{n} \right) \\ & + \frac{2k_6 \omega \tau}{1+(n\omega\tau)^2} \left[\cos n(\alpha+u) - n\omega\tau \sin n(\alpha+u) - (-1)^n e^{-\left(\frac{\pi-\alpha-u}{\omega\tau}\right)} \right] \\ & + \frac{2(I_1 + A_5)\omega\tau_2}{1+(n\omega\tau_2)^2} \left(1 + e^{-\frac{\alpha}{\omega\tau_2}} (n\omega\tau_2 \sin n\alpha - \cos n\alpha) \right) \\ & + \frac{k_1}{n+1} (\cos((n+1)\alpha - \theta_1) - \cos((n+1)(\alpha+u) - \theta_1)) \\ & - \frac{k_1}{n-1} (\cos((n-1)\alpha + \theta_1) - \cos((n-1)(\alpha+u) + \theta_1)) \\ & + \frac{2k_1 \sin(\theta_1 - \alpha)\omega\tau_1}{1+(n\omega\tau_1)^2} \left(e^{-\frac{u}{\omega\tau_1}} (n\omega\tau_1 \sin n(\alpha+u) - \cos n(\alpha+u)) + \cos n\alpha \right. \\ & \left. - n\omega\tau_1 \sin n\alpha \right) \end{aligned} \right] \quad (8)$$

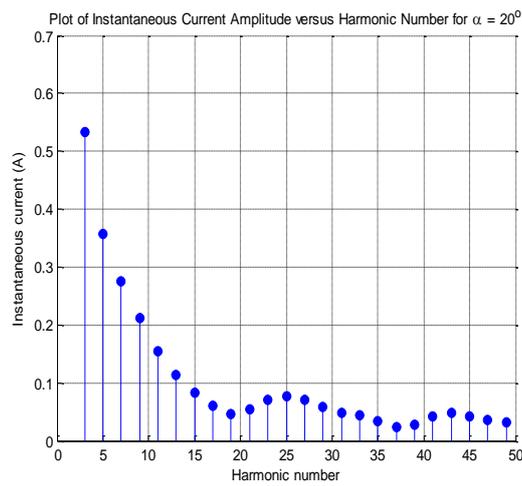
$$B_n = \frac{1}{\pi} \left[\begin{aligned} & \frac{k_3}{n+1} [\sin((n+1)(\alpha+u)-\theta_2) + (-1)^{n+1} \sin \theta_2] \\ & - \frac{k_3}{n-1} [\sin((n-1)(\alpha+u)+\theta_2) - (-1)^{n-1} \sin \theta_2] \\ & + \frac{2}{n} (A_6((-1)^n - \cos n(\alpha+u)) - A_5(1 - \cos n\alpha)) \\ & + \frac{2k_6 \omega \tau}{1+(n\omega\tau)^2} \left[n\omega\tau \cos n(\alpha+u) - n\omega\tau(-1)^n e^{-\left(\frac{\pi-\alpha-u}{\omega\tau}\right)} + \sin n(\alpha+u) \right] \\ & + \frac{2(I_1 + A_5)\omega\tau_2}{1+(n\omega\tau_2)^2} \left(n\omega\tau_2 - e^{-\frac{\alpha}{\omega\tau_2}} (n\omega\tau_2 \cos n\alpha + \sin n\alpha) \right) \\ & + \frac{k_1}{n-1} (\sin((n-1)(\alpha+u)+\theta_1) - \sin((n-1)\alpha + \theta_1)) \\ & - \frac{k_1}{n+1} (\sin((n+1)(\alpha+u)-\theta_1) - \sin((n+1)\alpha - \theta_1)) \\ & + \frac{2k_1 \sin(\theta_1 - \alpha)\omega\tau_1}{1+(n\omega\tau_1)^2} \left(n\omega\tau_1 \cos n\alpha + \sin n\alpha \right. \\ & \left. - e^{-\frac{u}{\omega\tau_1}} (n\omega\tau_1 \cos n(\alpha+u) + \sin n(\alpha+u)) \right) \end{aligned} \right] \quad (9)$$

The next section shows the harmonic spectrum obtained by simulating the harmonic components A_n and B_n of equations (8) and (9) respectively.

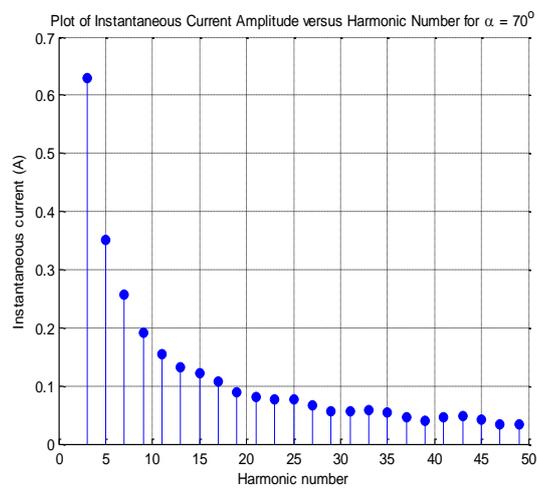
Harmonic Spectrum results



(a): Harmonics Spectrum of the controller at a Firing angle ' α '= 10°



(b): Harmonics Spectrum of the controller at a Firing angle ' α '= 20°



(c): Harmonics Spectrum of the controller at a Firing angle ' α '= 70°

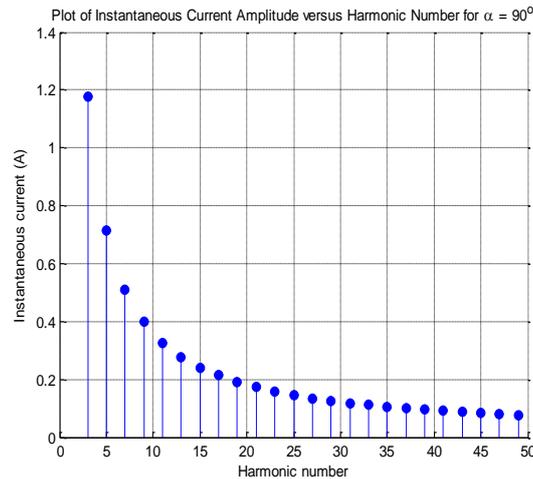
(d): Harmonics Spectrum of the controller at a Firing angle ' α ' = 90°

Fig.2: (a-d): Harmonics Spectrum of the controller at different Firing angles

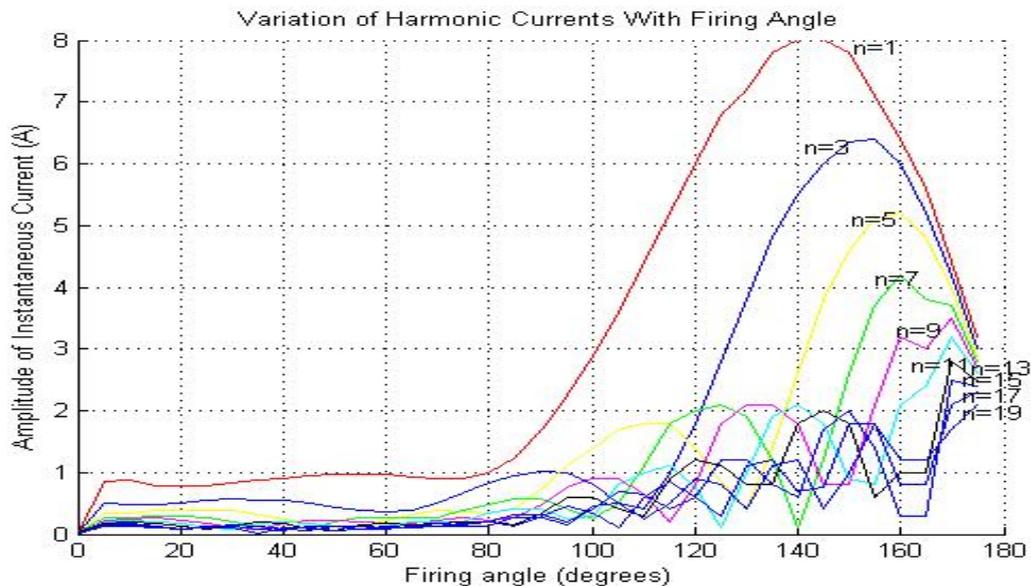


Fig. 3: Variation of Harmonic Current with Firing Angle

DISCUSSION OF RESULTS

The variation of the harmonic spectrum of the input current with the harmonic number is displayed for increasing firing angles of the drive in Fig. 2. From this figure, it is obvious that the magnitude of the current harmonic content and hence the amount of distortion produced by the drive is high at the 3rd and 5th harmonics whereas, it is considerably reduced at a higher harmonic number. A similar deduction [6] can be interpreted from figure 3 where a very high harmonic content is present in the input supply current when the drive is operated between 120 to 170 degrees at a frequency range of 150 – 650Hz.

CONCLUSION

The implication of this work is that, communication equipment and circuits operating within this range of frequencies (150Hz – 650Hz) will be adversely affected at such significant harmonic

levels resulting in distortions and interference of communication systems. Also, signalling in traction systems. can be affected by such a significant level of supply input current harmonics

REFERENCES

1. Okoro, C .C (1982) “Performance Evalution of a DC motor fed from an asymmetrical Single – Phase Bridge” Proceedings IEE, vol. 129, PTB No. 5
2. Redl R. (1994). Power factor correction in single – phase switching –mode power supplies – an overview”. Int. J. Electronics, vol. 77, No.5. 555-582.
3. Okoro, C.C and Osunde, O.D (2007) “The input power factor problem for industrial drives” Proceedings of International Conference and Exhibition on power system Lagos, Nigeria
4. Osunde, O.D, Okoro, C.C and Awosope C.O.A, (2011) “Characterisation of an Asymmetrical Single – Phase DC machine drive” proceedings of the 3rd IEEE International Conference on Adaptive Science and Technology ICAST 2011” Abuja, Nigeria
5. Osunde, O.D (2010) “Input Power Factor problem and Correction for Industrual Drives” Ph.D thesis of the University of Lagos, Nigeria.
6. Sen P.C. (1991). Thyristorised DC Drives. John Wiley and Sons Inc. 1st Edition. Florida. Krieger Publishing Company.

EXTINCTION ANGLE CONTROL (EAC) AN ACTIVE METHOD FOR POWER FACTOR CORRECTION IN INDUSTRIAL DRIVE

Osunde, O.D

Department of Electrical/Electronics Engineering
Faculty of Engineering, University of Lagos, Lagos, Nigeria
Email: osundave2@yahoo.com; dosunde@unilag.edu.ng

ABSTRACT

Equipment connected to an electricity distribution network usually needs some kind of power conditioning, typically rectification, which produces a non - sinusoidal line current due to the nonlinear input characteristics. With the steadily increasing use of such equipment, line current harmonics have become a significant problem. Harmonics are unwanted frequency components, which arise from the use of semi-conductor controllers. Modern industries and applications such as the steel plants, traction systems, industrial drives, furnace heating, Aluminum smelting etc generate voltage and current harmonics which have adverse effects on equipment designed for operation with sinusoidal waveforms. The harmonics generated results in distortion of line voltages, degradation of power factor of electrical equipment thereby increasing the reactive power consumption and also overall running cost of equipment. In this presentation, the single – phase AC – DC drive which produces a high input current harmonics and a low power factor is employed in the study. EAC provides control of the gating signals of the drive and a detailed mathematical analysis of the behavior factors – Harmonic factor (HF), Displacement (DF) and the Power factor of the drive. Simulation and laboratory experimentation demonstrates an improved power factor (PF)

Keywords: Harmonics Power Factor (PF) Displacement Factor (DF) Harmonic Factor (HF) Drives

INTRODUCTION

There have been many reported problems associated with harmonics within an industrial plant [1-4] and a high input current harmonics have been established to exist in ac supply to drives [5-6] resulting to a low input power factor. It is to be noted that the presence of harmonics in the supply waveforms have a wide-ranging effects on the supply system. These include: Communication system interference. Degradation of equipment performance and effective life Sudden equipment failure\Protective system mal-operation\Increased power transmission losses Overheating in transformer, shunt capacitor, power cables, AC machines and switchgear leading to pre-mature ageing and poor power factor. Many research efforts aimed at improving poor power factor problem have been made in the past by various researchers [7-9] and a lot of study is still on going.

In this work, the extinction angle (EAC) control technique aimed at improving the poor power factor of industrial drives is being investigated. The research gives a description of the circuit topology and a mathematical analysis of the control technique. Results of simulation and laboratory experiment shows an improved power factor close to unity.

Circuit Topology

The drive circuit and its associated waveforms of input currents and voltages is displayed in Figs. A and B. In the single- phase ac – dc drive shown in Fig. A, the thyristors T_1 and T_2 have being replaced by switches S_1 and S_2 . The switching actions of S_1 and S_2 can be performed by gate turn-off thyristor (GTO's). The characteristics of GTO's are such that a GTO can be turned - on by applying a short – positive pulse to its gate as in the case of normal thyristors and can be

turned – off by applying a short negative pulse to its gate. The fundamental component i_1 of the supply current ‘i’ leads the supply voltage.

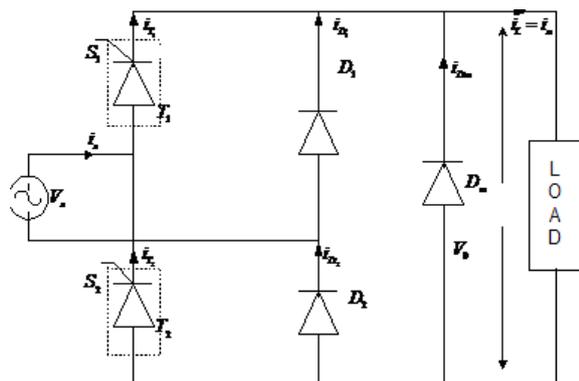


Fig. A: Circuit layout

METHODS

Operation

In an extinction angle control, switch S_1 is turned on at $\omega t = 0$ and turned off by forced commutation at $\omega t = \beta$. Switch S_2 is turned on at $\omega t = \pi$ and is turned off at $\omega t = (\pi + \beta)$. The output voltage is controlled by the extinction angle β . The waveforms for voltage and current through the switches are shown in Fig. B.

Analysis

The average output current is

$$V_{dc} = \frac{1}{\pi} \int_0^{\pi} V_m \sin \omega t d(\omega t) \tag{1}$$

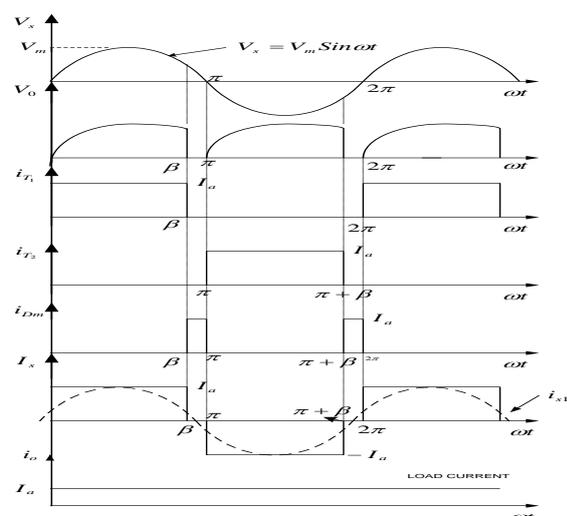


Fig. B: Waveforms of current and voltages

$$V_{dc} = \frac{1}{\pi} \int_0^{\beta} V_m \sin \omega t d(\omega t)$$

$$V_{dc} = \frac{1}{\pi} \int_0^{\beta} V_m \sin \omega t d(\omega t)$$

$$\begin{aligned}
&= \frac{1}{\pi} V_m \left| -\cos \right|_0^\beta \\
&= \frac{V_m}{\pi} [1 - \cos \beta] \quad (2)
\end{aligned}$$

V_{dc} can be varied from $\frac{2V_m}{\pi}$ to 0 by varying ' β ' from π to 0

$$\therefore \text{The maximum average output voltage is } V_{dm} = \frac{2V_m}{\pi} \quad (3)$$

Hence, the normalized average output Voltage V_n is;

$$V_n = \frac{V_{dc}}{V_{dm}} = \frac{\frac{V_m}{\pi} (1 - \cos \beta)}{\frac{2V_m}{\pi}}$$

$$= \frac{1}{2} (1 - \cos \beta) \quad (4)$$

The rms output voltage is given by: $V_{rms} = \left[\frac{1}{\pi} \int_0^\beta V_m^2 \sin^2 d(\omega t) \right]^{\frac{1}{2}} \quad (5)$

$$= V_m \left[\frac{1}{\pi} \int_0^\beta \frac{1}{2} - \frac{\cos 2\omega t}{2} d(\omega t) \right]^{\frac{1}{2}}$$

$$= V_m \left[\frac{1}{\pi} \left| \frac{\omega t}{2} - \frac{\sin 2\omega t}{4} \right|_0^\beta \right]^{\frac{1}{2}}$$

$$= V_m \left[\frac{1}{\pi} \left(\frac{\beta}{2} - \frac{\sin 2\beta}{4} \right) \right]^{\frac{1}{2}}$$

$$= \frac{V_m}{\sqrt{2}} \left[\frac{1}{\pi} (2\beta - \sin 2\beta) \right]^{\frac{1}{2}} \quad (6)$$

Similarly, the instantaneous input current can be expressed in Fourier series

$$\text{as } i_s(t) = I_{dc} + \sum_{n=1,2,3,\dots}^{\infty} (a_n \cos n\omega t + b_n \sin n\omega t) \quad (7)$$

where,

$$I_{dc} = \frac{1}{2\pi} \int_0^{2\pi} i_s(t) d(\omega t) \quad (8)$$

$$= \frac{1}{2\pi} \int_0^{\pi+\beta} i_s(t) d(\omega t)$$

$$= \frac{1}{2\pi} \left[\int_0^{\beta} I_a d(\omega t) - \int_{\pi}^{\pi+\beta} I_a d(\omega t) \right]$$

$$= \frac{I_a}{2\pi} \left[|\omega t|_0^{\beta} - |\omega t|_{\pi}^{\pi+\beta} \right]$$

$$= \frac{I_a}{2\pi} [\beta - 0 - (\pi + \beta) + \pi] = 0$$

$$\therefore I_{dc} = 0 \quad (9)$$

$$a_n = \frac{1}{\pi} \int_0^{\pi+\beta} i_s(t) \text{Cos}n\omega t d(\omega t) \quad (10)$$

$$= \frac{1}{\pi} \left[\int_0^{\beta} I_a \text{Cos}n\omega t d(\omega t) - \int_{\pi}^{\pi+\beta} I_a \text{Cos}n\omega t d(\omega t) \right]$$

$$= \frac{I_a}{\pi} \left[\left| \frac{\text{Sinn}\omega t}{n} \right|_0^{\beta} - \left| \frac{\text{Sinn}\omega t}{n} \right|_{\pi}^{\pi+\beta} \right]$$

$$= \frac{I_a}{n\pi} [\text{Sinn}\beta - 0 - (\text{Sinn}(\pi + \beta) - \text{Sinn}\pi)]$$

$$= \frac{I_a}{n\pi} [\text{Sinn}\beta - (\text{Sin}\pi \text{Cos}\beta n + \text{Cos}\pi \text{Sinn}\beta - \text{Sin}\pi n)] = \frac{2I_a}{n\pi} \text{Sinn}\beta \quad \text{For } n = 1, 3, 5, \quad (11)$$

$$= 0 \quad \text{for } n = 2, 4, 6, \quad (12) \quad b_n = \frac{1}{\pi} \int_0^{\pi+\beta} i_s(t) \text{Sinn}\omega t d(\omega t) \quad (13)$$

$$= \frac{1}{\pi} \left[\int_0^{\beta} I_a(t) \text{Sinn}\omega t d(\omega t) - \int_{\pi}^{\pi+\beta} I_a(t) \text{Sinn}\omega t d(\omega t) \right] = \frac{I_a}{\pi} \left[\left| \frac{-\text{Cos}n\omega t}{n} \right|_0^{\beta} - \left| \frac{-\text{Cos}n\omega t}{n} \right|_{\pi}^{\pi+\beta} \right]$$

$$= \frac{I_a}{n\pi} \left[\{ \cos 0^\circ - \cos n\beta \} - \{ \cos n\pi - \cos n(\pi + \beta) \} \right] \frac{I_a}{n\pi} [\cos 0^\circ - \cos n\beta + (\cos n\pi \cos n\beta - \sin n\pi \sin n\beta) - \cos n\pi] =$$

$$\frac{I_a}{n\pi} [1 - \cos n\beta + \cos n\pi \cos n\beta - \sin n\pi \sin n\beta - \cos n\pi] \quad \therefore \quad b_n = \frac{2I_a}{n\pi} (1 - \cos n\beta) \quad \text{For } n = 1, 3, 5, (377)$$

$$= 0 \quad \text{for } n = 2, 4, 6. (14)$$

since,

$$I_{dc} = 0,$$

the instantaneous input current can now be written as:

$$i_s(t) = \sum_{n=1,3,5,\dots}^{\alpha} \sqrt{2} I_n \sin(\omega t + \phi_n) \quad (15)$$

where,

$$\phi_n = \tan^{-1} \frac{a_n}{b_n} \quad (16)$$

$$= \tan^{-1} \left[\frac{\frac{2I_a}{n\pi} \sin n\beta}{\frac{2I_a}{n\pi} (1 - \cos n\beta)} \right] = \tan^{-1} \left[\frac{\sin n\beta}{(1 - \cos n\beta)} \right] = \tan^{-1} \left[\frac{\sin \left(\frac{n\beta}{2} + \frac{n\beta}{2} \right)}{2 \sin^2 \frac{n\beta}{2}} \right]$$

$$= \tan^{-1} \left[\frac{\left(\sin \frac{n\beta}{2} \cos \frac{n\beta}{2} + \cos \frac{n\beta}{2} \sin \frac{n\beta}{2} \right)}{2 \sin^2 \frac{n\beta}{2}} \right]$$

$$= \tan^{-1} \left[\frac{2 \sin \frac{n\beta}{2} \cos \frac{n\beta}{2}}{2 \sin^2 \frac{n\beta}{2}} \right] = \tan^{-1} \left[\frac{\cos \frac{n\beta}{2}}{\sin \frac{n\beta}{2}} \right]$$

hence

$$\tan \phi_n = \frac{\cos \frac{n\beta}{2}}{\sin \frac{n\beta}{2}} \quad (17)$$

but,

$$\cos^2 \phi_n + \sin^2 \phi_n = 1 \quad (18)$$

$$1 + \frac{\sin^2 \phi_n}{\cos^2 \phi_n} = \frac{1}{\cos^2 \phi_n} \quad 1 + \tan^2 \phi_n = \frac{1}{\cos^2 \phi_n} \quad (19)$$

Substituting equation (17) into equation (19),

$$1 + \frac{\cos^2 \frac{n\beta}{2}}{\sin^2 \frac{n\beta}{2}} = \frac{1}{\cos^2 \phi_n}$$

simplifying gives;

$$\cos^2 \phi_n = \sin^2 \frac{n\beta}{2} \quad (20)$$

hence,

$$\cos \phi_n = \sin \frac{n\beta}{2}$$

Displacement factor (DF) becomes,

$$DF = \cos \phi_1$$

$= \sin \frac{\beta}{2}$ leading (21) Thus, the rms value of the nth harmonic component of the input current is:

$$I_{s_n} = \frac{1}{\sqrt{2}} (a_n^2 + b_n^2)^{\frac{1}{2}} \quad (22)$$

$$= \frac{1}{\sqrt{2}} \left[\left(\frac{2I_a}{n\pi} \sin n\beta \right)^2 + \left(\frac{2I_a}{n\pi} (1 - \cos n\beta) \right)^2 \right]^{\frac{1}{2}}$$

$$= \frac{2I_a}{\sqrt{2n\pi}} \left[\sin^2 n\beta + (1 - 2\cos n\beta + \cos^2 n\beta) \right]^{\frac{1}{2}}$$

$$= \frac{2I_a}{\sqrt{2n\pi}} \left[1 + (1 - 2\cos n\beta) \right]^{\frac{1}{2}}$$

$$= \frac{2I_a}{\sqrt{2n\pi}} \left[2(1 - \cos n\beta) \right]^{\frac{1}{2}}$$

$$\begin{aligned}
&= \frac{2I_a}{\sqrt{2n\pi}} \left[2 * 2 \sin^2 \frac{n\beta}{2} \right]^{\frac{1}{2}} \\
&= \frac{4I_a}{\sqrt{2n\pi}} \left[\sin^2 \frac{n\beta}{2} \right]^{\frac{1}{2}} \quad (23)
\end{aligned}$$

Hence,

$$I_{s_n} = \frac{2\sqrt{2}}{n\pi} I_a \sin \frac{n\beta}{2} \quad (24)$$

The rms value of the fundamental current (i.e. n=1) is:

$$I_{s_1} = \frac{2\sqrt{2}}{\pi} I_a \sin \frac{\beta}{2} \quad (25)$$

Next, the rms input current is:

$$\begin{aligned}
I_s &= \left[\frac{1}{\pi} \int i_s^2(t) d(\omega t) \right]^{\frac{1}{2}} \quad (26) \\
&= \left[\frac{1}{\pi} \int_0^\beta I_a^2 d(\omega t) \right]^{\frac{1}{2}} \\
&= I_a \left[\frac{1}{\pi} \omega t \Big|_0^\beta \right]^{\frac{1}{2}} \\
&= \frac{I_a}{\sqrt{\pi}} [\beta - 0]^{\frac{1}{2}} \\
&= I_a \sqrt{\frac{\beta}{\pi}} \quad (27)
\end{aligned}$$

The expression for the harmonic current factor is [10]:

$$HF = \left[\left(\frac{I_s}{I_{s_1}} \right)^2 - 1 \right]^{\frac{1}{2}} \quad (28)$$

Substituting equations (25) and (27) in equations (28), it becomes:

$$\begin{aligned}
 &= \left[\frac{\left\{ I_a \sqrt{\frac{\beta}{\pi}} \right\}^2}{\left\{ \frac{2\sqrt{2}I_a}{\pi} \sin \frac{\beta}{2} \right\}^2} - 1 \right]^{\frac{1}{2}} \\
 &= \left[\left(\frac{\sqrt{\beta}}{\sqrt{\pi}} * \frac{\pi}{2\sqrt{2}\sin \frac{\beta}{2}} \right)^2 - 1 \right]^{\frac{1}{2}} \\
 &= \left[\frac{\beta * \pi^2}{8\pi \sin^2 \frac{\beta}{2}} - 1 \right]^{\frac{1}{2}} = \left[\frac{\beta\pi}{8\sin^2 \frac{\beta}{2}} - 1 \right]^{\frac{1}{2}} \\
 &= \left[\frac{\beta\pi}{4(1 - \cos\beta)} - 1 \right]^{\frac{1}{2}} \tag{29}
 \end{aligned}$$

The expression for the input current power factor is [10]:

$$PF = \frac{I_{s1}}{I_s} \cos\phi_1 \tag{30}$$

And from equation (21),

$$\cos\phi_1 = \sin \frac{\beta}{2} \tag{31}$$

Hence substituting equations (25), (27) and (31) into equation (30) and simplifying,

$$\begin{aligned}
 &= \frac{2\sqrt{2}}{\pi} \sin \frac{\beta}{2} * \sin \frac{\beta}{2} \\
 &\quad \frac{I_a \sqrt{\frac{\beta}{\pi}}}{I_a \sqrt{\frac{\beta}{\pi}}} \\
 &= \frac{2\sqrt{2}}{\pi} * \frac{\sqrt{\pi}}{\sqrt{\beta}} * \sin^2 \frac{\beta}{2}
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{2\sqrt{2}}{\sqrt{\pi\beta}} \sin^2 \frac{\beta}{2} = \frac{2\sqrt{2}(1-\cos\beta)}{2\sqrt{\pi\beta}} \\
 &= \frac{\sqrt{2}(1-\cos\beta)}{\sqrt{\pi\beta}} \tag{32}
 \end{aligned}$$

Simulation

The functional relationship between the behaviour factors and the output voltage is obtained by simulating equations; (4), (21), (29), and (32) using Matlab programming tool. The results of the simulations are displayed in Fig. C. Also, the relationship of the behaviour factors of the drive and the extinction angle is obtained by simulating equations (21), (29) and (32) using matlab programming tool. The results of this simulation are displayed in Fig.D.

RESULTS

Figure C, shows the simulation results of the relationship between the behaviour factors of the single – phase ac – dc drive with the output voltage for the EAC technique.

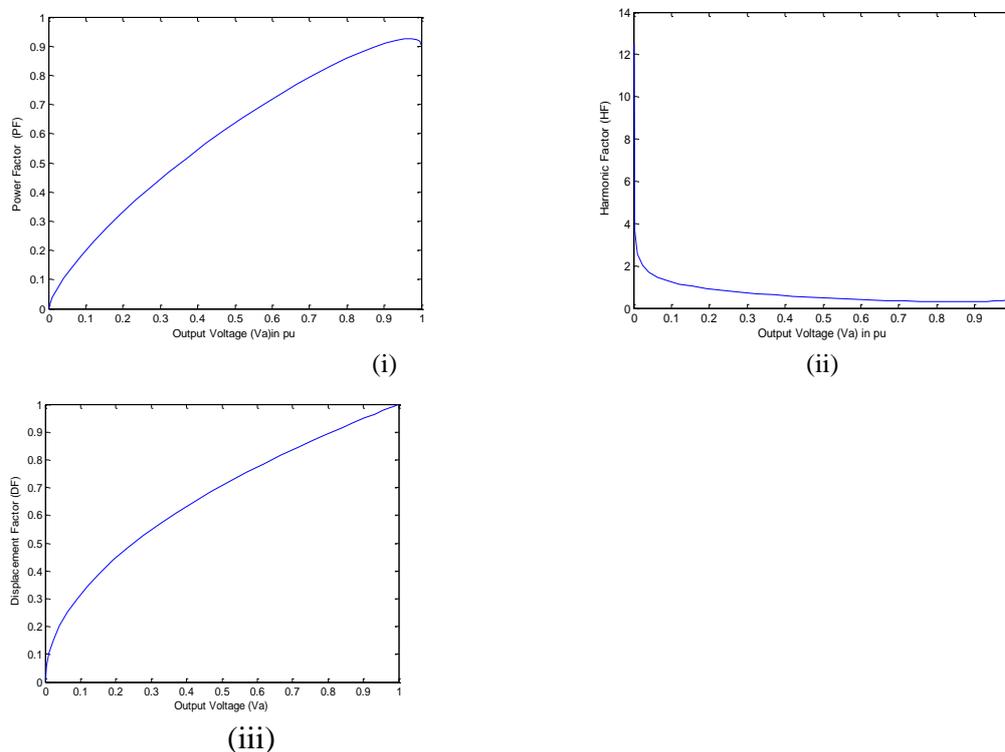


Fig. C: Relationship of behavior factors and output voltage for Extinction Angle PFC Control technique.

Figure 4, shows the simulation results of the relationship between the behaviour factors of the single – phase ac – dc drive with the extinction angle for the EAC technique.

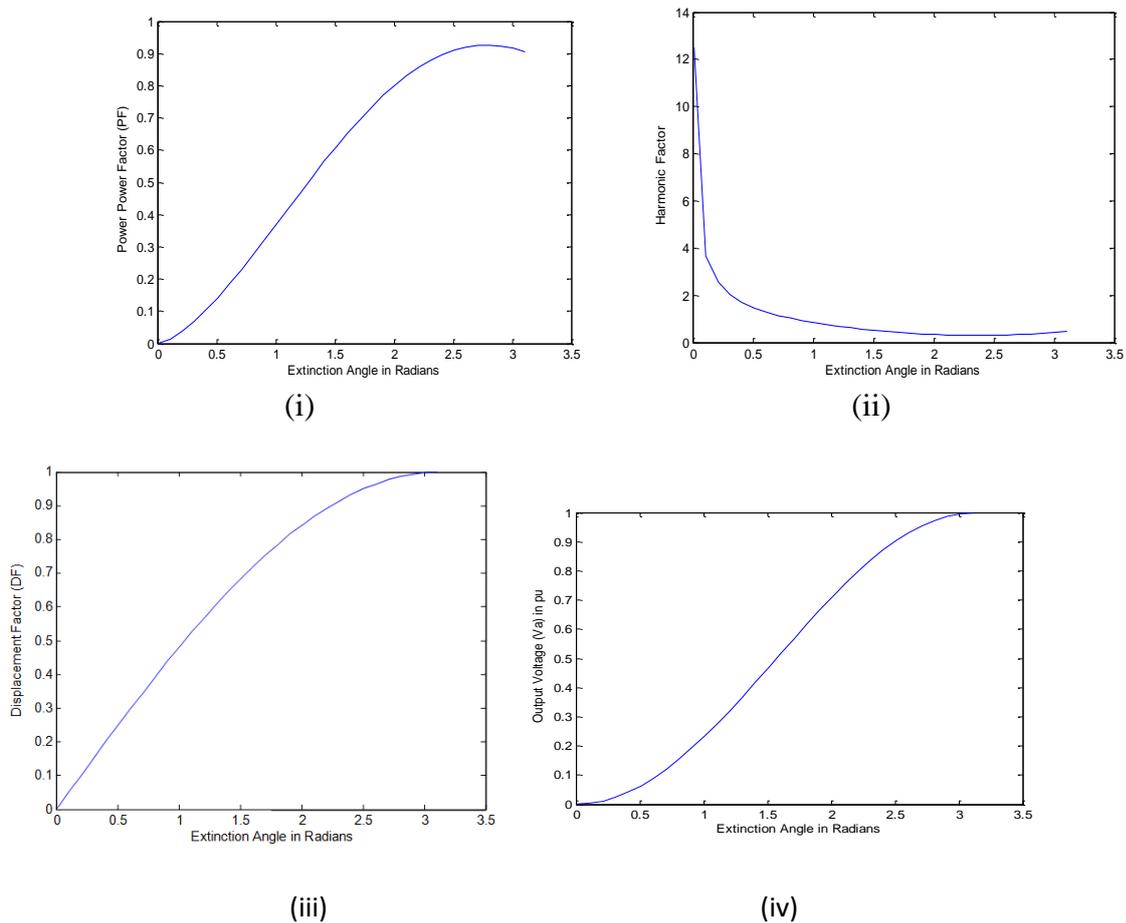


Fig. D: Relationship of behavior factors and extinction angle for Extinction Angle PFC Control technique

Fig.E: Relationship between the output voltage and extinction angle for Extinction Angle PFC Control technique

Experimental results

The circuit was set up in the laboratory and the waveforms of input voltage and current was obtained as displayed in Fig. F.

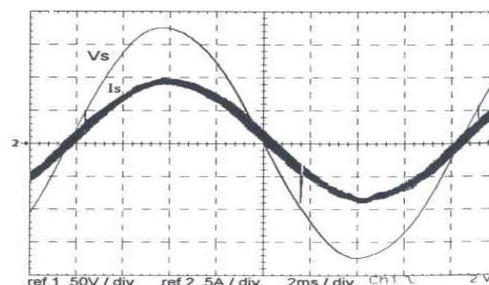


Fig. F: Results of laboratory experiments for Extinction Angle Control (EAC).

DISCUSSIONS

It should be made clear that the performance of the asymmetrical bridge converter with extinction control are similar to those with phase control (PAC) discussed in previous

presentation [6], except that the power factor is leading as displayed in Fig. F whereas, with the phase angle control (PAC) technique, the power factor is lagging.

A critical look at the input waveforms of this technique reveals that the component of the input current leads the input voltage and the displacement factor and power factor is leading the supply voltage. This feature is required in some applications desirable to stimulate a capacitive load and to compensate for the line voltage drops.

CONCLUSION

The results reveal that as the extinction angle and the output voltage is increased, power factor is increased progressively. Also, the displacement factor is increased whereas, the harmonic factor is decreased. As expected of single – phase drives, it provides a variable output voltage for a varying power factor. This has been established in this work.

REFERENCES

1. K. H. Bezold, J. Forster and H.Zander: “Thyristor Converters for Traction DC motor Drives”, IEEE Conference Record, ISPC-72, New York, 1972.
2. K.H.Liu, Y.L.Lin: “Current waveforms Distortions in Power Factor Correction Circuits Employing Discontinuous – Mode Boost Converters”. PESC. Conf. Proc. 1989. Pp. 825 – 829
3. P. Enjeti, Sireen and I. Pitel,: “Analysis and Design of a new active filter to cancel neutral current harmonics in three phase four wire electric distribution systems, “IEE Trans. Ind. Application, vol.30,no. 6, Nov/Dec. 1994.pp.1565-1572
4. P.T. Krein: “Elements of Power Electronics”.New York, Oxford University Press, 1st edition, 1998.
5. Okoro, C.C and Osunde, O.D: “The Input Power Factor Problem for Industrial Drives” Proceedings of International conference and Exhibition on Power Systems. Lagos. 23rd – 25th July, 2007
6. Osunde, O.D: “Simulation Model of An Input Power Factor Of A Single – Phase AC- DC Drive” Proceedings os the 7th International Conference on Power and Telecommunications, Warri, 11th – 13th October, 2011.
7. R. Redl: “Power factor correction in single – phase switching –mode power supplies – an overview”. Int. J. Electronics, vol. 77, No.5, pp.555-582, 1994
8. R. Erickson, M. Madigon and S. Singer: “Design of a simple high power factor rectifier based on the flyback converter”. Proceedings of IEEE, Applied power Electronics Conference (APEC), 1990, 792-801.
9. Okoro, C.C, Awosope and Osunde, O.D: “Correction of Input Power Factor problem in Industrial Drives” Proceedings of the International Conference in Engineering and Technology (IET 2011). August 8th – 10th 2011. Pp. 78 – 87
10. R.H Muhammed: “Power Electronics: Circuits, Devices and Applications”. 2nd Edition. Prentice Hall, Englewood Cliffs, NJ, 07632.

A LINGUISTIC FUZZY EXPERT SYSTEM FOR CONTAGIOUS DISEASES DETECTION AND ISOLATION

M. S. Osigbeme¹, F. O. Ogunwolu² & A.A Omoare³

¹Department of Electronics and Control Engineering, Nnamdi Azikiwe University, Awka.

²Department of System Engineering, University of Lagos, Akoka, Lagos State

³Department of Medical Microbiology and Parasitology, University of Ilorin, Kwara State.
mykaelosi@yahoo.com

ABSTRACT

This paper presents an electronic expert system platform to detect and diagnose existing and new cases of contagious diseases as they occur with minimal contact with the index patient(s) and healthcare personnel with a confidence level that can be used to initiate or suggest appropriate follow-up action(s). The aim is to use ICT tools for patient-diagnosis, raise a red flag in real-time and thus contain contagious cases which may degenerate into an epidemic by providing a way to analyze vague and ambiguous input data from visible and reported symptoms in patients. A re-useable expert system which makes use of fuzzy reasoning techniques and design methodology was used in this work. The expert system is premised on rule-based fuzzy logic which captures the ambiguity, imprecision and nuances involved in disease reporting and detection using the Mamdani model. The software developed for the fuzzy expert system, called SOSIC, presents its diagnosis with fuzzy values between 0 to 1 corresponding to its level of confidence for the fuzzy inputs. The current approach to e-diagnosis and detection of contagious diseases using our SOSIC software is not completely contactless, thus ongoing investigations are geared towards improving SOSIC to be contactless. The developed fuzzy expert system software provides a safe procedure with minimum contact between patients and healthcare personnel to address early detection and diagnosis issues that may help forestall chain-infection and epidemics. The developed fuzzy based expert system can be further extended to accommodate the detection of a wider array of symptoms as new cases arise; thus this paper fulfils an identified need in safe healthcare practice.

Keywords: Disease Control, SOSIC Diagnosis, Preventing Diseases, Quarantining, Contagious Diseases.

INTRODUCTION

An average scenario of patients trying desperately to see a doctor especially in public hospitals and primary health care leaves much to be desired; experiences such as undue waste of time, frustration and delays, exploitation and lackadaisical attitude of some of the healthcare givers. In a developing country such as Nigeria, where there is consistent trade union and government disagreements over salaries, entitlements, working conditions and health care facilities, life threatening situations and conditions may further be compromised by these healthcare institutions. This is further complicated by the fact that diseases outbreaks usually have debilitating consequences, endangering even the healthcare givers' health and the populace if not detected, isolated and controlled. It is therefore a matter of urgency and necessity for a review of the health institution's modus operandi in tandem with recent developments and best practices available in other climes.

This work advocates a way for healthcare givers to examine patients in emergencies with a view to minimizing contact with yet to be properly diagnosed patients that may be a host to contagious diseases such as Influenza (flu), Chickenpox and Ebola among others. By minimal contact, nurses and other lower cadre healthcare givers who hitherto are the first to receive patients on arrival in the emergency units of hospitals and clinics are allowed to have a general idea of the case they are

dealing with at hand based on an expert system comparable to MYCIN such that during the window period prior to when a patient finally sees the doctor, the patient who we can refer to as the index case has not infected the medical personnel or even other patients in the general patient out-ward unit.

The disease prevention and isolation approach we have chosen for this expert system is to help protect everybody involved either directly or indirectly in the event of a disease outbreak by helping to contain the spread, kick start quarantine procedures where necessary and proffer initial solutions verifiable by trained medical personnel if necessary and thus serve as an electronic form of first aid pending final diagnosis by trained personnel or serve as a referral to Emergency Diseases Hospitals (EDH) if available. This work allows healthcare personnel and even the patients-to-be-diagnose to respond to basic or simple questions from the software package we have developed and which is designed to be resident in the familiar personal computer and available in the general open ward for out-patients and administrable to patients positioned at about one metre away from healthcare personnel. We thus hope that by this structured information related approach, it will be able to help reduce the severity for spreading of contagious diseases bearing in mind that there is normally an ample amount of time wasted while waiting for the doctor or waiting in a queue.

Related Work

The use of computers to aid health care givers and patients have been available as far back as 1970s with the design and deployment of MYCIN, a medical expert system for diagnosing ailment and based on rule base reasoning [1] that are premised on certainty factors of symptoms present in patients. CASNET was also designed to help medical personnel to detect ailments and diseases in patients by considering the most significant result of tests. It uses semantic network representation formalism, having nodes which represent disease states with attached weights to determine how they relate under some appropriately defined relationship. Due mainly to the dynamic nature of diseases occurrence [8], complexity in its spread and sensitive factors involved in treatment and isolation, coupled with the professional expertise needed for building, verifying and deploying tools for patient diagnostic purposes, much has not really been done in the scientific community for this specific area. This assertion can be observed in the recent (2014) outbreak of the Ebola Viral Disease (EVD) in West Africa where standard health procedures supported with ICT tools could have helped in preventing the death of the healthcare givers who probably due to the fact that EVD was not rampant and with symptoms similar to fever, malaria, flu, etc which are not contagious may have initiated very low alert levels in dealing with the case. An ICT supported healthcare system using expert system's artificial intelligence and capability to control and analyze huge data in real-time will provide the necessary large database that can contain all possibility of the symptoms of a disease including Emerging infectious diseases (EIDs) for which [5] puts the number to be increasing globally over the past 50 years with estimates of the proportion of EIDs that involve pathogens transmitted from animals to humans, or *zoonoses*, ranging from 60% to 75% of contagious diseases. Although the number according to [5] of "Emerging zoonoses can become devastating if they become transmissible from person to person. For example, the complete genetic characterization of the pandemic (in) 1918 (of the) "Spanish Flu" virus suggests it not only originated from an avian influenza virus, but that the pandemic virus was in fact an adapted avian influenza virus; these findings show that zoonotic agents can result in severe impacts with minimal genetic changes, in this case increased severity and facilitated human to human transmission, some of which are already present in the current circulating avian viruses." EBVs zoonotic agents include Bats, Monkeys, Apes and Duikers (African Antelopes). Vrhova et al in [5] further went on to point out that "society would be better prepared to detect and prevent EIDs if we can get "ahead of the curve": if we are able to identify risky situations before the first cluster of cases in humans

are identified in hospitals”. The increasing use of ICT and its tools has witness an unprecedented growth in almost all areas including security and crime detection [9], in teaching and learning [6] and healthcare cannot be left behind. The role of approximate reasoning in a medical expert system which was developed by [7] and called EMERGE uses a rule-based expert system for the analysis of chest pain in an emergency room environment to provide rapid decision making by utilizing certainty factors to indicate the seriousness of the patients illness. The EMERGE according to developers however lacked the ability to record nuance (high distinction) and did not intuitively appear to follow the same processes as the human reasoning process. Though our intent is purely to serve as an alternative to help advance diagnosis of diseases especially contagious ones in our healthcare system and to draw attention to this area of scientific support to the healthcare system we however state that the result of this work or the conclusion from the diagnostic software cannot serve as a substitute for the advice, diagnosis or treatment by a doctor or other trained health professionals.

METHODS

The diagnostic software designed is based on a mathematical model that allows application of rule-based fuzzy models to obtain a relationship between variables that interfere as signs and symptoms to collectively determine the state of a patient by representing these variables by means of if-then rules with vague or imprecise (ambiguous) predicates, such as:

If body temperature is High then Malaria susceptibility is High.

If body pressure is Low then Fever susceptibility is Low.

If Weight Loss is High then Chronic Condition is High.

This defines in a rather qualitative way the relationship between the patient’s body temperature, pressure and weight and the disease causative mechanism. However, due to the fact that human reasoning and response to data entry or collation is based on heuristics and ambiguity such that temperature may be reported as high, slightly high or very high. Pressure could be reported as normal or abnormal and weight loss could be interpreted as high, slightly high or severe. Thus to make such model operational, the meaning of the term ‘high’ or ‘low’ must be defined more precisely. This is done by using fuzzy sets, i.e., sets where the membership is changing. The Mamdani model was chosen for this project over the Takagi-Sugeno Model due to the ability of the model to deal with linguistic fuzzy since the latter is more adapted for data driven identification.

Mamdani Model

In this model, the antecedent (if-part of the rule) and the consequent (then-part of the rule) are fuzzy propositions:

$$R_i: \text{If } x \text{ is } A_i \text{ then } y \text{ is } B_i; \quad i=1, 2, \dots, K \quad 1.$$

Here A_i and B_i are the antecedent and consequent linguistic terms of patients’ symptoms as present (such as ‘Normal’, ‘Slightly large’, ‘Very High’ etc.), represented by fuzzy sets, and K is the number of rules in the model.

Fuzzy inference systems (FIS)

A FIS according to [10] “is a way of mapping an input space to an output space using fuzzy logic. A FIS tries to formalize the reasoning process of human language by means of fuzzy logic (that is, by building fuzzy IF-THEN rules).” The Mamdani-type inference expects the output membership functions to be fuzzy sets whose output, after the aggregation and defuzzification process is a single spike rather than a distributed fuzzy set. This output which is a singleton output membership function of the pre-defuzzified fuzzy set corresponds to the efficiency of the defuzzification process and the computation of the centroid of a two-dimensional function.

This linguistic fuzzy model is useful for representing qualitative knowledge based on available or visible symptoms and belief that the respondent, that is either the patient or nurse is giving accurate report of the symptoms using uncertain and ambiguous linguistic variables or ‘qualifying adjectives’ which contain more information than ‘crisp’ values of true or false, high or low, hot or cold as disease isolation depends more on the degree of causative elements in the patient’s body. For example early stages of a disease will manifest fewer symptoms compared to later and final states with each stage having its own unique signatures. By using membership functions the degree or extent of viral, pathogenic, bacterial, etc involvement, their stage of development, population, etc present in the patient’s immune system (the host) can be more understood. For example, a membership function mapping of body temperature and blood pressure is shown below.

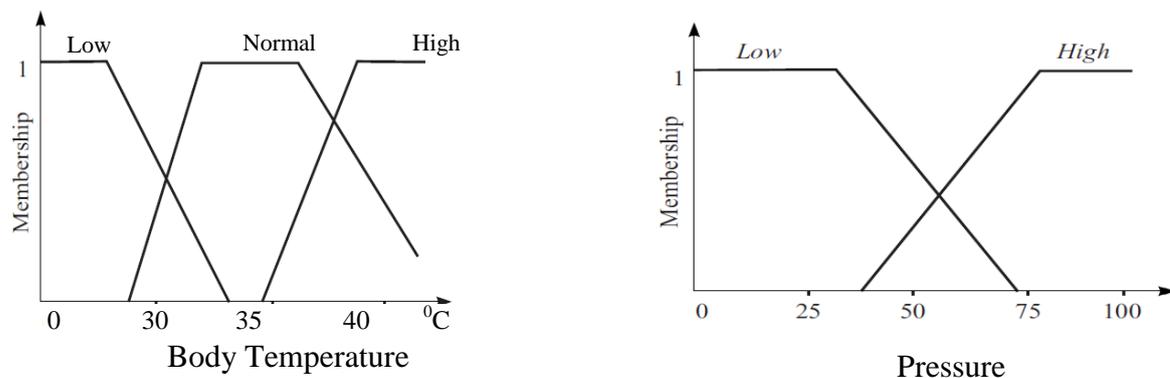


Figure 1.0 Membership Functions of present state of patient’s condition.

Since the input–output data of the system under study are available the membership functions can be constructed or adjusted automatically with the stringent rule that the qualitative relationship given by the rules is usually expected to be valid for a range of conditions.

Fuzzy Expected Interval, (FEI). To handle the fuzzy population distribution in the proposed inference system the equation below was used to obtain the upper and lower bounds in the computation of the Fuzzy Expected Interval, (FEI) from which a Fuzzy Expected value was computed.

$$\begin{aligned}
 UB_j &= \frac{\sum_{i=j}^n \text{MAX}(pi1, pi2)}{\sum_{i=j}^n \text{MAX}(pi1, pi2) + \sum_{i=j}^{j-1} \text{MIN}(pi1, pi2)} \dots\dots\dots 2 \\
 LB_j &= \frac{\sum_{i=j}^n \text{MIN}(pi1, pi2)}{\sum_{i=j}^n \text{MIN}(pi1, pi2) + \sum_{i=j}^{j-1} \text{MAX}(pi1, pi2)} \dots\dots\dots 3
 \end{aligned}$$

Software Implementation (SOSI Clinic)

A screenshot of the GUI accepting patients’ real-time symptoms which has been designed with the uncertainty of fuzziness and ambiguity or vagueness in responses of the patient under investigation or the resultant conclusions of the administering healthcare personnel such as the nurse on duty that is using the software is shown in figure 2.0 below. In using this tool, the user

will have to select the degree of presence of symptoms as visible on the patient or as reported by the patient under investigation. These actions fire the various membership functions in the fuzzy system by creating a membership function set and the software based on the selected inputs, uses its fuzzy inference system to obtain a unique value which depicts mathematically the state of the patient.

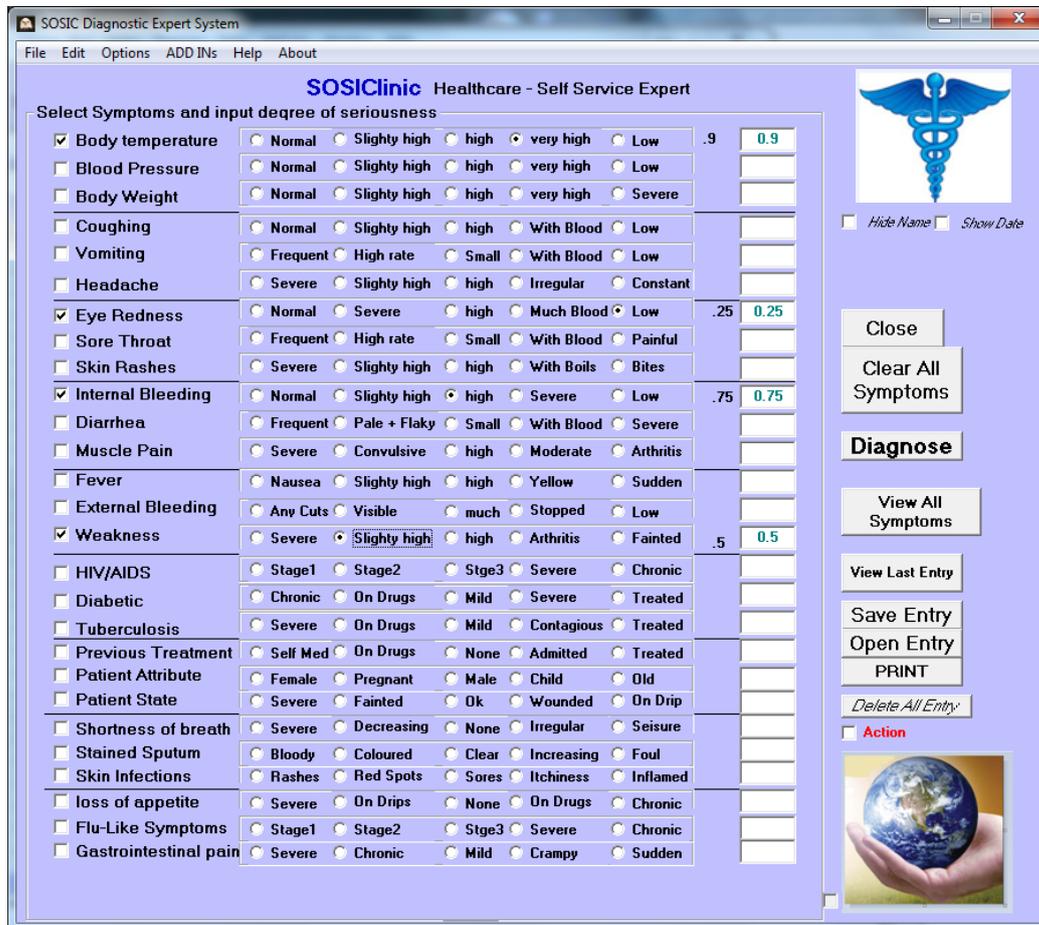


Figure 2.0 shows the SOSIC diagnostic console for inputting symptoms

RESULTS AND DISCUSSION

Figure 2.1 shows a screenshot of the window showing the results of the diagnosis by the SOSIC expert system for which fictitious values have been previously inputted recall in figure 2.0 above. The hypothetical case inputs were used to diagnose a severe case of typhoid and quarantine was not recommended since it was not directly contagious but due to the severity of the ailment, admission was recommended.



Figure 2.1 shows results of diagnosis of a Typhoid case

However in figure 2.2 below a severe condition of EVD was detected and quarantine was recommended for the patient. The Error in Judgment (EIJ) is further computed by the software to show the degree of her conviction and premise, an optional information that users or trained personnel can further use to validate the result of the diagnosis. The EIJ is based on the number and degree of symptoms fed into it by the patient or/and healthcare personnel. For example, while a patient with just internal and external bleedings may get a computation and diagnosis of EVD 0.8 may have a high EIJ or error function as high as 70% as the two symptoms are not enough to conclude such a critical judgment, however if other symptoms were inputted in her reasoning the EIJ will drop significantly.

CONCLUSION

We have presented a novel application of fuzzy sets and fuzzy logic in this work for transforming largely vague responses of patients and their symptoms directly into alert levels with verifiable level of confidence and error in judgment. The results of the hypothetical cases used to validate this model with participants about one metre away from the administering staff produced very promising results and the general sense of the majority of the participants in the systems' evaluation was that the software was a worthwhile development effort. The SOSIC software as an Expert system has allowed the modeling of complex interacting biological systems in patients to produce a unique solution for a line of action by depending on heuristic and intuitive information readily available from ill patients in real-time. We thus have been able to mitigate the window period of contagious disease spread as it makes its first appearance in the public domain through healthcare facilities by efficiently detecting and isolating the index case and by raising a red flag to curtail further spread. The importance of this tool cannot be overemphasized in a biological warfare where terrorist can take advantage of vulnerabilities in the system to create a biological mayhem and only a knowledge driven economy can survive such a war.

RECOMMENDATIONS

We recommend that appropriate authorities should collaborate and further develop this tool and adopt the outcome as a standard procedure for healthcare, this will definitely help nip in the bulb cases that would have hitherto claimed lives due to very low alert levels as history has continue to show that diseases take advantage of man's low alert levels to claim lives including the healthcares'. We therefore recommend the use of ICT tools such as this for general patient diagnostic measure, as a standard proactive procedure irrespective of whether the patient will be admitted, referred or rejected.

REFERENCES

1. Shortliffe, E.H., (1976); "Computer-Based Medical Consultation: MYCIN" Elsevier Publishing, North-Holland, NY
2. Kandel, Abraham; (1992); "Fuzzy Expert Systems" CRC Press, Inc. Boca Raton, Florida, USA. Pp 23 – 41.
3. Babuska, R, (2002); "Neuro-Fuzzy Methods for Modeling and Identification" in edited Advances in Intelligent Paradigms and Applications, Springer-Verlag, Heidelberg. Pp 161–186.
4. Friedl, L., Ceccato, P., (2010); "Human Health Societal Benefit Area: Infectious Disease" in Critical Earth Observations Priorities: Human Health Infectious Diseases SBA Report.
5. Vrbova L, Stephen, C., Kasman, N., Boehnke, R., Gibson, B., Brauer M., Patrick D., (2009); "Systematic Review of Surveillance Systems for Emerging Zoonotic Diseases" www.nceh.ca/sites/default/files/Zoonoses_Surveillance_May_2009.pdf. Retrieved on 25th July, 2014.

6. Reamon, D.T, Sheppard, S.D, (1997); “The Role of Simulation Software in an Ideal Learning Environment” Proceedings of DETC'97 ASME Design Engineering Technical Conference September 14-17, 1997, Sacramento, California. USA.
7. Hudson, D.L, Cohen, M.E, (1992); “The Role of Approximate Reasoning in a Medical Expert System” in Abraham Kandel’s “Fuzzy Expert Systems” CRC Press, Inc. Boca Raton, Florida. Pp 165 – 179.
8. Reddy, K.S, (2003); “Prevention and Control of Non-Communicable Diseases: Status and Strategies”www.icrier.org/pdf/wp104.pdf. Retrieved on 2nd July, 2014.
9. Badiru, B.B, Asaolu, O.S, Omitaomu, A.O, (2006); “Eyewitness Information Management System using Neuro-Fuzzy Classification Schemes.” Journal of Information Science and Technology. JIST Vol. 2(3) 2006.
10. Ardil, E., Sandhu, P.S., (2010); “A soft computing approach for modeling of severity of faults in software systems.” International Journal of Physical Sciences Vol. 5(2), pp. 074-085, February, 2010. <http://www.academicjournals.org/IJPS>.

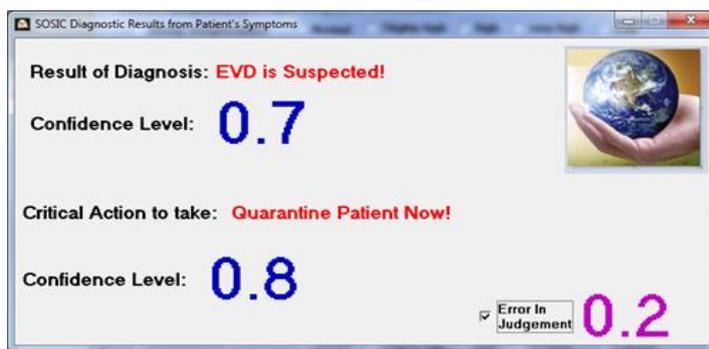


Figure 2.2 shows results of diagnosis of a contagious EVD case

DYNAMIC RESPONSE OF MICROBIAL SYSTEM OF THE NIGER DELTA TO CRUDE OIL (HYDROCARBONS) POLLUTION

O.O. Olanipekun^{1,*}, A.O. Ogunbayo¹, S.C.U. Nwachukwu² & R. A. Bello¹

¹Department of Chemical Engineering, University of Lagos, Yaba, Lagos.

²Department of Microbiology, University of Lagos, Yaba, Lagos.

oolanipekun@unilag.edu.ng

ABSTRACT

The activity of indigenous microbial system is a required tool to remediate an environment that has been contaminated by hydrocarbons. This work deals with the dynamic response to crude oil contaminants of undefined microbial systems in three selected communities of the Rivers State of Nigeria. The activities of indigenous (undefined) consortia were studied and compared using Respiratory technique. The soil samples were incubated with 2 % (v/v) crude oil in mineral salt medium at 37 °C in three phases of two weeks in a shake flask at 150 rpm. At the end of the last phase, components of the crude oil degraded by the undefined consortia in the soils were identified with the gas chromatographic techniques. The results obtained showed that the consortia from the different soil samples exhibited different degrees of capacities to degrade the crude oil. On the whole, 50.00 to 85.70 % of hydrocarbon components of the crude oil were degraded thus making the areas potentially suitable for *in-situ* bioremediation. The study has shown that the obtained microbiological characteristics and activities of the soils are adequate for bioremediation technologies.

Keywords: *Microbial activities, Undefined Consortium, Crude oil, Bioremediation, Soil.*

INTRODUCTION

Rivers State is one of the highly ranked oil-producing states of Niger-Delta of Nigeria, and a lot of petroleum production and activities have directly exposed this area to large or repeated spills or leaks frequently. The presence of hydrocarbon pollution in the environment poses a great hazard for aerial, terrestrial and aquatic life, and the impact of these pollutants is of great public concern due to the severe ecosystem imbalances caused by them (Whyte *et al.*, 1997; Biccaet *al.*, 1999; Margesinet *al.*, 2003). Regardless of the level of pollution, they are potentially dangerous to the microfauna and microflora, and have detrimental effects on the ecosystem (Amundet *al.*, 1987; Akpofureet *al.*, 2001). As a result there are worldwide concerns about remediating and restoring environments of hydrocarbon pollution (Biccaet *al.*, 1999).

Microbial influenced remediation and restoration have been accepted as a promising tool to cleaning up hydrocarbon contaminated environments (soil, water, and estuaries). It has gained a wide application in combating the menace of hydrocarbon pollution to the environment which is usually encountered in the oil and gas industries. Apart from being environmentally friendly, because it does not introduce additional chemicals to the environment, bioremediation usually competes well on a cost basis, especially in biodegrading petroleum products and most solvents (Admassu and korus, 1996). Going by the success story of application of bioremediation in so many hydrocarbon contaminated places for instance in Prince William Sound in Alaska after the Exxon Oil spill in 1989 (Boopathy, 2000), the method can also be employed in cleaning the contaminated environments in Niger Delta area of Nigeria.

Bioremediation systems or technologies are used in cleaning up environment such as soil, water and air contaminated with hydrocarbons. It is basically an application of biodegradation, which is a microbial driven process to clean up the environments contaminated with organic compounds (hydrocarbons). The effectiveness of these systems thrives on the ability to enrich

and maintain microbial populations and activities within the target environment. This is achieved with two major inputs like operational conditions and the organic contaminants as illustrated in Figure 1. The operational conditions include the physical and chemical properties of the environment, which are the environmental variables that govern the soil (environment) microbial activities, populations and communities. Other factors include toxicity, bioavailability and degradation rate of the contaminants. Finally, the strategic methods of optimizing the system are also inputs in the bioremediation system. From the foregoing, it is important that the evaluation of the activity of the microbiota of the soil is vital for well-designed and implemented bioremediation efforts. Soil biological investigations, such as measurement of soil respiration, enzyme activities and microbial counts (depending on the desired information) can give information about the presence of viable microorganisms and on the impact of the effects of environmental stresses, such as hydrocarbon contamination on the metabolic activity and biogeochemical cycles taking place in soils (Margesinet *al.*, 2000).

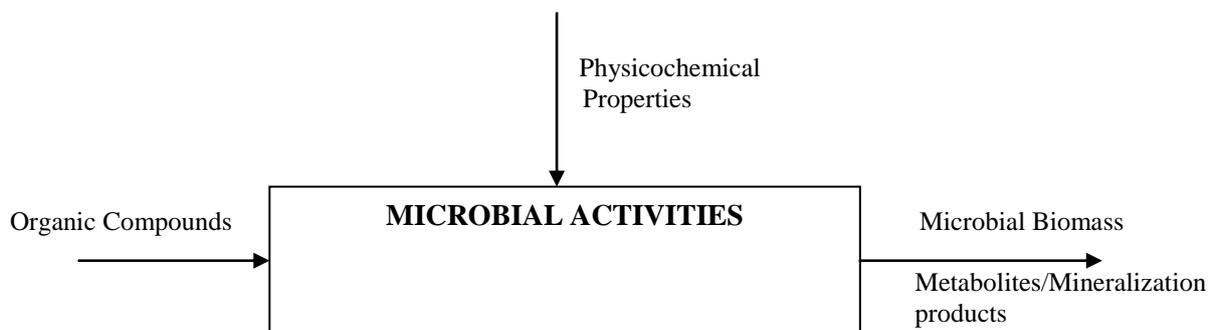


Figure 1: Bioremediation System.

The engineering of bioremediation processes relies on information about the site and about the candidate microorganisms. This work aims at obtaining this basic information such as response of the microbial system which can enhance the bioremediation technologies involved in the Niger Delta, particularly Rivers State of Nigeria. The activities of pristine and contaminated sites will also be compared with a view to improving the developed bioremediation technologies.

METHOD

Sample Sites and Collection: The methods used in the works of Margesinet *al.* (2003), Uzoamaka *et al.* (2009) and Obire and Anyanwu (2009) were integrated and adopted in this work. This involved soil samples, both contaminated with crude oil and pristine (uncontaminated), serving as control were collected from surface soil (0-15 cm depth) from three communities (as sites) in River states. These communities are, Tai (Pete), Ebubu (Eleme) and Gokana and they are abbreviated as RTP, REE, and RGK respectively in this study (see Figure 2). The soil sample collections were made from 3-4 random points per sample sites and mixed to form a composite soil sample with a sterile scoop and transferred aseptically into sterile polyethylene bags.

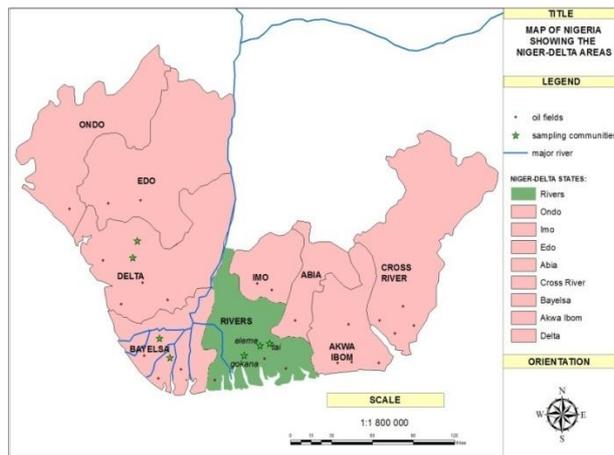


Figure 2: Map of Nigeria (Niger Delta area) Showing Sample sites in River State

Microbial Activities Analysis: Respirometric technique was used, since it allows an in depth analysis of the microbial population dynamics. (Margesinet *al.* 2003; Eze and Eze, 2010). The soil respiration was measured from incubation of 100g soil samples kept in hermetically sealed 250 ml glass flask for 21 days at room temperature (see Figure 3). To achieve this, 100 ml conical flask containing 50 ml of 0.50 mol dm^{-1} of NaOH solution was used to capture the CO_2 produced from the respiration.



Figure 3: Set up for the respiratory study.

The conductance of the NaOH solution was measured using Jency Model 712 Conductance Instrument after each incubation time (1, 3, 5, 7, 13, 17 and 21 days). The microbial activity was monitored in triplicate for the released CO_2 (Crittter *et al.*, 2004). The produced CO_2 was calculated from the following equation.

$$m = 22 \left[\frac{\lambda_1 - \lambda_x}{\lambda_1 - \lambda_2} \right] VC \quad 1.0$$

Where λ_x is the conductivity value of the sample, λ_2 is the conductivity value of Na_2CO_3 , λ_1 is the conductivity value of NaOH, V is the volume of the standard NaOH solution, C is its concentration in mol dm^{-3} and m is the estimated mass of absorbed CO_2 in mg.

Crude Oil Utilization-ability of the Un-defined Consortium in the Environment: The abilities of the un-defined consortium in the sampled soils were confirmed by inoculating 10 g of each sample in separate cotton plugged 250 ml Erlenmeyer flasks containing sterile liquid

minimal salt medium (whose composition was same as used in the estimation of hydrocarbon utilizing bacteria and fungi above). The liquid medium and crude oil were autoclaved separately at 121 °C at 1 atm. pressure for 15 min. sterile crude oil which served as source of carbon and energy was added at 1-2 % (v/v) to make up a final volume of 90 ml sterile liquid minimal salt medium. Control flask containing the liquid medium and the 1-2 % crude oil but without soil sample was also prepared. The flasks were monitored and agitated in water bath shaker for a period of 14 days. This is the first enrichment. For second enrichment phase, 10 ml of aliquot of each soil sample was transferred to fresh 90 ml medium containing 1-2 % (v/v) crude oil and also monitored for 14 days in water bath shaker at 15 rpm. The same procedure was repeated for the third enrichment phase. These were to re- confirm the biodegradation abilities of the undefined consortium. At the end of each phase, microbial loads were determined by plating aliquots (0.1 ml) from 10⁻³ and 10⁻⁴ dilutions of samples on PDA plates and 10⁻⁵, 10⁻⁷ and 10⁻⁸ dilutions on NA plates. Hydrocarbon utilizing isolates were obtained from the last phase of enrichment using the method used by previous researchers (Nwachukwu, 2000; Omotayo et al., 2012). The residual hydrocarbons present in the media after the last phase of enrichment were determined by GC/MS analysis (Omotayo *et al.*, 2012; Malatova, 2005).

RESULT AND DISCUSSION

The respirometry technique has allowed an in-depth analysis of the microbial population dynamics, by comparing the activities of indigenous microbial population in both pristine (uncontaminated) and contaminated soils. The plots of accumulated carbon (IV) oxide production against time of incubation are shown in Figures 4- 6. The cumulative values obtained reflect the distinct behavior for the contaminated and uncontaminated soil samples.

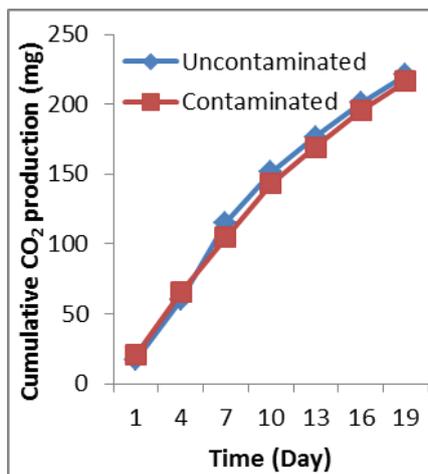


Figure 4: Accumulated CO₂ production during 21 days incubation of soil samples from Eleme, Rivers State, REE

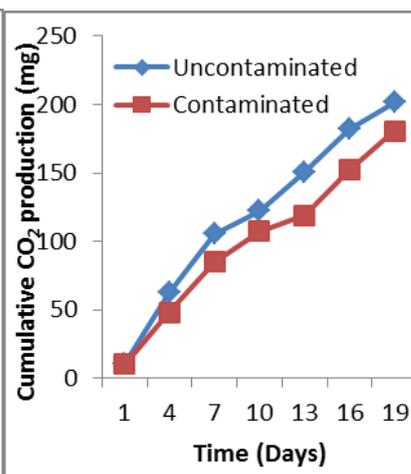


Figure 5: Accumulated CO₂ production during 21 day incubation of soil samples from Gokana, Rivers State, RGK

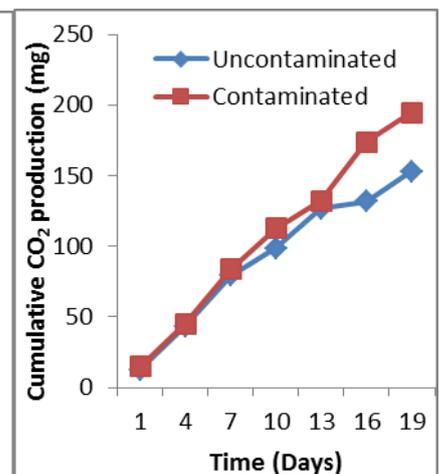


Figure 6: Accumulated CO₂ production during 21 days incubation of soil samples from Tai, Rivers State, RTP

The results obtained as reflected in Figures 4 and 5 (representing Eleme and Gokana, communities in Rivers State respectively) showed that the activities of microbes in uncontaminated soils (actual) are higher than that of the contaminated (potential). This was similar to the observation reported by other researchers (Margesin *et al.*, 2003). The results indicated that there was a decrease in the total heterotrophs in the contaminated soils apparently due to the toxic effects of the crude oil. Moreover, the indigenous microbial systems lack adequate abilities to mineralize the crude oil hydrocarbons. This is an indication that such

environments would require enhancement (biostimulation or bioaugmentation) to be remediated or restored.

The results plotted in Figure 6, depicting the microbial activities in Pete, Rivers State showed that the potential activity of the indigenous microbes was higher than that of the actual. Thus there is a strong positive response from the indigenous microbial population, indicating their biodegradative contributions. This suggests that the microbial activities of this site were not so impacted and interfered with by the crude oil pollution or the recovery of the site had improved by the time this study started.

Table 1: Kinetic Parameters of Growth of the Undefined Consortium as function of CO₂ generation at the sites

Location	Description of Soils used	Lag Time, (hr)	Specific Growth Rate(mg/l/hr)	Mean Generation Time(hr)
REE	A	33.6	1.06	0.65
	B	28.8	0.61	1.13
RGK	A	14.4	1.14	0.61
	B	36	0.96	0.72
RTP	A	24	0.44	1.56
	B	33.6	0.46	1.5

Key: A- uncontaminated soil, B- contaminated soil, RTP-Tai (Pete), REE-Ebubu (Eleme) and RGK-Gokana

These observations are further strengthened by the kinetic parameters generated for the sites as a function of carbon (iv) oxide production (Table 1). In the locations (REE and RGK), where the actual activities were greater than the potential activities, the specific growth rates were also higher while the mean generation times were lower. This is an indication that increase in activities was as result of increase in the growth rate. In other words, when activity was higher, less time would be required by the microbial population to double itself.

Furthermore, this may imply that the biodegradability potential of hydrocarbons in soils of these sites was high, and that the soil could be successfully remediated by natural attenuation. In other words, not only were viable hydrocarbons utilizing microbes present but they were efficient in mineralizing the hydrocarbons.

Biodegradability in the undefined Environments (Soils)

The biodegradability of the total petroleum hydrocarbon, (TPH) of Nigerian crude Oil within the un-defined consortium of microbial population in the Niger Delta soils was qualitatively evaluated after the last phase of two-week enrichment technique using Gas Chromatography, GC. Table 2 shows the microbial load of the soil samples while Figures 6-11 show the chromatograms of the residuum hydrocarbons after the enrichment period.

It was observed that the biodegradation or utilization of the hydrocarbons in the crude oil by the un-defined consortium resulted in the growth of the microbial populations, as there were increases in the microbial load of both bacteria and fungi during the period of enrichment as shown in Table 2.

The results showed that all the soil samples harbored some population (consortium) of hydrocarbon degraders whose activities resulted in the biodegradation of hydrocarbons in the crude oil. Consequently, this could be the reason for the disappearance of majority of the

components of petroleum hydrocarbons. It is a strong implication that the indigenous consortium in the Niger Delta of Nigeria, though non-defined, could effectively biodegrade crude oil. This is in agreement with the result of previous work, which reported the degradation ability of indigenous microorganisms on component of petroleum hydrocarbons (Margesinet *al.*, 2003). Consequently, there is need to encourage the use of bioremediation in the region.

Table 2: Indigenous Microbial Populations in Enrichment Medium

Site Location	Site Description	Microbial Type	Phase I (cfu/g)	Phase II (cfu/g)	Phase III (cfu/g)
REE	A	Bacteria	2.00×10^8	1.60×10^9	1.50×10^{10}
		Fungi	ND	0.43×10^6	6.25×10^6
	B	Bacteria	7.2×10^8	3.18×10^9	6.00×10^{10}
		Fungi	7.50×10^6	0.93×10^6	1.05×10^7
RGK	A	Bacteria	2.35×10^8	2.40×10^9	5.00×10^{10}
		Fungi	1.35×10^6	3.30×10^6	5.75×10^6
	B	Bacteria	7.18×10^8	7.00×10^9	2.00×10^{10}
		Fungi	7.40×10^6	3.37×10^6	5.50×10^6
RTP	A	Bacteria	3.45×10^8	8.25×10^9	5.00×10^{10}
		Fungi	3.65×10^6	2.70×10^6	1.25×10^7
	B	Bacteria	5.93×10^8	1.20×10^9	5.50×10^{10}
		Fungi	3.35×10^6	2.98×10^6	1.75×10^7

Key: A-uncontaminated soil, B- contaminated soil, RTP-Tai (Pete), REE-Ebubu(Eleme) and RGK-Gokana.

The analysis of crude oil hydrocarbons by GC-MS is a tool to evaluate the biodegradation process and can play an important role in validating the CO₂ evolution data as a tool for evaluating hydrocarbons degradability.

In comparing the chromatographic properties of the sample from different locations, control flasks (not containing soil either crude oil contaminated or not) and the experimental flasks (containing soil either crude oil contaminated, A or not, B) shown in Figures 6-11, some disappearances of the hydrocarbons could be related to abiotic factors such as weathering, dissolution, evaporation and others. A similar result was observed in some previous work (Malik and Ahmed 2012) and these factors were known to have contributed to the disappearance and decrease of significant quantities of the aliphatic and aromatic hydrocarbons particularly the fractions with low molecular weights.

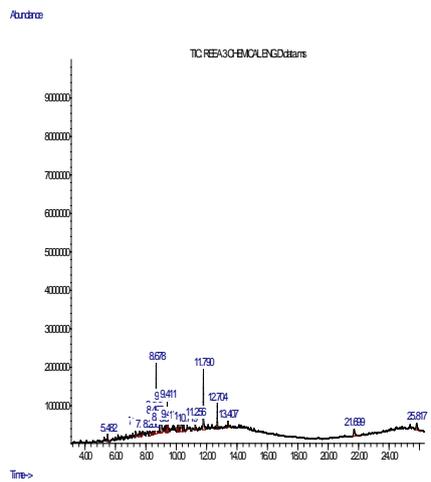


Figure 6: chromatograms of crude oil in mineral salt medium with soil sample of REEA after the last phase enrichment.

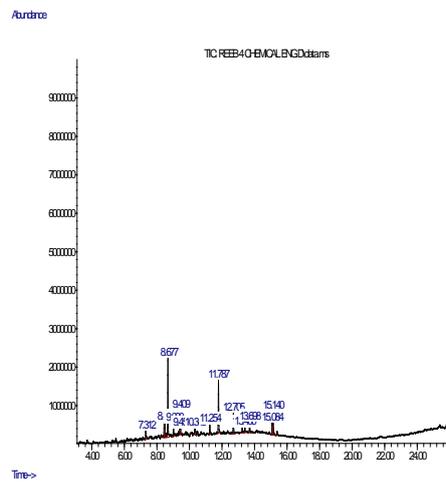


Figure 7: GC chromatograms of crude oil in mineral salt medium with soil sample of REEB after the last phase enrichment.

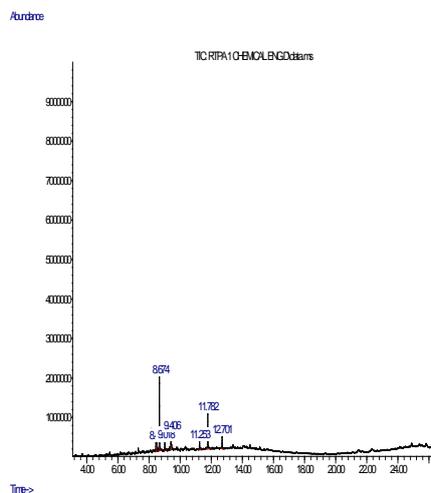


Figure 8: GC chromatograms of crude oil in mineral salt medium with soil sample of RTPA after the last phase enrichment.

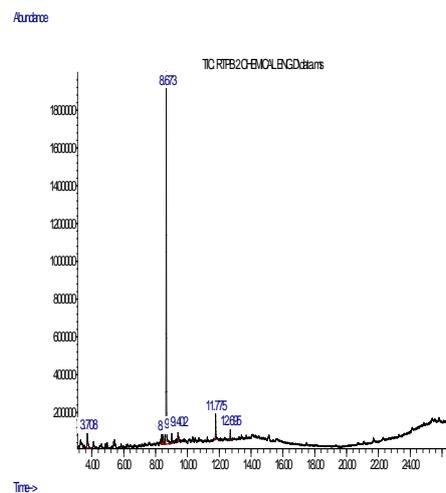


Figure 9: GC chromatograms of crude oil in mineral salt medium with soil sample of RTPB after the last phase enrichment.

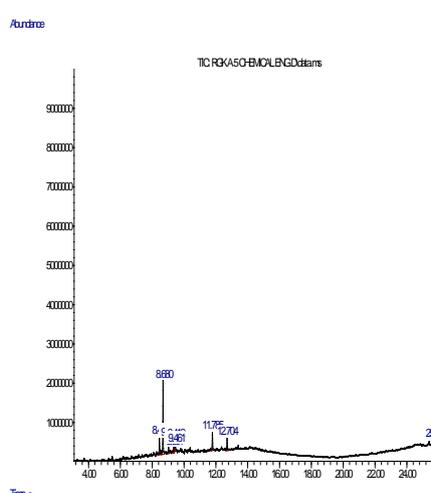


Figure 10: GC chromatograms of crude oil in mineral salt medium with soil sample of RGKA after the last phase enrichment.

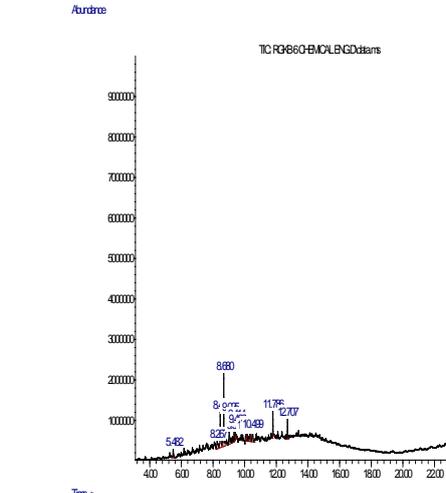


Figure 11: GC chromatograms of crude oil in mineral salt medium with soil sample of RGKB after the last phase enrichment.

Chromatographic characteristic of various soil samples showed removal or disappearance of different hydrocarbons. The degree of disappearance was found to be more in the location RGKA and RTPB, where 2, 6, 11- trimethyl dodecane and 2, 6- dimethyl heptadecane respectively were the only identified hydrocarbon peaks in chromatograms (Table 2). The 2, 6- dimethyl heptadecane was identified in every other locations except in RGKA while 2, 6, 11- trimethyl dodecane was not only found in locations such as REEA, REEB, RGKB and RTPB. This could be explained that consortium of hydrocarbon utilizing microbes present in different locations have different capabilities. Hence, there is need of bioaugmentation with selected strains to degrade the recalcitrant molecules.

The location REEB was found to have least biodegradation capability of 50 % when comparing its chromatographic properties with other locations. This could be attributed to depressed microbial activities and lower percentages of hydrocarbon utilizers observed for this location during the respiratory study and microbiological properties carried out on the site (Figure 3). Therefore, activities of the consortia as with the respiratory study validated the major observation in the disappearances of the hydrocarbons. It could be deduced that the disappearances of the hydrocarbons in the crude oil were actually proportional to the microbial activities.

Table 3: Interpretation of the Gas Chromatograph Analysis Showing Residual Hydrocarbons (After the last two weeks of degradation in enrichment)

CRUDE OIL	CONTROL	REEA	REEB	RGKA	RGKB	RTPA	RTPB
2-methyl Naphthalene	xxx						
2, 6, 10- trimethyl Dodecane							
2, 7- dimethyl Naphthalene	xxx						
1,7- dimethyl Naphthalene	xxx						
2, 3, 6- trimethyl Naphthalene	xxx	xxx	xxx		xxx		
Tridecane							
Heptadecane							
2, 6- dimethyl heptadecane	xxx	xxx	xxx		xxx	xxx	xxx
Hexadecane	xxx						
2, 6 ,11-trimethyl Dodecane	xxx			xxx		xxx	
Nonadecane							
Heptacosane							
Heneicosane							
Dodecane			xxx				
Tricosane							
Hexadecane	xxx	xxx	xxx				
Octadecane							
5- butyl docosane							
Hexacosane							
Octacosane							
% Biodegradation		62.5	50	87.5	75	75	87.5

Key: xxx- indicates Presence, A-uncontaminated soil, B- contaminated soil, RTP-Tai (Pete), REE-Ebubu (Elem) and RGK-Gokana

CONCLUSION

This study has really focused on the acquisition of knowledge of response of microbial system of some soils from Rivers State of Nigeria. It presented the biodegradation ability of the naturally present consortium of microorganisms in the samples.

It has been established that with slight exception, application of bioremediation in this region is possible.

In sites such as REE and RGK where biodegradation of the crude oil hydrocarbon components are relatively lower in comparison to RTP, there is the need to bioaugment and biostimulate the process of remediation in order to restore the environment.

ACKNOWLEDGEMENT

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REFERENCES

- Admassu, W. and Korus, R. A. (1996) Engineering of bioremediation processes: needs and limitations. In: *bioremediation: Principles and Applications*, ed. R. L. Crawford and D. L. Crawford, pp 13- 34. Cambridge University press, New York.
- Akpofure, E. A., Efere M. L. and Ayawei, P. (2001): Oil spillage in Nigeria's Niger Delta
- Amund, O. O., Adebowale, and Ugoji, E. O. (1987): Occurrence and Characteristic of Hydrocarbon-Utilizing Bacteria in Nigeria Soils Contaminated with Spent Motor Oil. *India Journal of Microbiology*, 27, 63-67.
- Bicca, F.C., Fleck, L.C. and Ayub, M.A.Z. (1999): Production of biosurfactant by hydrocarbon degrading *Rhodococcus ruber* and *Rhodococcuserythropolis*. *Revista de Microbiologia* 30, 31-37.
- Boopathy, R. (2000) Factors Limiting Bioremediation Technologies. *Bioresource Technology* 74: 63- 67.
- Bundy, J.G., Paton, G.I. and Campbell, C.D. (2002). Microbial communities in different soil types do not converge after diesel contamination. *J. Appl. Microbiol.*, 92: 276–288.
- Critter, S. A. M, Freitas, S. S. and Airobi, C. (2004). Comparison of Microbial activity in some Brazilian Soils by microcalorimetre and respirometric methods. *Thermochimica Acta*, 410, 35-46.
- Eze, V. C. and B. N. Eze (2010) "Isolation and Characterization of Microorganisms involved in the Degradation of Refined Petroleum Products Polluted Sites in Elele, Rivers State Nigeria, *Int. Journal of Current Research*, 8: 91- 95.
- Malatova, K. (2005). Isolation and characterization of hydrocarbon degrading bacteria from environmental habitats in western New York State. A thesis of Master of Science, Department of chemistry. Rochester,
- Malik, Z. A. and Ahmed S. (2012). Degradation of petroleum hydrocarbons by oil field isolated bacterial consortium. *African Journal of Biotechnology*, 11(3), 650-658.
- Margesin, R., Labbe, D., Schinner, F., Greer, C.W. and Whyte L.G. (2003): Characterization of Hydrocarbon-Degrading Microbial populations in contaminated and Pristine Alpine Soils. *Applied and Environmental Microbiology*, 69, 3085-3092.
- Margesin, R., Zimmerbauer, A. and Schinner F. (2000). Monitoring of bioremediation by soil biological activities. *Chemosphere*, 40.339-346.
- Nwachukwu, S. C. U. (2000) Enhanced rehabilitation of tropical aquatic environment polluted with crude oil petroleum using *Candida utilis*. *Journal of Environmental Biology*, 21(3), 241-250
- Obire, O. and Anyanwu, E. C. (2009) "Impact of various Concentration of Crude oil on Fungal Populations of Soil," *Int. J. Environ. Sci. Tech.*, 6(2), 211- 218 Spring.
- Omotayo, A. E., Ojo, O. Y. and Amund, O. O. (2012) Crude oil Degradation by Microorganisms in Soil Composts. *Research Journal of Microbiology* 7(4) 209-218.
- Onifade, A.A. and F.A Abukar (2007) "Bioremediation of crude oil in the Niger Delta area of Nigeria using enhance natural attenuation" *Res. J. Anim. Sci.* 2.498-504.
- Uzoamaka, G.O., Floretta, T. and Florence, M.O. (2009) Hydrocarbon degradation potentials of indigenous fungal isolates from petroleum contaminated soils. *J. Phy. Nat. Scs.* 3(1) 1-6.

Whyte, L.G., Bourbonniere, L., Bellerose, C., Greer, C.W. and Nahir, M. (1997): Biodegradation of petroleum hydrocarbon by psychrotrophic *Pseudomonas*-strains possessing both alkane (UK) and naphthalene (nap) catabolic pathways. *Applied Environmental Microbiology*, 63, 3719-3723.

MODELING OF VELOCITY AND THERMAL BOUNDARY LAYER WITH CONJUGATE HEAT TRANSFER

Pius Okpara & Emmanuel O.B. Ogedengbe*

Energhx Research Group, Department of Mechanical Engineering, Faculty of Engineering, University of Lagos, Akoka-Yaba, Lagos, 101017, Nigeria
ogedengbe@energhx.com, gmt4popat2012@gmail.com, marc.rosen@uoit.ca

ABSTRACT: Numerical simulations of boundary layer play a significant role in the study and interpretation of physical experiments for theoretical explanations of boundary layer disturbances. Crank-Nicolson differential method, which is widely favoured for finite-difference modelling of boundary layer equations, is reviewed. The stability of this method is compared with other numerical approaches in order to establish the appropriate scheme for applications involving conjugate heat transfer between solid and fluid systems. Specific application to the analysis of cabin comfort in automobiles is anticipated.

Keywords: *Thermal, boundary layer, Velocity, Conjugate heat transfer, Crank-Nicolson method*

INTRODUCTION

Generally, fluid is defined as any substance or matter in a readily distorted form such that it deforms continuously when subjected to a shear stress or an unbalanced external force no matter how small [5]. When real fluid motions are observed carefully, two basic types of motions are seen. The first is a smooth motion in which fluid elements or particles appear to slide over each other in layers or laminae. This motion of fluid is called laminar flow. The second distinct motion is characterized by a random or chaotic motion of individual particles, eddies of different sizes are observed. This motion is called turbulent flow [11]. The influence of viscosity is dominant in the boundary layer region, especially with increasing Reynolds number. When fluid is moving over a solid surface, there is a significant impact of viscosity (and thermal conductivity) within the velocity and thermal boundary layer, particularly represented in a conjugate heat transfer system of a solid (flat plate) and a fluid. Thus the flow past a surface is divided into two regions: a region far from the surface of the body in which the effects of such fluid properties as viscosity and thermal conductivity are negligible and a region close to the surface where these properties are not negligible. This thin layer of fluid in which the effects of viscosity and thermal conductivity are important is called a boundary layer [9]. If one is interested in fluid momentum, Boundary layer can be described as a region where fluid particles' local velocity, u_0 is 99% of the free stream velocity of the ambient fluid, u_∞ [2]. Studies on boundary layer flows have significantly increased our understanding of effective velocity and temperature within the zone of the boundary layer. In view of its importance, boundary layer flow over a moving surface with temperature dependent viscosity has been taken up in the present study. In many practical fields, there are significant temperature differences between the surface of the hot body and the free stream. These temperature differences cause density gradients in the fluid medium. This means that the boundary layer flow should not be confined to fluid with uniform viscosity. It is known that this physical property may change significantly with temperature. Conjugate heat transfer (CHT) is the process regarding the interaction between the heat conduction inside the solid body and the heat transfer in the surrounding fluid.

Boundary layer flows form one of the most important pillars in modern computational fluid dynamics [10]. The fundamental governing equations of fluid dynamics are the cornerstone of computational fluid dynamics. These governing equations are the continuity equation: $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$ [3], momentum equations:

$$U \frac{\partial u}{\partial x} + V \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \text{ and } U \frac{\partial v}{\partial x} + V \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) [1][13]$$

and finally, energy equations: $U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial x^2} + \frac{u(T)}{\rho C_p} \frac{\partial^2 T}{\partial y^2}$ [4]. They are the mathematical statements of the conservation laws of physics upon which all fluid dynamics is based. (The first law of thermodynamics) [8].

In recent years studies on boundary layer theory have been on the increase due to their wide range of applications in engineering and in industry such as in high speed flows (fighter aircrafts), in industrial flow e.g. conveyor belts [6][7]. Flows over moving at surfaces have found vast applications in high speed flows in nuclear reactors, pollutants emission in refineries, materials handling in industries [12]. Thus the results of boundary layer flow over moving at surface with temperature dependent viscosity will no doubt find its application in these and similar areas. Most importantly, this study will form the basis for further mathematical studies on such boundary layer flows. With this enormous significant increase in applications, it is imperative that this present study is undertaken. This study, will investigate boundary layer flow over moving flat surface with temperature dependent viscosity with the notion of solving the velocity and thermal boundary layer equation in laminar flow by discretizing the equation using the Finite-Volume Method and then does the simulation using Visual studio.

METHODS

2.1 Model Development

We consider model formulation of steady, two-dimensional flow in the (x, y)-plane in Cartesian coordinates. Consider the fluid flow geometry for a boundary layer flow over a moving flat surface (Car headliner or roof in Fig. A) with temperature dependent viscosity fluid flowing over it (moist, water or air).

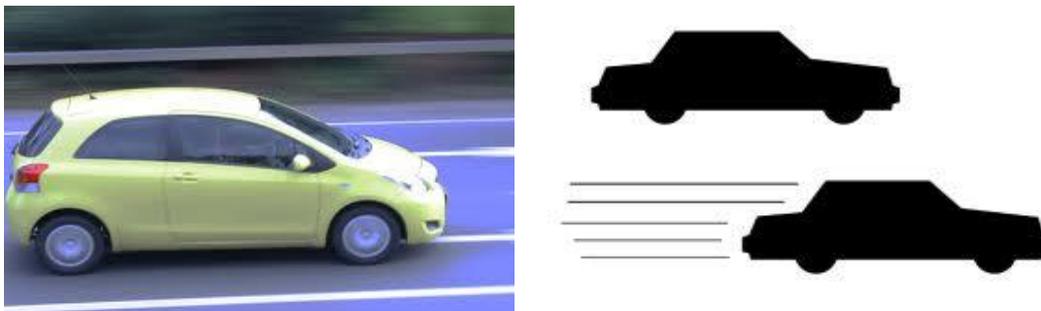


Figure A: Schematic view of a car in motion.

The boundary layer thickness, $\sigma(x)$ is as shown below.

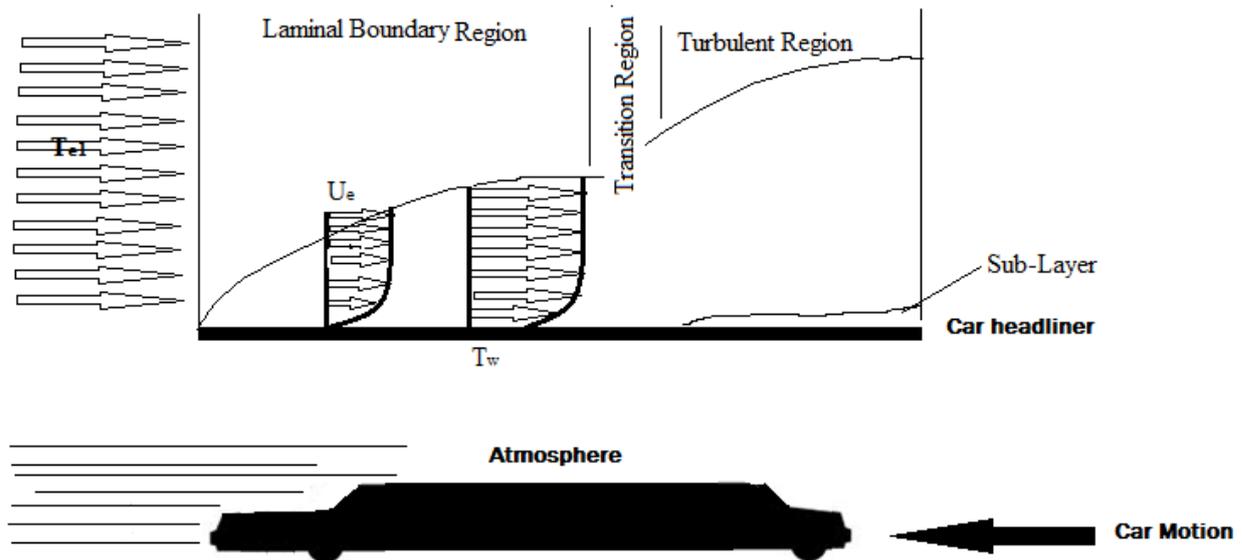


Figure B: Velocity and Thermal Boundary layer flow geometry with conjugate heat transfer on a moving car model.

2.2 Governing Equation

The governing boundary layer equations of the flow will be transformed to a dimensionless system of equations using a similarity variable (x,y) . The resulting set of coupled non-linear ordinary differential equations will be solved numerically by applying shooting iteration technique with Crank-Nicolson approach.

We consider the following conditions:

- ✓ Steady flow
- ✓ Two-dimensional flow
- ✓ Laminar boundary layer flow
- ✓ Viscous incompressible Newtonian fluid
- ✓ Moving flat surface with variable plate velocity (Car headliner or roof), $U_p(x)$ and streaming free stream edge velocity $U_e(x)$ parallel to the surface.
- ✓ No suction and injection at the solid surface. This means that $v(x; 0) = V(x; 1) = 0$.
- ✓ The temperature of the flat surface, T_w is assumed to be uniform.
- ✓ Boundary layer flow over a moving flat surface with temperature dependent viscosity, the viscous term, μ , is temperature dependent hence it is now given by $\mu(T)$.

Following Ling and Dybbs model [14] this temperature dependent dynamic viscosity is given by:

$$\mu(T) = \frac{\mu_{\infty}}{1 + \tau(T - T_{\infty})} \quad (1)$$

Two dimensional boundary layer equations for boundary layer flow over a moving at surface with temperature dependent viscosity are given by:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad \text{Continuity Equation} \quad (2)$$

$$U \frac{\partial u}{\partial x} + V \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \frac{\partial^2 u}{\partial y^2} \quad \text{x-Momentum Equation} \quad (3)$$

$$0 = -\frac{1}{\rho} \frac{\partial p}{\partial y} \quad \text{y-Momentum Equation} \quad (4)$$

$$U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial x^2} + \frac{\mu(T)}{\rho C_p} \frac{\partial^2 T}{\partial y^2} \text{Energy equation} \quad (5)$$

Boundary conditions:

1. at the wall: $u(x; 0) = U_p(x)$; $v(x; 0) = 0$; $T(x; 0) = T_w$
2. at the edge: as $y \rightarrow \infty$; $u(x; \infty) = U_e(x)$; $v(x; \infty) = 0$; $T(x; \infty) = T_\infty$

Y-momentum equation analysis: Pressure across the boundary layer and edge are constant.

$$\text{i.e.} \quad \frac{\partial p}{\partial y} = \frac{\partial T}{\partial y} = 0 \quad \text{implies } p = p(x).$$

Therefore:

$$-\frac{1}{\rho} \frac{dp}{dx} = U_e \frac{\partial U_e}{\partial x} \quad (6)$$

X-direction boundary layer equation becomes:

$$U \frac{\partial u}{\partial x} + V \frac{\partial u}{\partial y} = U_e \frac{\partial U_e}{\partial x} + \frac{1}{\rho} \frac{\partial}{\partial y} \left(\mu(T) \frac{\partial u}{\partial y} \right) \quad (7)$$

We assume power law variations in $U_p(x)$ and $U_e(x)$, i.e

$$U_p(x) = X^n U_w \quad (8)$$

$$U_e(x) = X^n U_\infty \quad (9)$$

Where:

U_∞ And U_w are constant reference velocities

Pressure gradient is given as:

$$n = \frac{x}{U(x)} \frac{dU(x)}{dx} \quad (10)$$

Where:

$$U_x = (U_\infty + U_w) X^n = B_0 X^n; \quad (11)$$

$$B_0 = U_w + U_\infty \quad (12)$$

Since both the fluid and the surface are moving. This means that we consider the boundary layer flow at a specific given local point. Therefore, we deal with local variables and in non-dimensional terms, we define the Reynolds number based on distance x along the wall, hence this local Reynolds number is given by:

$$Re_x = \frac{U(x) \cdot x}{\nu} = \frac{\rho U(x) \cdot x}{\mu_\infty} \quad (13)$$

2.3 resolving the Velocity Boundary Layer Using Finite Volume Method

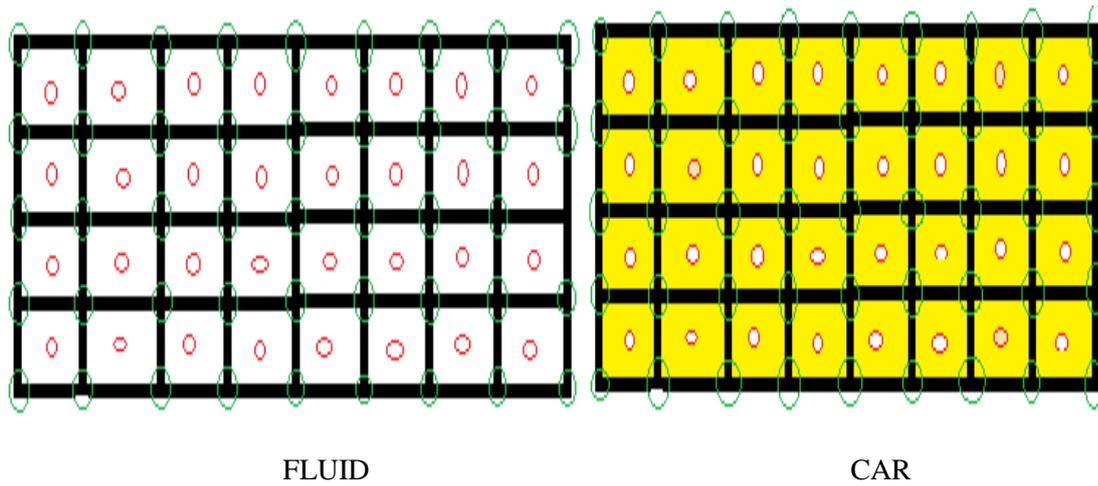


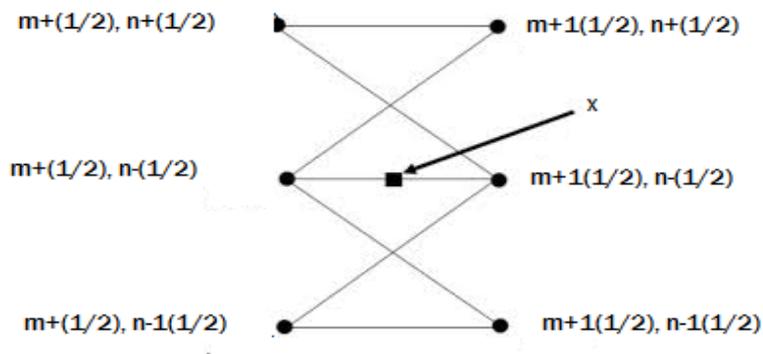
Figure C: Discretization of the flowing fluid and overhead roof computational domain.

Where:

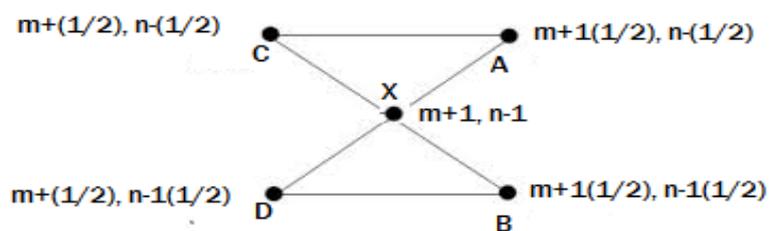
 Or  is the control Volume

 Are the grid nodes (boundary nodes)

 Are the finite volume computational nodes



(a)

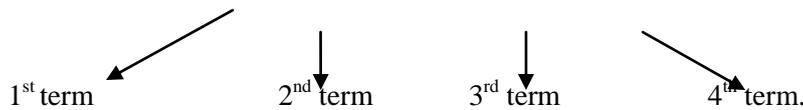


(b)

Figure 4: (a) momentum equation molecule and (b) continuity equation molecule

STEP 1. Discretizing Momentum Dimensionless Equation

$$f'_i \xi_i \frac{f'_i}{\xi_i} + \bar{V}_i \frac{\partial f'_i}{\partial \eta} = (1 - f'^2_i) \beta_i + \frac{\partial^2 f'_i}{\partial \eta^2}$$



1ST Term: $f'_i \xi_i \frac{f'_i}{\xi_i}$

$$\xi f' \frac{\partial f'}{\partial \xi} \approx \frac{\xi_{m+1} f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \left[f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} - f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \right]}{\Delta \xi} \quad (14)$$

2ND Term: $\bar{V}_i \frac{\partial f'_i}{\partial \eta}$

$$\bar{V} \frac{\partial f'}{\partial \eta} \approx \frac{1}{2} \bar{V}_{m+(\frac{1}{2}),n-(\frac{1}{2})} \left(\frac{f'_{m+(\frac{1}{2}),n+(\frac{1}{2})} - f'_{m+(\frac{1}{2}),n-(\frac{1}{2})}}{2\Delta \eta} + \frac{f'_{m+(\frac{1}{2}),n+(\frac{1}{2})} - f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})}}{2\Delta \eta} \right) \quad (15)$$

3RD Term: $(1 - f'^2_i) \beta_i$

$$\beta(1 - f'^2) = \beta_{m+1} \left(1 - f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \cdot f'_{m+(\frac{1}{2}),n-(\frac{1}{2})} \right) \quad (16)$$

4TH Term: $\frac{\partial^2 f'_i}{\partial \eta^2}$

$$\frac{\partial^2 f'}{\partial \eta^2} \approx \frac{1}{2} \left[\frac{f'_{m+(\frac{1}{2}),n+(\frac{1}{2})} - 2f'_{m+(\frac{1}{2}),n-(\frac{1}{2})} + f'_{m+(\frac{1}{2}),n-(\frac{1}{2})}}{(\Delta \eta)^2} + \frac{f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} - 2f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} + f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})}}{(\Delta \eta)^2} \right] \quad (17)$$

NOTE: The following are very important:

- ❖ The essence of averaging $\frac{\partial f}{\partial \eta}$ at point m and m+1 is the essential characteristics of the Crank-Nicolson method.
- ❖ We discretized in order to linearize continuity and momentum equation.
- ❖ Linear function f' at m+1 are known
- ❖ The only known value of transformed momentum equation is $\bar{V}_{m,n}$

- ❖ The known value of $\bar{V}_{m,n}$ allow us to solve for f' in the transformed momentum equation, then we used the value of \bar{V} gotten to evaluate the transformed continuity equation to get \bar{V} .
- ❖ The crank-nicolson method is implicit because we solve for all the value of f' at all times.
- ❖ Implicit methods are known to be very stable and it allows large step sizes in the ξ_1 direction with good accuracy.

Putting the terms expression together, we have:

$$\frac{\xi_{m+1} f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \left[f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} - f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \right]}{\Delta \xi} + \frac{1}{2} \bar{V}_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \left(\frac{f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} - f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})}}{2\Delta \eta} + \frac{f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} - f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})}}{2\Delta \eta} \right) = \beta_{m+1} (1 - f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \cdot f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})}) + \frac{1}{2} \left[\frac{f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} - 2f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} + f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})}}{(\Delta \eta)^2} + \frac{f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} - 2f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} + f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})}}{(\Delta \eta)^2} \right] \quad (18)$$

Equation 18 is called the finite volume momentum equation and it contains an unknown $f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})}$, $f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})}$, and $f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})}$ which has the form:

$$A_{m+(\frac{1}{2}),n-(\frac{1}{2})} f'_{m+1(\frac{1}{2}),n+(\frac{1}{2})} + B_{m+(\frac{1}{2}),n-(\frac{1}{2})} f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} + C_{m+(\frac{1}{2}),n-(\frac{1}{2})} f'_{m+1(\frac{1}{2}),n-1(\frac{1}{2})} = D_{m+(\frac{1}{2}),n-(\frac{1}{2})} \quad (19)$$

On comparing the coefficient :

$$A_{m+(\frac{1}{2}),n-(\frac{1}{2})} = \frac{V_{m+(\frac{1}{2}),n-(\frac{1}{2})}}{4\Delta \eta} - \frac{1}{2(\Delta \eta)^2}$$

$$B_{m+(\frac{1}{2}),n-(\frac{1}{2})} = \xi_{m+1} f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} \frac{1}{\Delta \xi} + \beta_{m+1} f'_{m+1(\frac{1}{2}),n-(\frac{1}{2})} + \frac{1}{(\Delta \eta)^2} \quad (20)$$

$$C_{m+(\frac{1}{2}),n-(\frac{1}{2})} = - \left\{ \frac{V_{m+(\frac{1}{2}),n-(\frac{1}{2})}}{4\Delta \eta} + \frac{1}{2(\Delta \eta)^2} \right\}$$

$$D_{m+(\frac{1}{2})n-(\frac{1}{2})} = \beta_{m+1} + \xi_{m+1} f'_{m+(\frac{1}{2})n-(\frac{1}{2})} \frac{1}{\Delta \xi} - \bar{V}_{m+(\frac{1}{2})n-(\frac{1}{2})} \frac{f'_{m+(\frac{1}{2})n+(\frac{1}{2})} - f'_{m+(\frac{1}{2})n-1(\frac{1}{2})}}{4\Delta \eta}$$

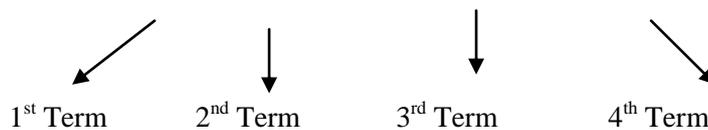
$$+ \frac{f'_{m+(\frac{1}{2})n+(\frac{1}{2})} - 2f'_{m+(\frac{1}{2})n-(\frac{1}{2})} + f'_{m+(\frac{1}{2})n-1(\frac{1}{2})}}{4\Delta \eta}$$

Since at $m+1(1/2)$ level (A, B and C), f' are unknown and at point $m+(1/2)$, f' are known then, it is possible to drop the $m + (\frac{1}{2})$ and $m + 1(1/2)$ notation. Therefore, we have:

$$A_{n-(\frac{1}{2})} f'_{n+(\frac{1}{2})} + B_{n-(\frac{1}{2})} f'_{n-(\frac{1}{2})} + C_{n-(\frac{1}{2})} f'_{n-1(\frac{1}{2})} = D_{n-(\frac{1}{2})} \quad (21)$$

STEP 2. Discretizing Continuity Dimensionless Equation

$$\xi \frac{\partial f'}{\partial \xi} + \beta f' + \frac{\eta}{2} (\beta - 1) \frac{\partial f'}{\partial \eta} + \frac{\partial V}{\partial \eta} = 0$$



1ST Term: $\xi \frac{\partial f'}{\partial \xi}$

$$\xi \frac{\partial f'}{\partial \xi} = \frac{1}{2} \xi_{m+1} \left\{ \frac{f'_{m+1(\frac{1}{2})n-(\frac{1}{2})} - f'_{m+(\frac{1}{2})n-(\frac{1}{2})}}{\Delta \xi} + \frac{f'_{m+1(\frac{1}{2})n-1(\frac{1}{2})} - f'_{m+(\frac{1}{2})n-1(\frac{1}{2})}}{\Delta \xi} \right\} \quad (22)$$

2ND Term: $\beta f'$

$$\beta f' = \frac{1}{4} \beta_{m+1} \left\{ f'_{m+(\frac{1}{2})n-(\frac{1}{2})} + f'_{m+(\frac{1}{2})n-1(\frac{1}{2})} + f'_{m+1(\frac{1}{2})n-(\frac{1}{2})} + f'_{m+1(\frac{1}{2})n-1(\frac{1}{2})} \right\} \quad (23)$$

3RD Term: $\frac{1}{2} \eta (\beta - 1) \frac{\partial f'}{\partial \eta}$

$$\frac{1}{2} \eta (\beta - 1) \frac{\partial f'}{\partial \eta} = \frac{1}{4} \eta_{n-1} (\beta_{m+1} - 1) \left\{ \frac{f'_{m+(\frac{1}{2})n-(\frac{1}{2})} - f'_{m+(\frac{1}{2})n-1(\frac{1}{2})}}{\Delta \eta} + \frac{f'_{m+1(\frac{1}{2})n-(\frac{1}{2})} - f'_{m+1(\frac{1}{2})n-1(\frac{1}{2})}}{\Delta \eta} \right\} \quad (24)$$

4TH Term: $\frac{\partial V}{\partial \eta}$

$$\frac{\partial V}{\partial \eta} = \frac{1}{2} \left\{ \frac{V_{m+\frac{1}{2},n-\frac{1}{2}} - V_{m+\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} + \frac{V_{m+1\frac{1}{2},n-\frac{1}{2}} - V_{m+1\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} \right\} \quad (25)$$

Substituting the finite difference equations in equation (23) to (26) into continuity equation, we have:

$$\begin{aligned} & \frac{1}{2} \xi_{m+1} \left\{ \frac{f'_{m+1\frac{1}{2},n-\frac{1}{2}} - f'_{m+\frac{1}{2},n-\frac{1}{2}}}{\Delta \xi} + \frac{f'_{m+1\frac{1}{2},n-1\frac{1}{2}} - f'_{m+\frac{1}{2},n-1\frac{1}{2}}}{\Delta \xi} \right\} + \frac{1}{4} \beta_{m+1} \left\{ f'_{m+\frac{1}{2},n-\frac{1}{2}} + \right. \\ & \left. f'_{m+\frac{1}{2},n-1\frac{1}{2}} + f'_{m+1\frac{1}{2},n-\frac{1}{2}} + f'_{m+1\frac{1}{2},n-1\frac{1}{2}} \right\} + \frac{1}{4} \eta_{n-1} (\beta_{m+1} - 1) \left\{ \frac{f'_{m+\frac{1}{2},n-\frac{1}{2}} - f'_{m+\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} + \right. \\ & \left. \frac{f'_{m+1\frac{1}{2},n-\frac{1}{2}} - f'_{m+1\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} \right\} + \frac{1}{2} \left\{ \frac{V_{m+\frac{1}{2},n-\frac{1}{2}} - V_{m+\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} + \frac{V_{m+1\frac{1}{2},n-\frac{1}{2}} - V_{m+1\frac{1}{2},n-1\frac{1}{2}}}{\Delta \eta} \right\} = \\ & 0 \end{aligned} \quad (26)$$

Everything variables are known in equation (26) except, $V_{m+1\frac{1}{2},n-\frac{1}{2}}$. Collecting like terms, the equation above becomes;

$$\begin{aligned} V_{m+1\frac{1}{2},n-\frac{1}{2}} = & V_{m+1\frac{1}{2},n-1\frac{1}{2}} + V_{m+\frac{1}{2},n-1\frac{1}{2}} - V_{m+\frac{1}{2},n-\frac{1}{2}} + 2\Delta \eta \left[\left(-\frac{1}{4} \beta_{m+1} - \right. \right. \\ & \left. \frac{1}{2\Delta \xi} \xi_{m+1} - \frac{1}{4\Delta \eta} \eta_{n-1} (\beta_{m+1} - 1) \right) f'_{m+1\frac{1}{2},n-\frac{1}{2}} + \left(-\frac{1}{4} \beta_{m+1} - \frac{1}{2\Delta \xi} \xi_{m+1} + \frac{1}{4\Delta \eta} \eta_{n-1} (\beta_{m+1} - \right. \\ & \left. 1) \right) f'_{m+1\frac{1}{2},n-1\frac{1}{2}} + \left(-\frac{1}{4} \beta_{m+1} + \frac{1}{2\Delta \xi} \xi_{m+1} - \frac{1}{4\Delta \eta} \eta_{n-1} (\beta_{m+1} - 1) \right) f'_{m+\frac{1}{2},n-\frac{1}{2}} + \\ & \left. \left(-\frac{1}{4} \beta_{m+1} + \frac{1}{2\Delta \xi} \xi_{m+1} + \frac{1}{4\Delta \eta} \eta_{n-1} (\beta_{m+1} - 1) \right) f'_{m+\frac{1}{2},n-1\frac{1}{2}} \right] \end{aligned} \quad (27)$$

For the purpose of simplification, four new variables are in introduced called the continuity equation coefficients, on comparing with

$$\begin{aligned}
V_{m+1\left(\frac{1}{2}\right),n-\left(\frac{1}{2}\right)} &= V_{m+1\left(\frac{1}{2}\right),n-1\left(\frac{1}{2}\right)} + V_{m+\left(\frac{1}{2}\right),n-1\left(\frac{1}{2}\right)} - V_{m\left(\frac{1}{2}\right),n-\left(\frac{1}{2}\right)} \\
&+ 2\Delta\eta \left[(A_n^c) f'_{m+1\left(\frac{1}{2}\right),n-\left(\frac{1}{2}\right)} + (B_n^c) f'_{m+1\left(\frac{1}{2}\right),n-1\left(\frac{1}{2}\right)} + (C_n^c) f'_{m+\left(\frac{1}{2}\right),n-\left(\frac{1}{2}\right)} \right. \\
&\left. + (D_n^c) f'_{m+\left(\frac{1}{2}\right),n-1\left(\frac{1}{2}\right)} \right]
\end{aligned}$$

We have;

$$\begin{aligned}
A_n^c &= -\frac{1}{4}\beta_{m+1} - \frac{1}{2\Delta\xi}\xi_{m+1} - \frac{1}{4\Delta\eta}\eta_{n-1}(\beta_{m+1} - 1) \\
B_n^c &= -\frac{1}{4}\beta_{m+1} - \frac{1}{2\Delta\xi}\xi_{m+1} + \frac{1}{4\Delta\eta}\eta_{n-1}(\beta_{m+1} - 1) \quad (28) \\
C_n^c &= -\frac{1}{4}\beta_{m+1} + \frac{1}{2\Delta\xi}\xi_{m+1} - \frac{1}{4\Delta\eta}\eta_{n-1}(\beta_{m+1} - 1) D_n^c \\
&= -\frac{1}{4}\beta_{m+1} + \frac{1}{2\Delta\xi}\xi_{m+1} + \frac{1}{4\Delta\eta}\eta_{n-1}(\beta_{m+1} - 1)
\end{aligned}$$

From the boundary condition equation $V_1 = 0$ when $n = 1$, \bar{V} is related to V by the algebraic equation given as;

$$\bar{V} = \frac{\eta}{2}(\beta - 1)f' + V \quad (29)$$

Matrix Laboratory (MATLAB) or VISUAL BASIC could be the mathematical programming that can be used to solve the boundary layer equation in order to obtain the horizontal and vertical velocity distribution. The calculation proceeds in so many manner until all the values for f' and V have been obtained for the entire computational domain. Effects of various parameters of the flow such as velocity ratio and viscosity variation parameter will be investigated. Stability analysis will also be considered. Application of these studies include: high speed flows, pollutants emission, conveyor belts for materials handling, aerodynamics (airplanes, rockets, projectiles), hydrodynamics (ships, submarines, torpedoes), transportation (automobiles, trucks, cycles), wind engineering (buildings, bridges, water towers), and ocean engineering (buoys, breakwaters, cables)

CONCLUSION AND DISCUSSION

In this work, general overview of the project topic has been well understood at this half stage of the project which gave us a stepping approach finite volume method of velocity boundary layer solution using crank-nicolson approach in the methodology. We optimistic of a successful result at the final stage of approached methodology. The mathematical modeling relation has been well established.

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REFERENCES

1. Anderson, J. D. Jr., (1995 and 2005), Computational Fluid Dynamics: The Basics with Applications, McGraw-Hill Inc., New York.
2. Cengel, A.Y, Cimbala, J.M, (2006), Fluid Mechanics: Fundamentals and Applications, McGraw-Hill Inc., New York.
3. Cebeci, T, Cousteix, J, (2005), Modelling and Computation of Boundary Layer Flows, New Horizons Publishing, California.
4. Chorin, A.J, Marsden, J.E, (1992), A Mathematical Introduction to Fluid Mechanics, Springer Verlag, New York Inc.
5. McDonough, J. M,(2009), Lectures in Elementary Fluid Dynamics: Physics, Mathematics and Applications, University of Kentucky, Lexington, KY 40506-0503.
6. Mureithi, E. W, Mason, D. P, (2010), Local Non-Similarity Solutions For a Forced-Free Boundary Layer Flow With Viscous Dissipation, Mathematical and Computational Applications, Vol. 15, No. 4, pp 558-573.
7. Mureithi, E. W, Mason, D. P, (2001), On the Stability of a Forced-Free Boundary Layer Flow With Viscous Heating, Fluid Dynamics Research, vol. 31, pp 65-78.
8. Pozrikidis, C, (2009), Fluid Dynamics: Theory, Computation and Numerical Simulations, Springer-Verlag, New York.
9. Rodgers, D. F, (1992), Laminar Flow Analysis, Cambridge University Press, Cambridge.
10. Schlichting, H, Gersten, K, (2000), Boundary Layer Theory, Springer-Verlag, Berlin.
11. Shivamoggi, B.K, (1997), Theoretical Fluid Dynamics, John Wiley & Sons Inc, New York.
12. Zarrini, M., Pralhad, R. N (2010), Numerical Investigation of two-dimensional Boundary Layer Flow Over a Moving Surface, International Journal of Mathematical and Computer Sciences
13. Versteeg, H.K, Malalasekera, W, (1995), An Introduction to Fluid Dynamics: The Finite Volume Method, Addison Wesley Longman Ltd, London.
14. Hossain, A, Munir, S, (2000), Mixed Convection Flow From a Vertical Flat Plate With Temperature Dependent Viscosity, International Journal of Thermal Science, Vol. 39, pp 173-183.
15. Ali, M. E, (2006), The Effects of Variable Viscosity On Mixed Convection HeatTransfer Along a Vertical Moving Surface, International Journal Of Thermal Science, vol. 45, pp 60-69.

SOLVENT– INITIATOR COMPATIBILITY AND SENSITIVITY OF CONVERSION OF STYRENE HOMO-POLYMERIZATION

Kehinde A. J, Usman M. A & Owolabi R. U.*

University of Lagos, Chemical Engineering Department, Akoka, Yaba, Lagos, Nigeria
uthmanrash642@yahoo.com

ABSTRACT

In this study, efforts were made to synthesize vinyl polymers (Polystyrene, PS) using free radical solution polymerization. Four common solvents with dissimilar polarity; acetone, chloroform, benzene and toluene and two different initiators were finally selected after prior screening based on past experiences. The homo-polymerization was conducted in an ace round-bottom pressure flask of diameter 62 mm with thermo well which housed the thermometer. The reaction temperature was maintained at 120 °C using heater with temperature controller coupled with a magnetically driven stirrer. One hundred experimental runs of 8 different groups were carried out. Polymerization was conducted in the mass concentration of 0.1g for each initiator (Benzoyl Peroxide and its Blend). The key parameter considered is the volume ratio of Monomer to solvents under different types of solvents, initiators and reaction times. Initially, there was increase in conversion with solvent volume and time until at certain points where there was gradual decline in monomer conversion. Polymerization rate and monomer conversion were observed to be higher in polar solvents (acetone). Further presented in this study is the macromolecular architecture (molecular weight) and micro-structure of some of the solution polymerized monomer. A Kinetic model was also presented to predict the conversion with time profile of the polymerization process. Molecular weight determined were between acceptable ranges while the model presented though with considerable error margin but seems to respond just fairly at extremely low monomer conversion. Similar response was observed from earlier model reported in literature when tested with our experimental data.

Keywords: Vinyl polymers, Free radical, Solution Polymerization, Homo-Polymerization, Polarity.

INTRODUCTION

The serious growing trends in demands of polymers have challenged the status of the present digital age as plastic age. In terms of needs, polystyrene (PS) remains one of the giant fulcrums in the polymer industry. PS was first produced in 1930 by Dow and BASF in USA [1]. It is one of the most widely used thermoplastic in a variety of industrial applications such as packaging, consumer electronics, appliances and medical devices. After polyethylene, PS is among the widely produced polymer globally [1]. In 1996, world production capacity for styrene was near 19.2 million metric tonnes per year. Dow Chemical is the world's largest producer with a total capacity of 1.8 million metric tonnes in the USA, Canada, and Europe [2]. Asia is the overall leader in production and consumption of polystyrene, with 53% of total world production and 47% of total consumption of polystyrene in 2010. North America and Western Europe follow distantly at about 17–19% of the total production and consumption each. Asian consumption of all types of polystyrene is forecast to increase at an average annual rate of slightly over 3% during 2010–2015. Demand for polystyrene is driven by China which is the largest electronics and the second largest packaging industry in the world [3]. In the last decades, polymers were not only used as industrial bulk materials but also attracted great attention in high technology fields, e.g. nanotechnology, optics and biomaterials [4]. Each usage requires different

specifications for the polymers. Jones et al [5] in his report revealed the global trends in polymer production in the last six decades till recent time while the programme conducted by PERP program [6] specifically shows the PS end use consumption. Ring [7] report on PS similarly shows the PS production on selected country basis. The inference from the above trend is that to an industrialist, the most important reaction of styrene is reaction of styrene with itself.

The last three decades have witnessed already extensive investigation in the area of vinyl monomers homo-polymerization reaction engineering, most studies coming from both the Euro-American and the Asian researchers within the research circle of Chemistry, Material, Chemical and Polymer Engineering. Still, a formidable challenge remains by virtue of a bias trend noticed as voluminous part of the previous studies focused primarily on reactor and catalyst design for the polymerization process, its catalytic kinetics including subsequent models development capable of describing the reaction behaviour.

However, as an exemption from the above trend, the main production of PS is conducted by bulk and suspension free radical polymerization [8-10]. Malkin [11] used a series of alkyl methacrylates and styrene with a benzoyl peroxide initiator to study rheokinetics of polymer system. The research focused on the effects of initial concentration of initiator, reaction temperature, and time on the viscosity of the polymer system. Tefera [12] also investigated, both experimentally and theoretically, the free-radical suspension polymerization of styrene at different temperatures (i.e., 70 °C, 75 °C, and 80 °C) and initiator concentrations (i.e., AIBN: 0.15–0.45 wt.-% of styrene). Devonport [13] revisited the thermal initiation of styrene in the presence of TEMPO at 125 °C. They showed that low polydispersities and controlled molecular weights could be achieved under these conditions, although the degree of control was not as good as for unimolecular or bimolecular initiating systems. In recent years, [14] intensified research on styrene polymerization using supercritical CO₂ as a green solvent. RasulJhan [15] 2008 successfully investigated the performance of base catalysts (MgO, BaO, and CaO) on the degradation of polystyrene to styrene monomer where special focus was placed on mixing the catalyst with polystyrene particles in a reactor to increase the rate of degradation. Michael [16] 1997 studied the effect of free radical propagation rate coefficients of both methyl methacrylate (MMA) and styrene using Pulsed-Laser polymerization. The data reported in their article strongly supports the existence of either a radical-solvent or radical-monomer complex participating in the propagation reaction by modifying the reactivity of the reactants. The statement of [17] on the right use of initiator serves as our impetus for this study. Our interest in this study is to further investigate the use of varieties of initiators and solvents in improving the conversion of styrene to PS, achieving polymers of desired molecular weight and to create a link between the solvent properties and the polymer formation at any point in time under varied conditions.

METHODS

- ***Stage (i) : Reagents and Apparatus***

The under listed were the reagents and apparatus used during the experimental stage. All the glass wares prior to polymerization were inspected to ascertain that there was no trace of dirt or remnants of materials. Glass reactor was preferred to stainless steel in this study to actually view and monitor the reaction as it progresses and to further prevent radical reaction interference with the alloy wall (Fe, Cr, Ni, C) of the stainless steel

reacting vessel. A 100 ml Ace round-bottom pressure flask with thermo-well was used as the reactor and can withstand a maximum pressure of 60 psig at 120 °C. All the reagents used were of analytical grade, purchased from Sigma Aldrich in Germany and used as received except for styrene monomer which was de-stabilized.

Apparatus: Heater with a magnetic stirrer, Ace round-bottom pressure flask with thermo-well, Petri dish, Beakers, Separating funnel, Glass rod, Ubbelohde Viscometer, Measuring Cylinder, Stop watch, Water bath, Thermometer.

Reagents: Styrene (99%) inhibited by 10–15 ppm 4-tertbutylcatechol, Benzoyl Peroxide (75%), Benzoyl peroxide blend with dicyclohexylphthalate (contains 0.5% water), Methanol (CH₃OH) (99.8%), Sodium Sulphate (Na₂SO₄) (99%), Sodium Hydroxide (NaOH) (98%), Acetone (99.9%), Chloroform (CHCl₃) (99%), Benzene (99%) and Toluene (99.8%).

- **Stage (ii) : De-stabilization of the styrene monomer**
All the reagents were used as purchased without further purification except the styrene monomer which was de-stabilised. The removal was done as stated below following the report of [18]. The styrene monomer (100 ml) which contains a phenol (often 4-tert-butylcatechol) as a polymerization inhibitor was added to 100 mL of 10% NaOH solution. The mixture was strongly agitated and was allowed to settle by gravity in a separating funnel. The bottom layer consisting of the inhibitor was carefully drained off. The styrene was dried over anhydrous Na₂SO₄. As the sodium sulphate binds with any water that is present, it clumped after some minutes.
- **Stage (iii): Polymerization of styrene**
The reaction initiators include benzoyl peroxide and benzoyl peroxide blend with dicyclohexylphthalate while acetone, chloroform, benzene and toluene were the solvents used. Specific amount of each initiator and styrene monomer (constant throughout) were dissolved in desired and varying volume of solvent at different reaction times. The solution was manually charged into the reactor. The reaction temperature was maintained at 120 °C (± 2) under agitation provided by a magnetic driven bar stirrer at a speed of about 500 rpm. The pressure equal to the vapour pressure of the reaction mixture was maintained. After 10 minutes interval reaction time, the reactor was opened up, cooled to collect the resulting polymer solution.
- **Stage (iv): Polymer precipitation and solvents removal / recovery**
The clear polymer solution was added to about 2-3 ml of methanol in a beaker with continuous stirring to precipitate the polymer. The top clear solvent was decanted while the bottom polymer samples were air-dried to remove excess solvent and dried for 2 weeks at room conditions until a constant weight was reached.
- **Stage (i): Post polymerization analysis**
Monomer conversion into polymer and Polymerization rate were estimated. The synthesized PS were further subjected to solubility and density test in various solvents and molecular weight were also determined.
- **Monomer Conversion and Rate of Polymerization Estimation.**
Both the monomer conversion into polymer (x %) and rate of polymerization (R_p) were gravimetrically determined (Dried weigh method)

$$\% \text{ Conversion} = \frac{\text{Mass of Polymer}}{\text{Mass of monomer}} \times 100 \quad (1)$$

This is in form of the Mass concentration, it could also be in the form of Molar concentration

$$\begin{aligned} & \text{i.e } \% \text{ Conversion} \\ & = \frac{[\text{Polymer}]}{[\text{Monomer}]} \times 100 \quad (2) \quad \text{or in terms of volume} \end{aligned}$$

$$\% \text{ Conversion} = \frac{\text{Volume of Polymer}}{\text{Volume of Monomer}} \times 100 \quad (3)$$

We however gravimetrically calculated the polymerization rate (R_p) as

$$R_p = \frac{[\text{Polymer}]}{\text{Reaction time}} \left\{ \frac{\text{Mol}}{\text{l.s}} \right\} \quad (4)$$

$$\text{Where } [\text{Monomer}]_0 = \left[\left(\frac{\% \times \text{density of monomer}}{\text{Molecular Weight of monomer}} \right) \times 10 \right] \quad (5) \quad [19]$$

Polymer Molecular Weight Determination

The molecular weight of the polymer sample was determined using solution viscosity method found in the book of Bello [21]. Viscosities of concentrations of polymer solutions were measured with toluene as solvent at 30 °C using Ubbelohde glass viscometer. In viscosity method, the time taken for the polymer solution to flow through the capillary was compared with the time for a pure solvent. The flow time for the solvent is t_0 and that of polymer solution is t , the relative viscosity

$$\eta_r = \frac{t}{t_0} \quad (6)$$

$$\text{The specific viscosity, } \eta_{sp} = \eta_r - 1 \text{ or } \frac{t - t_0}{t_0} \quad (7)$$

The Solomon Gatesman Equation was used to determine the intrinsic viscosity

$$\eta = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{C} \quad [20] \quad (8)$$

Where C is the concentration of the sample. It is important to note that the intrinsic viscosity is not the viscosity as such but the volume per unit mass that the polymer occupies in a solution.

The Mark-Houwink-Sakurada Equation for viscosity of polyethylene and polystyrene found in the review of Herman, 1985 was used to calculate the intrinsic viscosity molecular weight.

$$\eta = KM^a \quad \frac{\text{mL}}{\text{g}} \text{ at a particular temperature} \quad [21-22] \quad (9)$$

K and a are constants which are dependent on the solvent, the type of the polymer and the temperature.

Table 2.1: Recommended Value of Mark-Houwink Constants For Polystyrene. [21]

Solvent	Temp. °C	K(ml/g) x 10 ⁻⁴	a	Molecular weight
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				Range x 10 ⁵
Toluene	-----	1.28	0.70	5.5-20.5
Toluene	-----	0.55	0.80	1.1-3.4
Toluene	-----	0.01	1.12	1.1-1.7
Toluene	30 °C	3.7	0.62	2.0-18
Butanone	40 °C	7.0	0.53	2.0-18

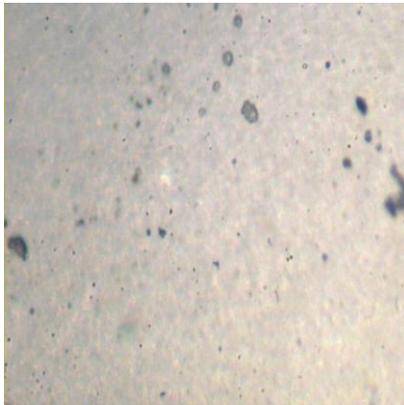


Fig 2: Microstructure of Polystyrene

Kinetic Model Development for Monomer Conversion

Considering the elementary steps shown below [24] i.e Initiation, Propagation and Termination steps, we have;

Initiation:



$$r_{R^*} = 2fk_I C_I$$

Chain Initiation:



$$r_{R^*} = -k_{CI} C_M C_{R^*}$$

Propagation:



Termination by combination:



Termination by disproportionation:



For the monomer conversion model, the following assumptions were made;

- i. Steady state approximation for radical concentration.
 - ii. Rate of initiation is equal to the rate of termination.
- Mass balance on the generated radicals gives

$$r_{R^{\bullet}} = 2fk_I C_I - k_{CI} C_M C_{R^{\bullet}} \approx 0 \quad (15)$$

$$C_{R^{\bullet}} = \frac{2fk_I C_I}{k_{CI} C_M} \quad (16)$$

Finally, we have our model as shown below

$$\ln(1 - x) = \frac{2R_P}{k_I C_M} \left[e^{-\frac{k_I t}{2}} - 1 \right] \quad (17)$$

RESULTS AND DISCUSSION

Table 1 and 2 describe the estimation of the solution viscosity molecular weight of the PS. The estimation was carried out using the Mark Houwink Sakurada equation of the form $\eta = 3.7 \times 10^{-4} \times M^{0.62}$ [21-22] at 30 °C where η is the intrinsic viscosity and M is the solution viscosity molecular weight. Solomon Gatesman equation described in Eq.8 was employed against the cumbersome graphical method for the determination of the intrinsic viscosity. Baastiaan [19] and lengthy list of researchers have satisfactorily used the equation. All the samples exhibited molecular weight within acceptable range except for sample ISC12 synthesized using chloroform as solvent which recorded a value above the acceptable range. Other samples synthesized using same solvent recorded relatively high molecular weight compared to others. However, from the behavior of our plots as shown in Fig 3 and 4, we could not actually establish any serious trend between the type of initiator, solvent used and reaction time to the molecular weight of the PS samples. The observed trend is irregular or fluctuating. This result is in contrary to the observation of Devonport [13] who had previously shown that number average molecular weights increased in an almost linear fashion with conversion. They revisited the thermal initiation of styrene in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) at 125 °C after conflicting results were reported almost simultaneously by [25-27]. Amarjit [28] also observed at ambient temperature enzyme mediated styrene polymerization that molecular weight of styrene increases with reaction time. Hui and Hamielec [29], studied the variations of number-average molecular weight with conversions at four temperatures (100, 140, 170, and 200 °C) and concluded that the molecular weights reduced throughout with the increase in conversion. Shi [30] also conducted similar study at four different temperatures (140, 160, 180, and 200 °C) and found that the number-average molecular weights did not vary significantly with conversions. The above are just few of the numerous inconsistency in molecular weight data with time or conversion. We however inspite of the above statements strongly believe in our data as report of [31] published on line in 2003 that the molecular weight of polymer formed at lower temperature increases proportionally with the reaction time. In the polymerization at 100 and 140 °C, the molecular weight is independent of reaction time. Reports from researchers globally which seem conflicting is due to the complex nature and sensitivity of polymerization reaction even to slight variations in thermodynamic conditions. Unlike simple molecules, polymers are not formed until appreciable n-1 number of self reactions has taken place.

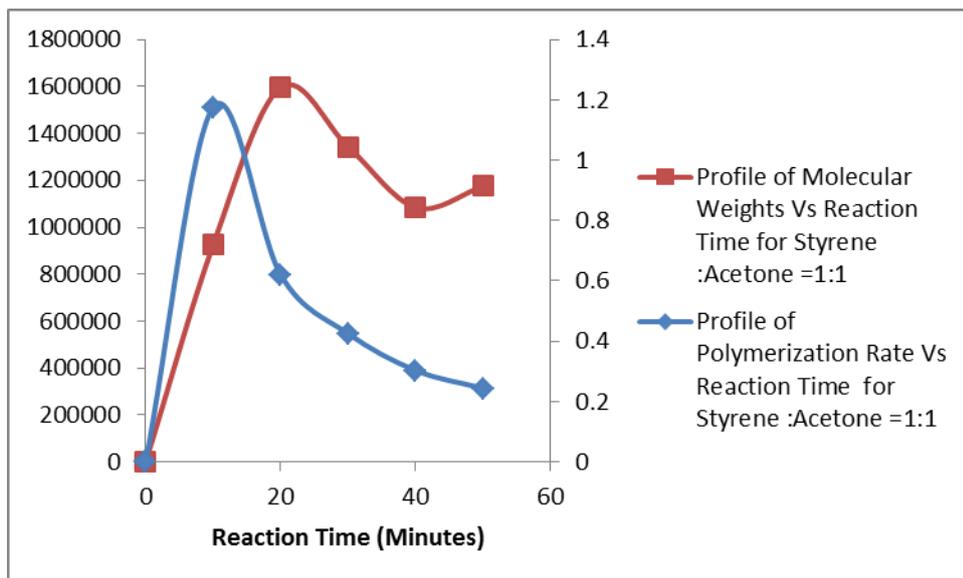


FIG 3: Molecular weight / Polymerization Rate (Rp) Reaction Time using BPO

Table 2.2 Molecular Weight Determination $t_0 = 69$ secs , [P] (g/ml) = 0.13 , Initiator : BPO Blend

Samples	t(sec)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\sqrt{[2(\eta_{sp} - \ln \eta_r)]}}{c}$	$M = \sqrt{\frac{\eta}{K}} \times 10^5$
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	89	0.290	1.290	2.041	10.83979
1SA13	88	0.275	1.275	1.948	10.05999
1SA14	87	0.261	1.261	1.851	9.25988
1SA15	88	0.275	1.275	1.948	10.05999
2SA12	77	0.116	1.116	0.856	2.66814
2SA13	82	0.188	1.188	1.364	5.66169
2SA14	83	0.203	1.203	1.463	6.33218
2SA15	79	0.145	1.145	1.062	3.77582
2SA16	77	0.116	1.116	0.856	2.66814
3SA13	76	0.101	1.101	0.752	2.16616
3SA14	88	0.275	1.275	1.948	10.05999
1SC12	103	0.493	1.493	3.300	23.54255
1SC13	93	0.348	1.348	2.413	14.19704
1SC14	89	0.290	1.290	2.041	10.83979
1SC15	91	0.319	1.319	2.229	12.48749
2SC13	92	0.333	1.333	2.331	13.42340
2SC15	90	0.304	1.304	2.146	11.74900
2SC16	91	0.319	1.319	2.229	12.48749

Table 2.3 Molecular Weight Determination $t_0 = 69$ secs , $[P]$ (g/ml) = 0.13 , Initiator : BPO

Samples	t (secs)	$\eta_{sp} = \frac{t-t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\sqrt{[2(\eta_{sp} - \ln \eta_r)]}}{c}$	$M = \sqrt[3]{\frac{\eta}{K}} \times 10^5$
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	95	0.377	1.377	2.595	15.96324
1SA13	92	0.333	1.333	2.331	13.42340
1SA14	89	0.290	1.290	2.041	10.83979
1SA15	90	0.304	1.304	2.146	11.74900
2SA12	88	0.275	1.275	1.948	10.05999
2SA13	89	0.290	1.290	2.041	10.83979
2SA14	87	0.261	1.261	1.851	9.25988
2SA15	82	0.188	1.188	1.364	5.66169
2SA16	78	0.130	1.130	0.960	3.20863
3SA13	80	0.159	1.159	1.164	4.38402
3SA15	79	0.145	1.145	1.062	3.77582
1SC12	86	0.246	1.246	1.756	8.50959
1SC13	89	0.290	1.290	2.041	10.83979
1SC14	92	0.333	1.333	2.331	13.42340
1SC15	95	0.377	1.377	2.595	15.96324
2SC13	97	0.406	1.406	2.779	17.84361
2SC15	82	0.188	1.188	1.364	5.66169
2SC16	85	0.232	1.232	1.659	7.75466
1SB13	80	0.159	1.159	1.164	4.38402
1SB14	77	0.116	1.116	0.856	2.66814
1SB15	75	0.087	1.087	0.647	1.69794

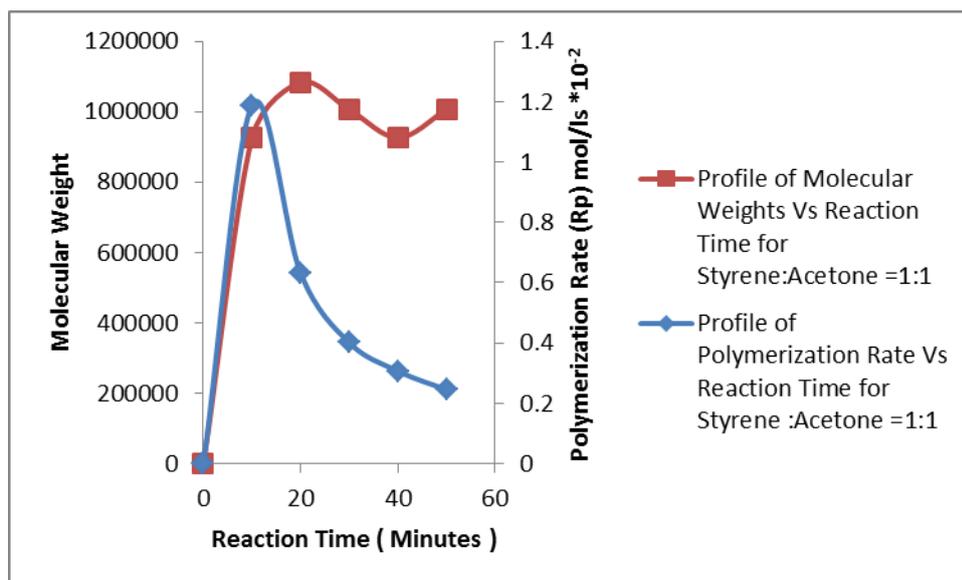


Fig 4: Molecular weight / Polymerization Rate (Rp) Reaction Time using BPO Blend

The production of polymers with end use properties is of significant importance to the polymer industry as its directly affects the physical, mechanical, optical and rheological properties of the final product [32]. Aside the molecular weight, the synthesized PS were further subjected to both solubility and density test as shown in Table 3. As expected, the samples were readily soluble in non-polar solvents and the density falls between the expected ranges which are in line

with reports in literature. Solvation of the PS sample was observed with acetone. Further investigation reveals that a product called Napalm was formed when PS dissolves in acetone. This was however, accidentally discovered in our studies.

Table 3: Solubility and Density Test of Synthesized PS

Solvents	Density(g/cm ³) ^{a,b}	Position of PS	Solubility
Acetone	0.791	Bottom	Solvated to form Napalm
H ₂ O	1.000	Top	Insoluble
Toluene	0.869	Bottom	Soluble
Ethanol	0.789	Bottom	Insoluble
Benzene	0.879	Bottom	Soluble
Chloroform	1.496	Top	Soluble

A= [33] , b = [34]

From our previous control experiment, the styrene monomer and initiator are all needed for polymerization. However, Gao and Penlidis [35] surprisingly cited experimental data from Hui and Hamielec [29] which showed that monomer conversion for styrene thermal and self-initiation reached 40% conversion after 5 hrs at 120 °C, and later 94% after 30 hrs. One advantage we identified from their work is the absence of initiator which on a credit side, reduces the production cost, we however considered it as sheer waste of time or just a mere academic exercise with no industrial value. BPO and its Blend, the two of which used in our studies gave convincing account of their roles as initiators where we experienced polymer build up as early as 10 minutes. Four solvents, on the basis of different polarity were investigated in the reaction to explore monomer, solvent, initiator and polymer compatibility. Fig 5 and Fig 6 showed the same trend. The curves showed that conversion vary markedly with the kind of solvent used. We clearly experienced two stages here namely, the acceleration and stationary stage which were more pronounced in acetone and chloroform and also occurred at roughly equal time of 10 minutes and 20-50 minutes respectively for all the solvents used irrespective of the initiator. Fig 9 exhibited similar behavior but with low conversion. We attributed the low conversion observed here to reduce radical formation for more diluted reaction mixtures. Fig 7 and Fig 8 introduced the decelerating stage into the profile in addition to the earlier trends. We further strongly believe that the decrease in concentration of the monomer with time was responsible for the decelerating stage. Fig 7 unexpectedly tends to resume to the earlier stationary stage. We attributed this to probably the gravimetric and most direct method used in our studies. The conversion of monomer to polymer was determined by direct stopping of the polymerization, isolating and weighing the resulting polymer. The handling of the polymer during precipitation, filtration and drying may lead to losses.

In all, highest conversions were observed in acetone a polar solvent irrespective of the type of initiator used and solvents volume. Toluene recorded the least conversion in all cases. We however established a relationship between the solvent properties, conversion and polymerization rate as shown in Fig10. The higher the polarity index of the solvents, the higher both the conversion and the polymerization rate. Polymerization rates were calculated from the molar conversion of styrene with respect to polymerization time.

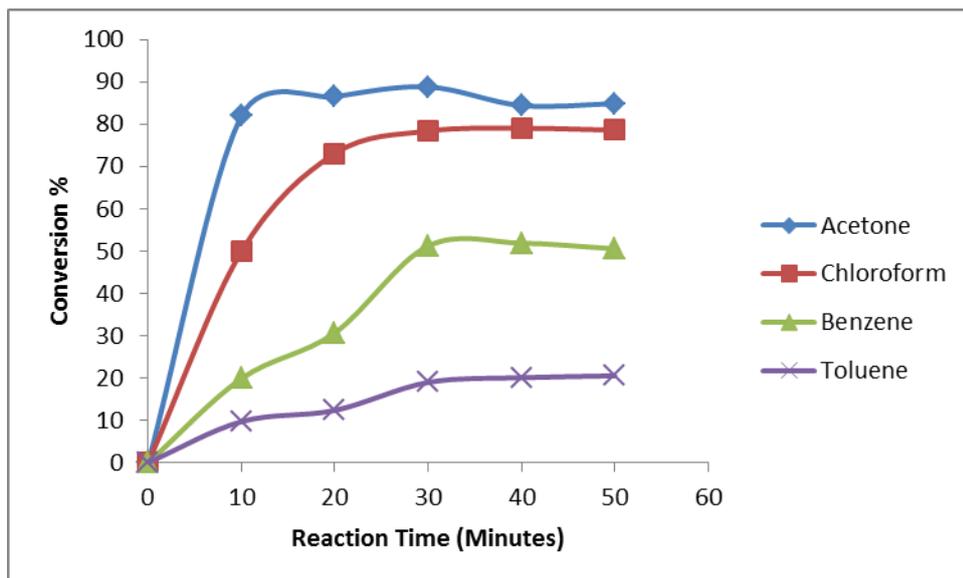


FIG 5 : Conversion Versus Reaction Time Profile at $\frac{\text{styrene}}{\text{solvent}} = 1$, BPO as Initiator

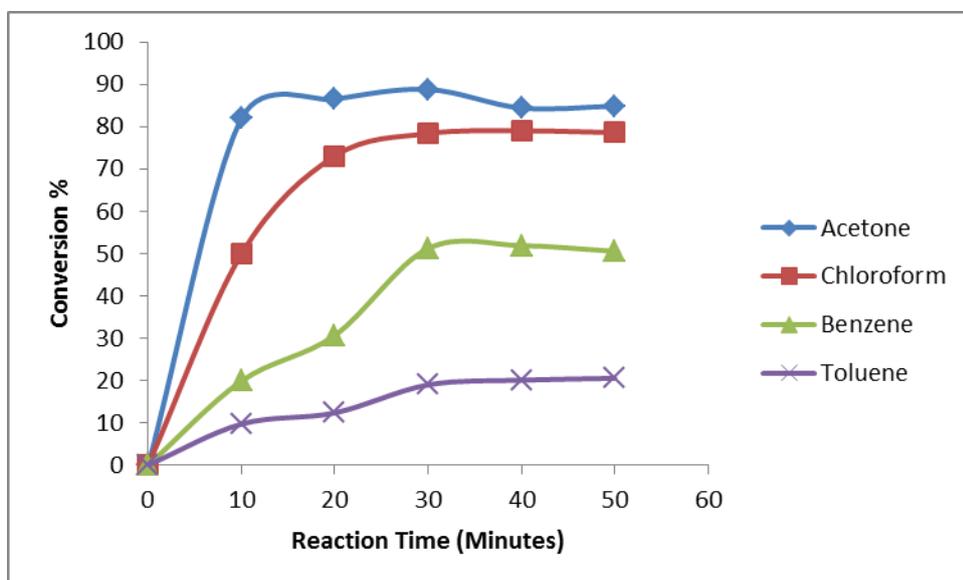


FIG 6: Conversion Versus Reaction Time Profile at $\frac{\text{styrene}}{\text{solvent}} = 1$, BPO Blend as Initiator

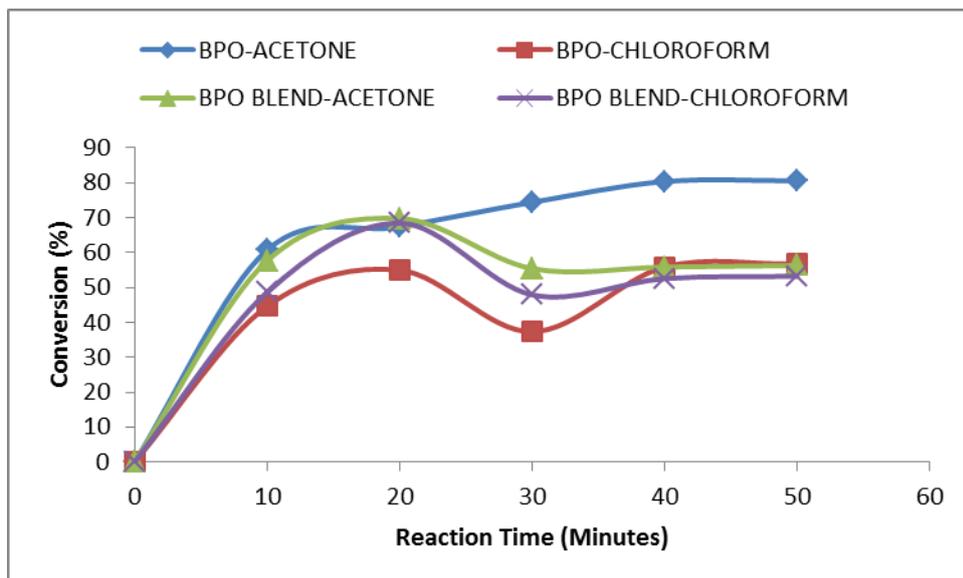


FIG 7: Conversion Versus Reaction Time Profile at $\frac{\text{styrene}}{\text{solvent}} = 0.5$

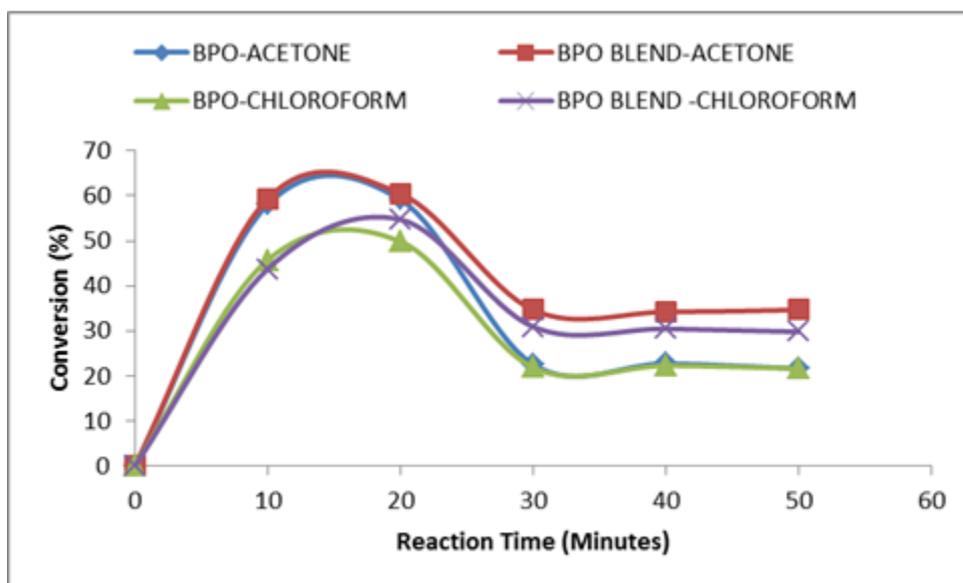


FIG 8: Conversion Versus Reaction Time Profile at $\frac{\text{styrene}}{\text{solvent}} = 0.33$

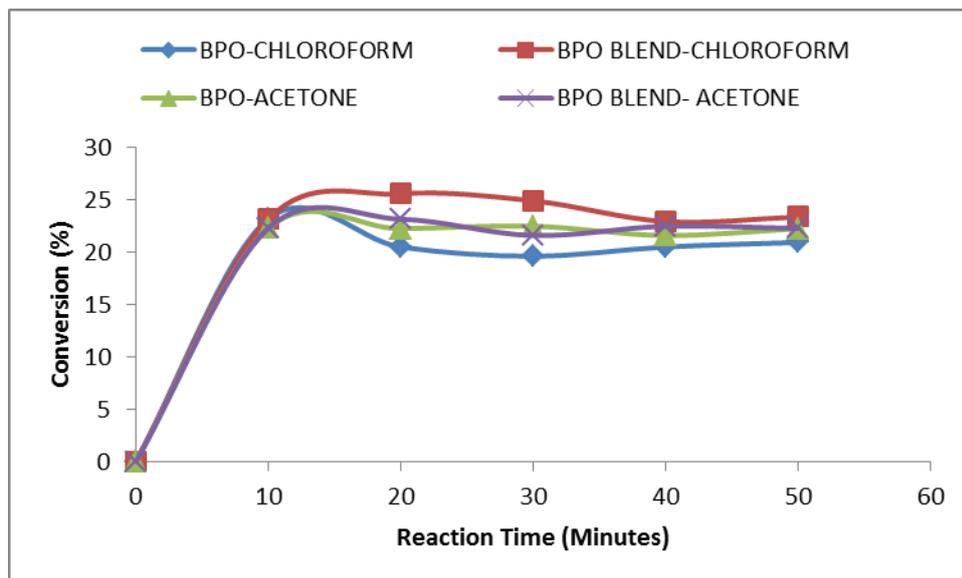


FIG 9: Conversion Versus Reaction Time Profile at $\frac{\text{styrene}}{\text{solvent}} = 0.25$

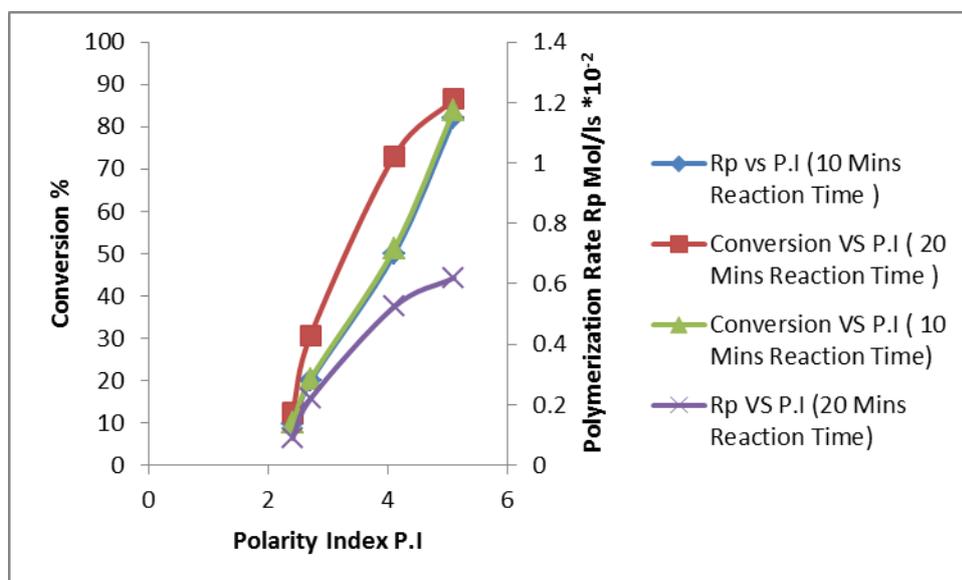


FIG 10: Polymerization Rate (Rp) /Conversion profile versus Polarity index (PI) using BPO

Figure 11- 13 similarly exhibited almost similar profiles for the different reaction times. Initially, the conversion increased as the volume of the solvent increases but later decreased at higher volume of solvent. This change of behaviour was noted at about after 5 to 10 ml of solvent. The reduced conversion observed was believed to be due to the reduced efficiency of the styrene polymerization at certain points. We have attributed the reduced efficiency to;

- Dilution of the initiator.
- Chain transfer to solvent.
- Reduced monomer concentration

Eq. (18) presented our model for the prediction of monomer conversion. The predictive capability of the kinetic model were demonstrated by a direct comparison of model predictions with experimental measurements on monomer conversion. Fig 13-14 compares the profile of the two data .The model responded just very fairly at extremely low conversion with a minimum error of 12.36%.

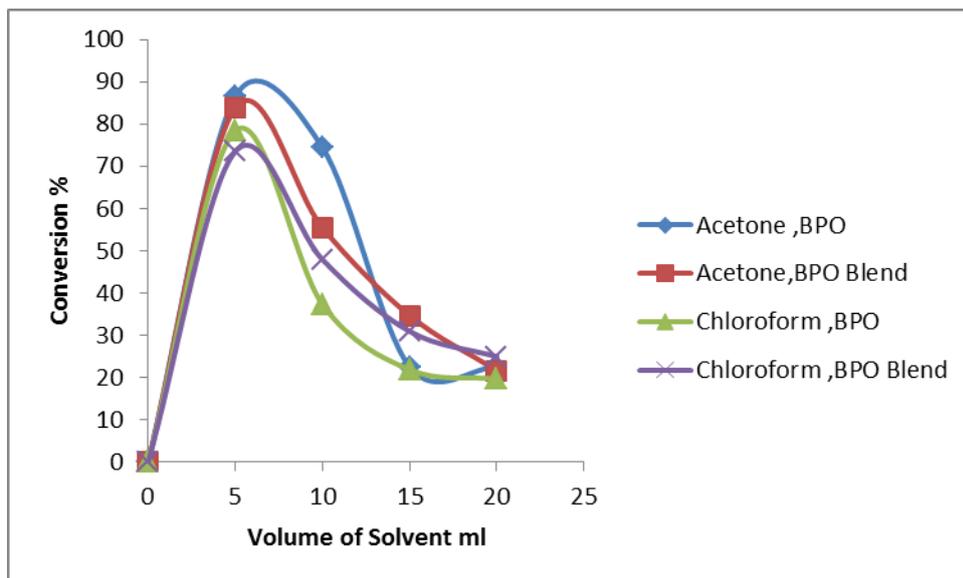


Fig 11: Conversion versus Volume of Solvent at 30 Minutes Reaction Time

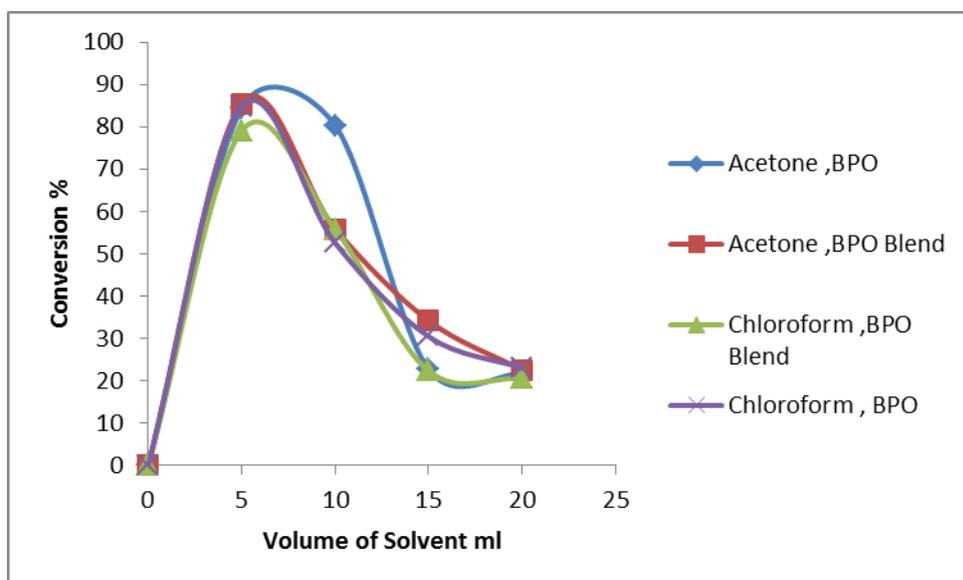


Fig 12: Conversion versus Volume of Solvent at 40 Minutes Reaction Time

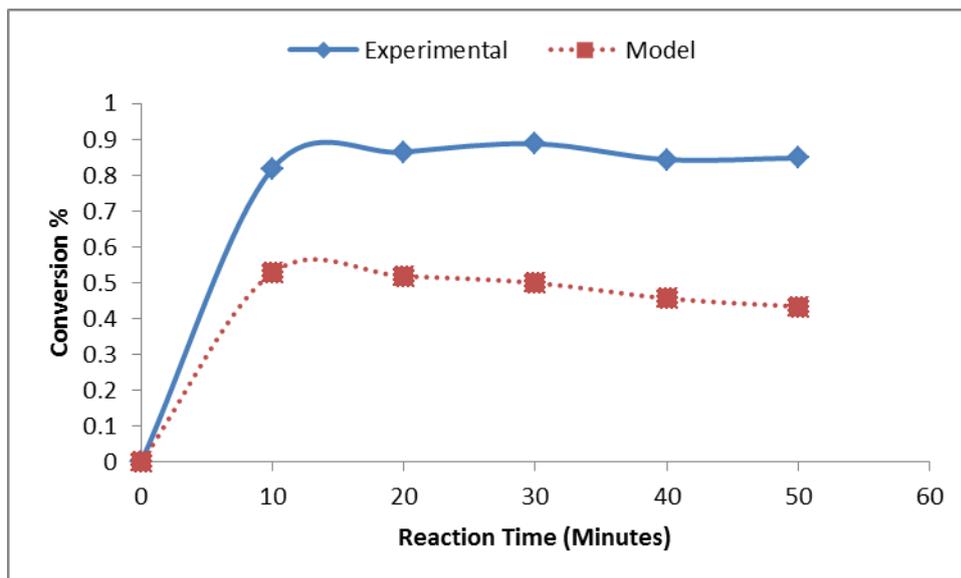


FIG 13: Experimental Data vs Model Data for high Conversion (Styrene: Acetone = 1:1) using BPO

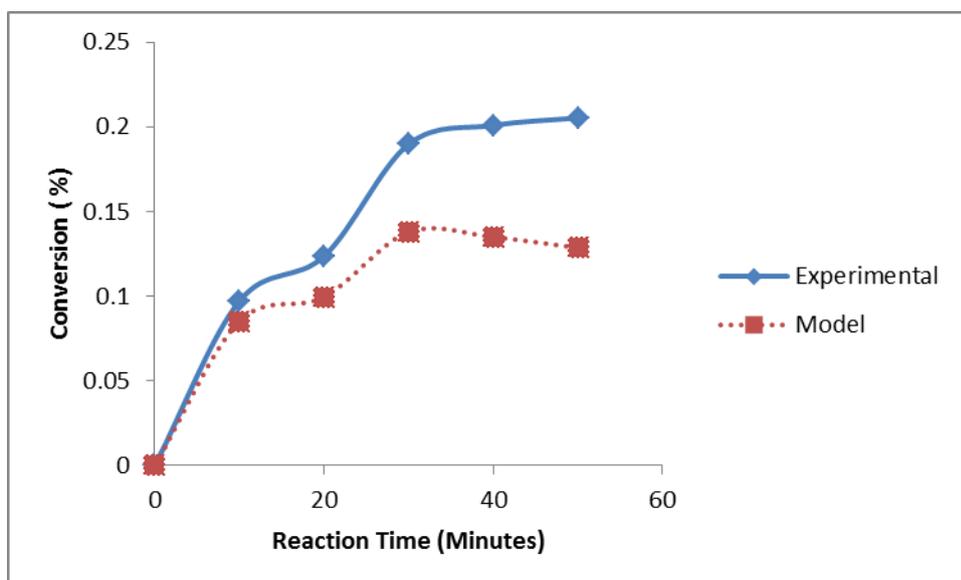


FIG 14: Experimental Data versus Model Data for low Conversion (Styrene: Toluene = 1:1) using BPO

Fig 2 shows some defects in the micro-structures of some of the PS samples. Tiny spots were observed. We suspect that the spots are parts of the solvent effects. The PS samples still contain remnants of solvents after de-solventization. These were gradually removed by evaporation while drying with time thereby creating defects in form of spots within the PS structure.

Fig 5-7 exhibited almost similar profile for different reaction times for all the four solvents used. In each case, highest conversions were observed in acetone a polar solvent irrespective of the type of initiator used and solvents volume. Toluene recorded the least conversion in all cases. As shown in Fig 10, the higher the polarity index of the solvents, the higher both the conversion and the polymerization rate. Figure 11- 12 similarly exhibited almost similar profiles for the different reaction times. Initially, the conversion increased as the volume of the solvent increases but later decreased at higher volume of solvent. This change of behaviour was noted at about after 5 to 10 ml of solvent.

Eq. (17) presented our model for the prediction of monomer conversion. Table 2-3 compares the experimental values with the model or predicted value. FIG 13-14 compares the profile of the

two data .The model responded just very fairly at extremely low conversion with a minimum error of 12.36 %. Our unsatisfactory response from the model prompted us to test the reliability of our data with similar model from Jiguang [36] as shown in eq (18).Their model as shown in FIG: 15 responded to our data similarly at low conversion where we were able to have intercept of 1.074 as against 1.000 and a initial monomer concentration of 13.31 mol / l as against 8.612 mol / l

$$\frac{1}{1-X} = 1 + k_p \left[\frac{k_{i1}}{k_{t1}} \right]^{\frac{1}{2}} [M_0] \theta = 1 + k_{1a} [M_0] \theta = 1 + K_1 \theta \quad (18)$$

$$\text{Where } k_{1a} = 9.46 \times 10^6 \exp\left(\frac{-9500}{T}\right) \quad (19)$$

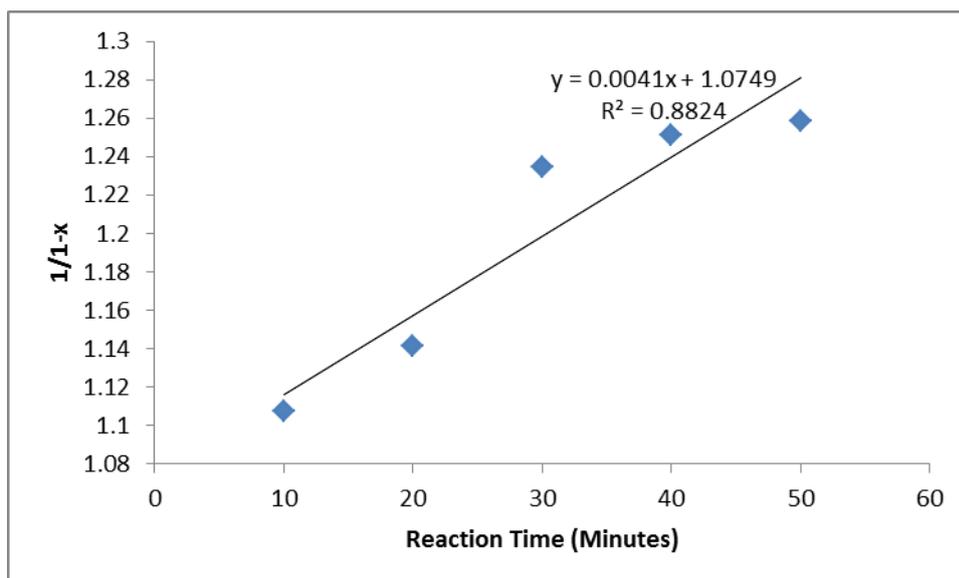


FIG 15: Graph of 1/1-x Vs Reaction time at low conversion for BPO

CONCLUSION

The polymerization technique adopted in this study is solution polymerization. Most free-radical polymerizations are highly exothermic, the introduction of solvent however allowed better temperature control through improved heat transfer, and also provided reduction in viscosity making stirring much easier. If excess heat is not adequately dissipated, the product temperature will rise with a subsequent rise in the rate of polymerization. At higher temperatures, runaway polymerization is possible. When that occurs, temperature can quickly exceed the boiling point of styrene monomer. Vapors may erupt violently from glass reactor vent or, excessive pressure can then be generated which may rupture the reactor. Such situation was not however experienced throughout which infer that we operated below or around the maximum pressure of 60 psig at 120 °C which the glass reactor can withstand.

In this polymerization, rate of reaction is limited, since the reaction temperature is limited by the the decomposition temperature of the styrene monomer. The potential health implication on the continuous use of organic solvents and their environmental impact, which may increase the cost

through additional separation processes to recycle the solvent, is a major drawback. Another potential issue is contamination of the polymer if removal of the solvent is difficult.

It is however clear from our results that the solvents are not actually spectators in the free radical reaction or just to provide an inert medium for heat dissipation but influence in a way the propagation step of the reaction. The different conversions obtained from the solvents used is an indication that their interaction in the reaction medium is felt. However, their choice should be strictly selective especially in terms of their relative inert roles, easy dissolution of the initiator used with a completely different boiling point compared to the solvents used during polymer precipitation.

As earlier stated, industrially, PS is synthesized using the bulk polymerization approach, similar high yield are obtained with purer products. To counter these advantages using the solution polymerization, there is no heat build up and as a result the process safety which cannot be quantified in terms of cost is guaranteed. Since acetone gave high conversion and chloroform gave high, molecular weight of polymers. The blend of both acetone and chloroform in various proportions is recommended to have a high conversion of monomer to polymer and polymer of high molecular weight.

REFERENCES:

- [1] Murat, O., 2012; Trends in Resin Markets and Growth Opportunities for Polystyrene Global Plastics Trade & Markets Conference, Istanbul.
- [2] Weissmermel, K., Industrial Organic Chemistry, 3rd Ed., VCH, New York, 19972. US Patent #4161573, assigned to Dow Chemical.
- [3] Research and Market, 2012; Global Polystyrene Industry - End Use Sectors in China Driving the Demand, World largest market research resource, Ireland.
- [4] Bledzki, A., Balard, H. and Braun, D. 1981; Kinetik der Polymerisation von Methylmethacrylat mit 1, 1,2,2-tetraphenyl-1,2-diphenoxyethan/, Makromol. Chem., 182: 3195-3206.
- [5] Jones, R.G, Ando, W and Chojnowski, J, 2000; Silicon Containing Polymers, Kluwer Academic Publishers, Dordrecht.
- [6] PERP Program, 2006; Polystyrene new report alert, Nexant Chem Systems Process evaluation / Research Planning Programme, South Broadway, White Plains, NY, 10601-4425.
- [7] Ring, K.L. 1999; CEH Marketing Research Report — Styrene, Chemical Economics Handbook (CEH)-SRI International, Menlo Park, CA.
- [8] Erdmenger, T Remzibecer, R., Hoogenbrom, R and Schubert, S.U., 2009; Simplifying the Free Radical Polymerization of Styrene: Micro-Wave Assisted High Temperature Autopolymerization. Aust.J.Chem. 62 :58-63.
- [9] Diaconescu, R.Z., Tuclose, S., Curteanu, 2002; A Case Study for Optimal Reactor Networks Synthesis: Styrene Polymerization, Polym.Plast.Technol.Eng, 41: 297-326.
- [10] Chen, Z., Pauer.W, Moritz H.U, Pruss, J.,and Warnecke, 1999; Modeling of the Suspension Polymerization Process using a Particle Population Balance Chem.Eng.Technol. 22: 609-616.
- [11] Malkin AY, Kulichikin SG., 1985; Rheokinetics of free-radical polymerization. Polymer, 25:778-784.

- [12] Tefera, N., Weickert, G., Bloodworth, R., Schweer, J. Free Radical Suspension Polymerization Kinetics of Styrene up to High Conversion, *Macromol. Chem. Phys.* 1994;195: 3067-3085.
- [13] Devonport, W., Michalak, L., Malmstrom, E., Mate, M., Kurdi, B., Hawker, C.J., Barclay, G.G., Sinta, R., 1997; Living free-radical polymerizations in the absence of initiators: controlled autopolymerization. *Macromolecules* 30, 7: 1929–1934.
- [14] McHale, R., Aldabbagh, F, Zetterlund, P.B, Okubo, M., 2007; Nitroxide-Mediated Radical Precipitation Polymerization of Styrene in Supercritical Carbon Dioxide, *Macromol.chem.phys* 208:1813-1822.
- [15] Rasul,J.M., Jasmin,S.,Abdur,R., 2008 ; Recovery of Styrene Monomer from Waste Polystyrene using Catalytic Degradation ,American Laboratory eNews Letter of Monday, February 18.
- [16] Michael ,D.Z.,Thomas ,P.D ,Gary ,D.W .,Kenneth , F.O.1997 ;The Effect of Solvent on the Homo-propagation Rate Coefficients of Styrene and Methylmethacrylate ,*Journal of polymer science and Polymer Chemistry* , 35 : 2311-2321.
- [17] Dhib, N and Al-Nidawy, R 2002: Modeling of Free Radical Polymerization of Ethylene Using Difunctional Initiators, *Chem.Eng.Sci*, 57: 2735- 2746.
- [18] Arai, K. and Saito, S. 1976; Simulation Model for the Rate of Bulk Polymerization over the Complete Course of Reaction. *J. Chem. Eng. Japan*, 9:302-313.
- [19] Sigma Aldrich, 2013,Polymer product from Aldrich , Product Information Guide. Aldrich Catalog No. Z412473.
- [20] Bastiaan, S., 2005 ; Characterization of Co-polymers by MALDI-TOF-MS, Ph.D Thesis, Technische Universiteit Eindhoven, Netherland.
- [21] Bello, M.A, 2001; *Polymers-The Chemistry and Technology of Modern Materials*, Concept Publication Limited, Lagos, Nigeria.
- [22] Herman, L.W; 1985; The Mark-Houwink-Sakurada Equation for the Viscosity of Linear Viscosity, *J. Phys. Chem. Ref. Data*, 14,2.
- [23] Goldberg, A.I, Hohenstein, W.P., and Mark, H, 2003; Intrinsic Viscosity - Molecular Weight Relationship for Polystyrene, *Journal of Polymer Science* , 5: 503-509.
- [24] Fogler, H.S., 1999; *Elements of Chemical Reaction Engineering*, Prentice Hall, International Series in the Physical and Chemical Engineering Sciences, 3rd ed.
- [25] Gaynor, S., Greszta, D., Mardare, D., Teodorescu, M., Matyjaszewski, K., 1994; Controlled radical polymerization. *Journal of Macromolecular Science—Pure and Applied Chemistry A* 31 ,11:1561–1578.
- [26] Mardare, D., Matyjaszewski, K., 1994; Thermal polymerization of styrene in the presence of stable radicals and inhibitors. *Polymer Preprints* 35:778–779.
- [27] Georges, M.K., Kee, R.A., Veregin, R.P.N., Hamer, G.K., Kazmaier, P.M., 1995; Nitroxide mediated free-radical polymerization process—autopolymerization. *Journal of Physical Organic Chemistry* 8, 4: 301–305.
- [28] Amarjit Singh, Decheng Ma, and David L. Kaplan, 2000 ; Enzyme-Mediated Free Radical Polymerization of Styrene , *Biomacromolecules* , 1: 592-596.
- [29] Hui , A.W., and Hamielec , A.E., 1972;Thermal Polymerization of Styrene at High Conversions and Temperatures - An Experimental Study , *J. Appl. Poly. Sci.*, 16: 749-769.
- [30] Shi Z, Shi , Z.J., Tong K. *Chem React Engng Technol* 1993; 9, 3:274–278.
- [31] Sueo , M., Miyuki, H., Masao , G ., Tsutomu , K. ,2003; Specific influence of temperature on γ -ray radiation induced polymerization of ethylene , *Journal of Polymer Science Part A: General Papers* ,3,8:3029-3030.
- [32] Verros ,G.D., 2003;Calculation of Molecular Weight Distribution in Non-Linear Free Radical Co-Polymerization ,*Polymer* ,44:7021-7032.

- [33] David, R.L, 1995; Handbook of Organic Solvents, CRC Press, USA .
- [34] Michael, A and Irene, A (2003) ,*Hand book of solvents synapse information resource*,Endicott,New York.
- [35] Gao, J., Penlidis, A., 1996. *A comprehensive simulator/database package for reviewing free-radical homopolymerizations*. Journal of Macromolecular Science—Reviews in Macromolecular Chemistry and Physics C 36 (2), 199–404.
- [36] Jiguang ,Q ., Wenping , G.,, Zheng , Z. ,(2002), *A kinetic study on bulk thermal polymerization of styrene* , Polymer ,43 ,7521–7527.

DESIGN OF AN INJECTION MOULDING MACHINE FOR POLYMER COMPOSITE

Ismail S.O., Ojolo S. J., Orisaleye J. I., & Olatunji O.O.

Mechanical Engineering Department, University of Lagos, Akoka, Lagos, Nigeria
tunjifemi@gmail.com, olatunjobafemi@yahoo.com

ABSTRACT

In the recent world, the polymer composite is fast replacing many of convectional metal/material in our applications. This is possible because of the advantages polymers offer over conventional materials. However, the cost of manufacturing is a major factor militating against the indigenous production of Polymer composite wares. In this paper, an injection moulding machine for High Density Polyethene (HDPE) and wood fibre composite was designed. A mould was also designed bases on the properties of the selected composite. Also, working drawings and material selection were obtained. From design calculation; the diameter of the injection plunger is 53mm, number of teeth required for the plunger rack and spur gear are 33 and 40teeth respectively. Torque and power obtained from the electric motor are 0.00134Nm and 0.13kw respectively.

Keywords: Design, Polymer composites, Injectionmoulding machine, Plunger rack.

INTRODUCTION

In the recent world, the polymer composite is fast replacing many of convectional metal/material in our applications. This is possible because of the advantages polymers offer over conventional materials. However, the cost of manufacturing is a major factor militating against the indigenous production of Polymer composite wares., thus, developing an injection moulding machine that will produce composite polymer wares and products such ascups, buckets, and fan blades, among others, at a low cost is conceived. This will provide job opportunity and improve the exporting power of our country. Polymers are generally produced as powders, pellets, and liquids. In order to produce polymeric products with desired shapes, thermoplastics must be melted and cool to a final product shape whereas thermosets must undergo further polymerization to complete cross linking reactions to finally solidify into the designed shape. These operations are called processing. Many factors influence the processing operations. Those include viscosity, orientation of heterogeneous phases, rate of reactions, and volatile formation. Among these factors, the viscosity consideration is by far the most dominant factors in processing. Viscosity is strongly influenced by temperature, share rate, molecular weight and its distribution, molecular structure of the polymeric chains and heterogeneity of materials. Thus, the study of flow behavior of polymeric materials, which is called rheology, is very important in understanding the proper conditions for processing (Husua, 2010).

The mould is probably the most important element of a molding machine. It is an arrangement, in one assembly, of one or a number of hollow cavities built to the shape of the desired product, with the purpose of producing large numbers of plastic parts. Thus the primary purpose of the injection mould is to determine the final shape of the molded part (shaping function). In addition to giving the final shape of the moulding, the mould performs several other tasks. It conducts the hot melt from the heating cylinder in the injection moulding machine and distributes the melt to the cavity (or cavities), vents the entrapped air or gas, cools the part until it is ejectable, and ejects the part without leaving marks or causing damage. The secondary tasks of a mould derived from these primary tasks include several mechanical functions such as accommodation of forces, transmission of motion, guidance and alignment of the mould components. The mould design, construction, the craftsmanship largely determine the quality of the part and its manufacturing

cost.

Gon-Yop (2008) investigated the material properties of polyethylene and wood fibre composites. The plastic injection moulding industry has evolved over the years from producing combs and buttons to producing a vast array of products for many industries including automotive, medical, and aerospace and consumer products (Mohd, 2009). Kazuya et al. (2004) studied the development of composites for ecological purposes (Ecomposites) using bamboo fibers and their basic mechanical properties. The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experimental results showed that the bamboo fibers (bundles) had a sufficient specific strength, which is equivalent to that of conventional glass fibers. They concluded that Bamboo fiber bundles have a potential ability to work as the reinforcement of polymer matrix. The tensile strength of the bamboo fiber bundle is as high as that of jute fiber (Kazuya et al., 2004). The objective of this paper is to design an injection moulding machine for Polymer composite and injection mould for a material that can be sourced locally. In this case, High Density Polyethylene with wood fibre was used as the filler. The research work involves design concept, operations and design analysis/calculations. These involve the design of injection plunger, motor selection, design of the handle, and the leverage on the handle of the machine. Also, assembly drawings of the machine, recommended materials and equipment for the construction of the designed machine were provided to assist investors that wanted to venture into construction of this machine.

METHODS

The composite used for the design of injection moulding machine is made of HDPE with woodfibre as the filler. This design is based on the result of material property obtained by Gon-Yop (2008) in his Development of Foam Injection Molding Technology for Polymer Composite Materials. The material properties obtained are as follow:

Table 1: The Material Properties of HDPE and Wood fibre foamed HDPE

PROPERTIES	HDPE	WOOD FIBRED FOAMED HDPE
DENSITY(g/cc)	0.95	0.88
WARPAGES(MM)	4.5	0.37
SHRINKAGE (%)	3.5	0.87
YOUNG MODULUS(Mpa)	141.1	181.4
TENSILE STRENGTH(Mpa)	4.898	5.059

Description of the Machine

The injection moulding machine for polymer composite is a piece of equipment containing majorly the injection unit and clamping unit. The injection unit consists of the plunger, driven by an electric motor. The plunger is enclosed inside a barrel made from nitride steel. An electric heater is mounted on a part of the barrel. Also, the clamping unit consists of the mould, the mould cavity, supporting platen, mould core, and injection pin. This design concept encompasses the maximum volume of the melt needed to fill the mould. This entails the plunger travel (**l**), diameter of the barrel (**d**), melt density (**p**) and melt mass (**m**); Design of barrel which includes diameter of the barrel and maximum piston travel; and Design for plunger. The design analysis involves:

a)The injection unit comprises of the:

1. Hopper,
2. Barrel,

3. Heater bands,
 4. Nozzle,
 5. Injection plunger.
- b) The clamping unit consists of the:
1. Mould,
 2. Platens, and
 3. Handle known as the locking device.
- c) The electrical panel comprises of:
1. Temperature control,
 2. Contactors,
 3. Thermocouple,
 4. Heat resistance wire, and
 - 5 Knob (control button).

Design Concept and Analysis

Determination of volume of Hopper

The volume of the circular hopper is given by;

$$V = \frac{m}{\rho} \dots\dots\dots (1)$$

$$V = \frac{2.5}{880} = 0.00284kg/m^3$$

Design of injection plunger

In the injection plunger design shown in Fig. 1.0, the volume of the melt (V) that the plunger can successfully pushed from the barrel can be determined by knowing the diameter of the plunger.

Using Fig. 1.0, the diameter of the plunger can be determined from Eq. (1) as:

$$V_1 = \pi r^2 l \dots\dots\dots (2)$$

The expression in Eq. (1) can be expressed in terms of diameter (d),

$$d = 2r$$

$$V_1 = \pi \frac{d^2 l}{4} \dots\dots\dots (3)$$

Also, volume (V) of the melt in the barrel can be obtained from Eq. (4), density of the melt, ρ
Mass of the melt, m

$$V_2 = \frac{m}{\rho} \dots\dots\dots (4)$$

Therefore,

$$V_1 = V_2$$

This implies that,

$$d^2 = \sqrt{\frac{4m}{\pi \rho l}} \dots\dots\dots (5)$$

Therefore, the plunger diameter can be determined from Eq. (5)

Taken $l = 1000mm$ and $m = 2.5kg$

$$\text{Therefore, } d = \sqrt{\frac{4 \times 2.5}{\pi \times 1140}} = 0.053m$$

d=53mm

Number of teeth required on the plunger rack

The number of teeth required is determined from Eq. (6)

$$\text{Number of teeth required on the plunger} = \frac{\text{Expected length of travel}}{\text{circular pitch distance}} \dots\dots\dots (7)$$

$$\text{expected length of travel} = \frac{\text{Length of plunger}}{5} = \frac{1000}{5} = 200\text{m}$$

Taken circular pitch distance to be 6,

$$\begin{aligned} \text{The number of teeth on the plunger rack} &= \frac{200}{6} \\ &= \mathbf{33\text{teeth}} \end{aligned}$$

Number of teeth required on spur gear (pinion)

The number of teeth required on the spur gear is determined from Eq. (10), circular pitch distance
Number of teeth required on spur gear,

$$N_p = \frac{\pi D_p}{P_d} \dots\dots\dots (8)$$

$$N_p = \frac{\pi \times 76}{6} = \mathbf{40\text{teeth}}$$

Motor selection

At the Injection rate of 110cm³/s,

$$Q = vA$$

Where **A** is the Area of the plunger head

At the speed of 1.21m/s

The angular velocity can be determined using;

$$\omega = \frac{v}{r} \dots\dots\dots (9)$$

$$\omega = \frac{1.21}{0.012} = \mathbf{101\text{rad/s}}$$

$$N = \frac{60\omega}{2\pi} \text{(Khurmi and Gupta, 2003)} \dots\dots\dots (10)$$

$$N = \mathbf{964.5\text{rpm}}$$

Using G80 type electric motor=0.112N and $r_s=0.012\text{m}$

$$\begin{aligned} T &= Fr_s \\ &= 0.112 \times 0.012 = \mathbf{0.00134Nm} \end{aligned}$$

$$\begin{aligned} \text{Power} &= T\omega \text{(Khurmi and Gupta, 2003)} \\ &= 0.00134 \times 964.5\text{rpm} = \mathbf{0.13kw} \end{aligned}$$

Design of Handle

In the design of the handle, the leverage on the handle (M_L) of the machine can be determined from Eq. (11),

$$M_L = m_h g D_L \dots\dots\dots (11)$$

$$m_h = \mathbf{5.39kg}$$

Distance with which the handle, d moves the platen=200mm

$$M_L = 5.39 \times 0.2 \times 9.81 = \mathbf{10.58J}$$

Determination of the Cooling Time

The cooling phase of the injection moulding process accounts for up to 75% of the overall cycle time. It therefore follows that a reduction in cooling time will in turn reduce the overall cycle time and hence, increases the throughput rate. Experimentally, cooling times are defined as the time taken for the pressure at the primary sensor to return to atmospheric, after the injection of a consecutive shot. The molten polymer cools and solidifies in the mould (Smith et al, 2008). The cooling system design was primarily based on the experience of the designer but the development of new rapid prototyping process makes possible to manufacture very complex channel shapes what makes this empirical former method inadequate. So the design of the cooling system must be formulated as an optimization problem.

The time required for the cooling the part produced in an injection moulding machine can be approximately obtained as follows:

Cooling time, $T_c = 150 \times \text{thickness of the thickest wall of part}$

Assuming a part of thickness of 1mm,

$T_c = 150 \times 1.0 = 150s$ (i. e 2.5 minutes)

Clamping Force

The clamping force is proportional to the projected area of the moulding and runner, and must be opposed by the clamping force. Although a proportion of the pressure produced by the injection cylinder is transmitted to the cavity, various losses occurring in the heating cylinder, nozzle and gate. Considering that force acts on the mould to open it can be calculated from the following expression:

$\text{Clamping force} = \text{Projected Area} \times \text{number of cavities} \times \text{Pressure} \times 0.8$

0.8 is the factor of safety.

$$\text{Pressure} = \frac{\text{Force transmitted by the plunger}}{\text{Area of the plunger}}$$

$$\text{Area} = \pi r^2$$

$$= 26.5^2 \times \pi = 0.00221 \text{m}^2$$

$$\text{Projected Area} = l \times b = 0.14 \text{m}^2$$

$$\text{Pressure} = 0.00221 / 0.112 = 0.0197 \text{N/m}^2$$

$$\text{Clamping force} = 0.0197 \times 1 \times 0.8 = 2.21 \times 10^{-3} \text{N}$$

Mould Design Consideration

Shrinkage is defined as the relative change in dimension between the length measured on the mold when it is cold and the length of the molded object after it has been cooled.

Shrinkage is defined mathematically as below;

$$\text{Shrinkage} = \frac{\text{Mould length} - \text{Part length}}{\text{Mould length}}$$

Shrinkage is a material property that shows the behavior of the material after the product is taken out of the mold and cooled. It shows the change in the dimensions of the product compared with the mold cavity size. The lower level of Shrinkage and the higher level allow for HDPE and wood composite is **0.97%** and **0.77%** respectively.

Design for Warpage

Warpage is defined as a non-uniform change in internal stresses resulting distortion or warp of the material. Along with the shrinkage, warpage is one of the factors that change the dimensions of the final product. For applications that require higher dimensional precisions, warping

behavior of the material is an important factor. One of the main factors that control the warping behavior of the material has been found to be the mould temperature. The mould temperature of 30 °C produces average warpage amount of 0.3133mm and 50°C produces average of 0.4392mm. The increase of 20°C in the mould temperature increases the height by 40%. Another factor that affects the warpage behaviour is the injection speed. Increase in the injection speed increases the amount of warping. Injection rates of 70cm³/sec results the average of 0.2833mm of warping and 110 cm³/sec results 0.4692mm.

Materials Selection

Materials are selected based on designed and metallurgical properties of the materials such as machinability, formability, weld-ability that greatly influenced the construction methods and other joining methods. Other factors considered are cost of the materials and mechanical properties of the materials. The materials used in the construction of this machine are medium carbon steel used for injection plunger, nitride steel barrel and nozzle. Mild steel was used for hopper, supporting plates, tie bars, platen, mould, bolts, and main frame. Other materials used are thermocouples, limit switches, knobs (control button), bolts, and 4-core Flexible wires, heat resistance wires, and contactors, red and light green paints.

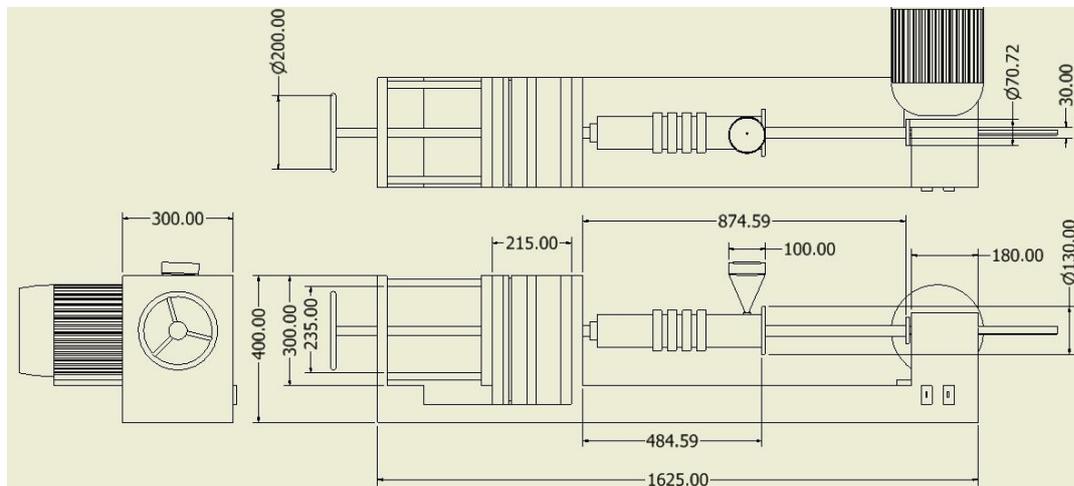
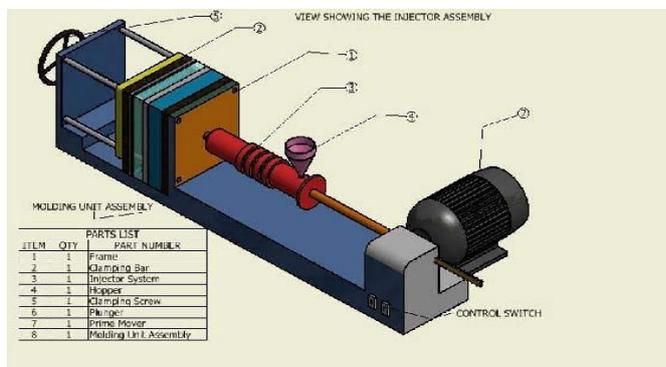


Fig. 1.0: The Plan View of the Injection Moulding Machine for Polymer Composite.



CONCLUSION

The injection moulding machine for HDPE and wood fibre composite was designed, the diameter of the injection plunger is 53mm; number of teeth required for the plunger rack and spur gear are 33 and 40 teeth respectively, torque and power obtained from the electric motor are 0.00134Nm and 0.13kw respectively. The mould was also designed based on the properties of the selected polymer composite. This work was designed for the small-scale production of small articles. For the economic growth of any nation, indigenous technology must be embraced. The small-scale investors that are willing to explore the vast economic advantages of locally available composite materials should be encouraged to embrace this technology.

REFERENCES

- Gon-Yop K. K., 2008. Development of Foam Injection Molding Technology for Polymer Composite Materials, Thesis submitted to the Department of Mechanical and Industrial Engineering University of Toronto, Toronto.
- Husna P. N., Hossain M. A., Sultana and S., Mollah M. M., 2010. Preparation of polymer composites using natural fiber and their physico-mechanical properties. *Bangladesh Journal of Science Industrial Research* 45(2), 117-122.
- Kazuya O., Toru F., Yuzo Y., 2004. Development of bamboo-based polymer composites and their mechanical properties, Elsevier publisher, *Composites: Part A* 35 (2004), 377–383.
- Kennedy P.K., 2009. Practical and Scientific Aspects of Injection Moulding Simulation, Doctoral Dissertation, Technical University of Eindhoven, Eindhoven, Netherlands
- Khurmi R. S and Gupta J.K., 2003. *Machine design*. S. Chand and Company Limited, New Delhi, India, 920-959.
- Mohd N. B. N., 2009. Sink marks defect on injection moulding using different raw materials. A thesis submitted for the award of the Degree of Bachelor of Mechanical Engineering with Manufacturing Engineering, Faculty of Mechanical Engineering, University of Malaysia Pahang, Malaysia.
- Netstal C., 1978. Instruction manual for injection moulding machine, Netsal Machine and Foundry Limited, Switzerland, 36-60
- Smith A.G., Wrobel L. C., McCalla B. A., Allan P. S., Hornsby P. R., 2008. A computational model for the cooling phase of injection moulding. *Journal of materials processing technology*, Elsevier publisher, 195, (1–3), 305–313
- Sharifah R. B. H., 2010. A study on the effect of Injection Moulding Process Parameters to the Properties of Injected Parts. A report submitted for the award of the Degree of Bachelor of Mechanical Engineering with Manufacturing Engineering, Faculty of Mechanical Engineering, University of Malaysia, Pahang, Malaysia.

A REVIEW OF IMPACT OF WATER RISE ON REAL ESTATE VALUE

E. O. Thontteh & M. M. Omirin

Department of Estate Management, Faculty of Environmental Science,
University of Lagos, Akoka, Lagos, Nigeria
estherthontteh@yahoo.com, momirin@unilag.edu.ng

ABSTRACT

Investors and building professionals would be more concerned if properties in areas susceptible to flooding reduce in value to a large extent since sustainability of value is the utmost goal of every investor. This paper examined impact of flooding on land and buildings in Oniru and Lekki Phase 1 areas of Lagos, Nigeria. Population considered for the study is practicing firms of The Nigeria institution of Estate Surveyors and Valuers in Lagos State. A systematic random sampling technique was adopted in sample selection giving a sample size of 55 for the study, out of which 48 was retrieved representing 87% of the sample size. Data was analyzed using descriptive statistics, relative importance index and correlation. The study explored the degree of influence of flood occurrence on land and building value in the study locations. Empirical findings showed that there exist a significant relationship between flooding and land price but not with rental values of office and residential buildings. A key implication of the finding is that the effect of flooding on land value, traffic as well as psychological effect on occupiers is severe. Hence, a concerted effort by government in the construction of drainages and embankments for easy passage of excess water needs to be adopted to prevent loss of property values, man-hour loss in traffic and advancement of good health.

Keyword: Demand, Flood, Health, Lagos, Land value, Traffic

INTRODUCTION

Disaster is the resultant effect of actualized hazard. Han (2012) defined a hazard as an activated threat to life, health, property or ecosystems. It involves something that could potentially be harmful. It is a phenomenon that can cause damage to life and property and destroy the economic, social and cultural life of people (Stone, 2009). Therefore, when a dormant hazard comes to fruition, it will cause physical damage or destruction, loss of life or drastic change to the environment and result in an incident, accident emergency event or disaster. Omojola (2009) also defined hazard as the climate-induced stresses on the city and are identified through observed trends and projections derived from global climate models (GCMs) and regional downscaling. He further stated that extreme events affected by climate change include heat waves, droughts, inland floods, accelerated sea level rise, and floods for coastal cities. According to Turnbull, Herbert and Mothorpe (nd) all real estate is subject to natural disaster which ranges from tornado, flooding, earthquake, landslide amongst others and the effect ranges from minor inconvenience to complete devastation. Furthermore, unlike many other natural disasters, the risk of flooding can be measured and it varies systematically across locations within a particular area.

Flooding according to Odunuga, Oyebande and Omojola (2012) is a serious disaster in the world, which not only causes serious damage but disturbs normal life and working conditions. Moreover, several reports have shown that thousands of lives and property worth billions in monetary terms have been lost in various affected areas in Lagos, Nigeria (Emordi, 2012). Furthermore, according to World Health Organization (WHO) flooding accounts for 40% of all natural disasters worldwide. The main health impacts are deaths, injuries, waterborne disease and emotional trauma during the flood event itself, during the restoration process, or from knock-on effects brought about by damage to major infrastructure including displacement of populations.

However, on average, the higher the water depth and the greater the flow velocity of a flood, the greater the damage to property (Gayelord, 2008).

Several studies have been conducted to assess relationship between flood and human health. However, its implication on land and building value has often been assumed without knowing the degree of variability in the study location. This study therefore focuses on impact of flood on land and buildings.

Empirical studies conducted outside the study location have found that real estate properties situated in designated flood plains are valued less than comparable properties situated outside the floodplain; usually by 4–12% in Australia (Lambley and Cordery, 2013), 15–35% in UK (Lamond, 2008), average of 5.8% in North Carolina (Bin and Polasky, 2003) and 1.27–4.7% in Japan (Fukozono and Ikeda, 2003). However, in Nigeria a negative impact of flooding on land and property value has often been assumed without knowing the degree of variability and impact. This assumption, though yet to be fully tested in the study area is a fundamental research gap which this paper has aimed to fill with the following research questions: does flooding affect land and building values in the study areas and to what extent has flooding impacted land and building values in the selected areas? This is to enable real estate managers, financiers, government agencies, residents, communities, insurers and investors to be well informed in order to fashion out necessary policy actions, adjustment coping strategy to enhance investment as well as its rate of return and profitability.

The overall purpose of this paper is to review the impact of flood disaster on the market value of land and buildings in selected locations in Victoria Island and Lekki Phase 1, Lagos, Nigeria while the specific objectives are as follows; to identify the general and specific effects of flood on land and building value in particular and to compare the magnitude of effects of flood disaster on land and property values in the selected areas.

Floods can devastate a country and have a range of impacts; short and long term upon their victims. The selected areas include Water Corporation Road in Oniru, Victoria Island, Lagos popularly referred to as Victoria Island annex and Admiralty Way, in Lekki Phase 1 as they have a common geographical location. The areas were selected because they form an extension of the Central Business District (CBD) where development is yet to fully take place in terms of building construction, furthermore, it is a preferred location for expatriates, hence its international outlook as rents and sales price are sometimes quoted in US dollars. In addition, the area, being regarded as an international market was selected in order to assist international investors on the choice of location for investment purpose. The areas examined at Oniru are Water Corporation Road being a low-lying area adjacent to ocean and beach, hence, its susceptibility to seasonal and frequent flooding and Admiralty Way in Lekki Phase 1. which is adjacent to Oniru and not directly on flood plain area.

The maintenance of property value is a key element in the sustainability of local communities (Bramley, Munro and Pawson, 2004). It is of importance not only to property owners and their agents, financiers and investors but also to local and national governments. If flooding leads to vacant and derelict property then local blight could ensue. A flood disaster can destroy decades of development gains in moments. People and buildings are often the most physically affected and needs more time to recover economically and psychologically (Lamond, 2008). The World Bank International Development Association (IDA) in its report of 2009 affirmed that impact of natural disasters in terms of fatalities and losses in economic growth is on the rise, and is more severe in developing countries. This situation will be exacerbated by the fact that natural disasters are expected to increase in frequency and severity due to climate change, increased urbanization and continued environmental degradation. Furthermore, a deep understanding of the

full impacts of flooding is necessary in order to guide investors and implement flood management policies in the best interests of all (Green, Vanderveen, Wierstra and Penningrowsell, 1994) as disasters pose an increasing threat to development efforts.

LITERATURE REVIEW

Flooding may result from increased volume of a body of water such as a river or lake that over flows or breaks levees which then result to some of the water escaping boundaries, in addition, it can also form where there is no stream as for example when abnormally heavy precipitation falls on flat terrain at such a rate that the soil cannot absorb the water or the water cannot run off as fast as it falls (Grima et al., 2011). Lakshmanan (2011) also added that flood is a state of high water level along a river channel or on the coast that leads to inundation of land which is not usually submerged. Against the belief that flooding will seemingly have a major adverse effect on real estate value, Kropp (2012) identifies the following as the most important value influencing factors of real estate: flooding or flood risk, demographic structure, neighborhood, traffic situation, business situation, social facilities, environment influences urban greening, legal situation, development status, contamination, types and degree of building and land use, protection of historical monuments, form and size of the property, topography, unemployment rate, cost of living, purchasing power, interest on capital and population development. Furthermore, Lamond (2008) concluded that measured impacts of flooding on property price are temporary in nature as they appear to be a reaction to flood events rather than to flood risk designation while the effect of flood status on property value is small relative to location, property size and type.

There are several extant literature both locally and internationally on the impact of flooding on lives and buildings based on events and data such as Omojola (2009), Emodi (2008), Lamond (2008) amongst others. However research on the effect of flooding on the market value of real estate seems to be limited.

Flood Risk Perception

According to Meldrum (2011) there are often no discounts in property price in flood plain areas as flood risk is subjective in nature. However, increasing risk perceptions correspond to decreasing property values. Furthermore, the difference in values of properties inside or outside a flood plain area reflects the subjective flood risk assessments made by investors and occupiers.

Yeo (nd) further reviewed the spatial and temporal effects of flood disclosure on property values in United States, Canada, New Zealand and Australia. He stated that disclosure of flood-liability whether by flooding or flood plain mapping should result in differentiation of market value between flood liable properties and those that are not. Furthermore, he stated that in Oregon, USA; in 1964 and 1971 flood had a depressing effect on land values particularly for water front land between 19% - 26%. However, it also affected lots that were apparently not flooded by 3% while the depressed effect lasted for 5-8 years; in Illinois, USA between 1986 -1987, flood had a more pronounced effect on property values by 15% - 21% for both flooded and non flooded property. Here the depressed effect lasted for more than 2 years.

In Ontario, Canada; in 1974 as a result of influence of flooding and flood disclosure at sites in Ontario province, assessments revealed no significant difference between flooded and non flooded areas either before or after major flood. In fact sales price were significantly higher after the flood. In addition rental value, sales price, assessed value and length of period for house sale in London between 1978 and 1989 found no significant difference between houses situated in and out of designated flood plain. In coromandel, New Zealand; in 1985 immediately after flooding, selling prices were significantly lower by 9% for all properties in the town including the non hazard areas for up to 4 years. Also in 1985 properties in Georges R. catchment in Australia fell by 25% and in 1991 properties in Parramatta R. catchment situated on highly flood

liable land fell by 11% but recovered within a year. As a result, Kellens, Zaalberg, Newtens, Vanneuville and De Maeyer (nd) affirmed that the study of risk perception involves the examination of people awareness, emotions and behavior with regard to hazards.

Flooding in Nigeria

Flooding refers to the inundation of an area by unexpected rise of water by both dam failure or extreme rainfall duration and intensity in which life and properties in the affected area are under risk (Nyarko, 2002). There is no doubt that globally natural disasters are on the rise. Over the past two or three decades, the economic losses and the number of people who have been affected by natural disasters have increased more rapidly (UNEP, 2007). Globally, about 200 million people were affected by natural disasters in the 1990s with about USD 63 billion lost in terms of market value of damaged properties (World Disaster Report, 2002). Historical studies indicate that major floods in Nigeria date back to the 1933 incident which occurred in Ibadan. Thereafter, there were others in Ibadan in 1951, 1960, 1963, 1980, 1985 and 2011. Ilorin, 1976; Lagos, 1985 and 1988; Cross river and Akwa Ibom, 1989 (Emordi, 2012). In fact flooding has become a recurring phenomenon in most cities in Nigeria with the most recent occurrences in Lagos on the 10th and 11th July, 2011 after about 12 hours of torrential rainfall which resulted into loss of lives, farmlands, household goods and landed properties. Flood disaster in Lagos is only an indication of the magnitude of flooding problem in Nigerian cities. Also on 29th June, 2012, a portion of Murtala Muhammed International Airport Road by Mobil Filling Station was submerged, as were some areas in Mafoluku, Oshodi, Victoria Island, Ikoyi, Lagos Island and some other parts of Eti-Osa Local Government Area. Many residents could not get to their offices and business places as most areas in the state were heavily flooded. Many properties were swept away and some major roads in the state were blocked (Vanguard Newspaper, June 30th, 2012).

Causes of the Frequent Flood Situation in Lagos, Nigeria

Human settlements may be affected by four types of flooding which includes localized flooding due to inadequate drainage; flooding from small streams whose catchment areas lie almost entirely within built-up areas; flooding from major rivers on whose banks the towns and cities are built; and coastal flooding from the sea or from a combination of high tides and high river flows from inland (Douglas et al., 2008). It is estimated that the required drainage channel to avert flooding is short by about 45%; and the existing ones are only about 30% maintained (Aderogba, 2011). Furthermore, causes of flooding in Lagos as affirmed by Aderogba (2011) includes the following: torrential rain, base water flow, spring water flow, filled/silted/dirty drainage channels, ocean/lagoon surge, illegal channelization of drains, constructions and reconstructions, blockage of canals, inadequate drainage channel, non-compliance with regulations, illegal structure on drainage channels, encroachment, negligence, collapsed bridges/culverts, farming along flood plains, and nature of terrain.

METHODS

This review is structured according to a series of questions that serve to demonstrate the spatial effects of flooding on land value. In this review, more attention is given to the assessed rather than perceived influences of flooding on land values in the study areas. The approach adopted includes document review, structured questionnaire and direct observation. For most qualitative studies, purposive sampling technique is used in which subjects are selected based on their relationship with the research question (Bryman, 2008). This study is no exception. Purposive sampling technique was used to select sample areas which include Lekki phase 1 and Victoria Island in Lagos, Nigeria. Lagos is the smallest State in the Federation yet with a population of about 13.5 million people and currently rated as the second African country after Cairo as having

reached mega city status (Omirin, 2013). Furthermore, Victoria Island is surrounded entirely by water, bordered by the Atlantic Ocean on the South, the mouth of the Lagos Lagoon on the West, the Five Cowrie Creek to the north North, and Oniru Estate on the East.

A quasi experimental approach was adopted in the study location for the purpose of assessing the variability of land and building values between areas susceptible to flooding because of their closeness to the ocean and beaches compared to other areas which are not. This is to facilitate the determination of the degree of variability of land and building values in the study area. The magnitude of the effect will be estimated from repeated sales and rental price, average mean, relative importance index and Pearson product –moment correlation. Correlation is a technique used to measure the degree of relationship between variables. It can be used descriptively to find the degree of relationship or inferentially to test hypothesis of significance. The populations considered for the study are the 318 practicing firms registered with The Nigerian Institution of Estate Surveyors and Valuers, Lagos State Branch. A systematic random sampling technique was adopted in the sample selection in which every 6th firm on the registration list was selected for the study. This gives a total of 55 firms, representing the sample size for the study location.

STUDY FINDINGS

Physical Effect of Flooding

Based on the rating provided by the respondents in table 1, the flood has higher impact on traffic than on any other areas observed in the study. The impact of flooding on traffic was found within the band of 4.5 and 5.0, and categorized as being very high. Following the impact on traffic, is the impact on buildings, with 4.13 and categorized the impact as high. Others in this same categorization are impact on on-going construction, 3.77, occupiers' health 3.32. The least effect was on open land, 3.29 and household item, 3.26. This implies that physical effect on traffic is high as it increases the number of waiting time at designated bus-stops, high traffic jam and slow movement of vehicles due to flooding of the roads. Impact on buildings was also rated high as it increases maintenance cost due to physical damage especially on façade of the building. This is followed by effect on on-going construction work on site as it increases labour and material cost as well as total construction time. Moreover, long term effects of flooding on psychological health may perhaps be even more important than illness or injury and at times emotional trauma may continue long after water has receded. Effect on open land was rated low with mean of 3.29 as well as effect on household items with the lowest mean of 3.26. This could be as a result of flood measure put in place during construction, for instance, raising the foundation high to avoid risk of been flooded.

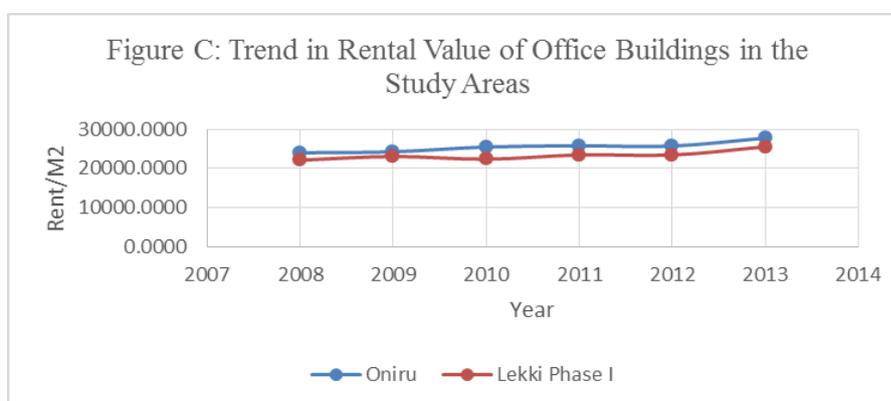
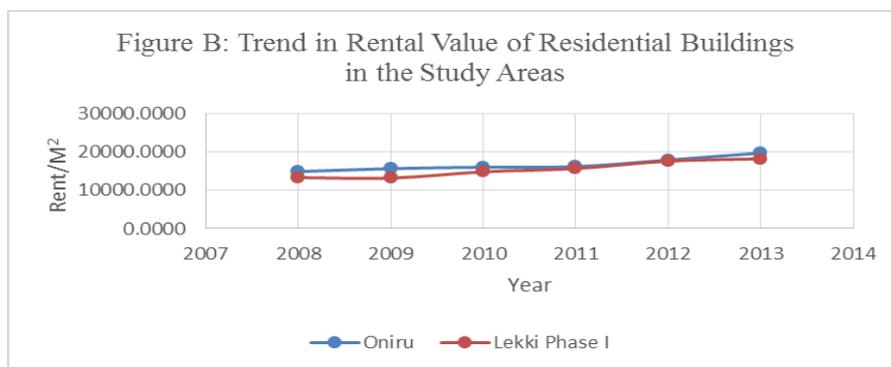
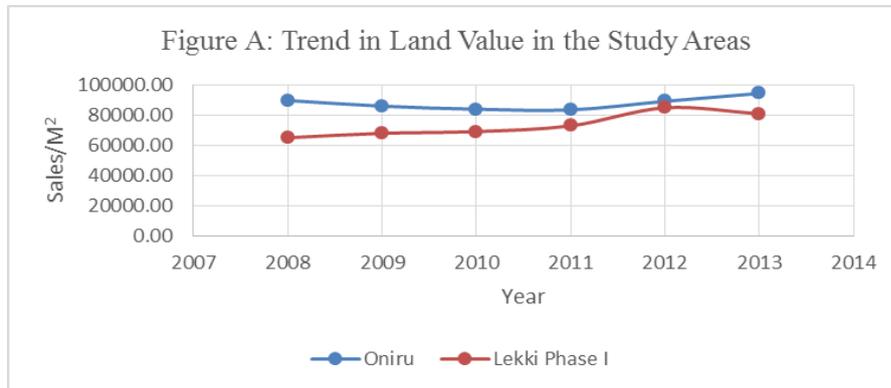
Table 1: Physical Effect of Flooding

	Std. Deviation	Mean
Effect of flood on traffic	0.771	4.54
Effect of flood on buildings	0.841	4.13
Effect of flood on on-going construction	0.729	3.77
Effect of flood on occupiers health	0.911	3.32
Effect of flood on open land	0.973	3.29
Effect of flood on household items	1.073	3.26

Land and Buildings Values in the Study Area

Figures A, B and C give and compare values of residential and office buildings in the two locations over a period of 2007-2013.

The occurrence of flooding showed a reduced demand on land and building averagely between 1-20%. 11-20% in Oniru while Lekki phase 1 only recorded between 1-10% reduction in respect of demand of land and building. Oniru further recorded high impact of flooding on market value than Lekki phase 1.



It was further observed that effect of flooding on rental value of residential and office buildings in the study area was mild as rent remained constant over a period of time. This could be adduced to the custom of rent payment per annum and in advance in the study area as well as cravings for the study location by investors for building development. This was evident in the study where respondents rated location higher than flooding or flood risk in determining market

Effect of Flooding on Demand for Land and Building

From the analysis, the effect of flooding on the rate of demand for land and building is rated averagely between 1-20%. This implies that the effect of flooding will reduce demand averagely by 1-20%. In Oniru, 33.3% of the respondents rated the effect flooding will have on demand below 1 to 10% and 45.8% provided similar rating in Lekki Phase I. About 45.8% rated the effect on demand between 11 and 20% in Oniru and 22.9% considered a similar view for Lekki Phase I. On this rating, the effect between the two locations stood at ratio 2 to 1 with Oniru having ratio 2 over Lekki Phase I. A similar ratio is shared on effect that is above 30%. This implies that the occurrence of flooding has a more negative implication on demand for land and buildings in Oniru than Lekki Phase 1.

Effect of Flooding on Market Value of Land and Building

Oniru recorded high effect of flooding on reduction of market value for land and buildings. Approximately 30% of the total respondents indicated impact is above 30% reduction for both sales and rental value in Oniru and only 10.4% for Lekki phase I on similar view. For degree of impact between 11-20% and between 21-30%, Oniru equally recorded high number and percentage of respondents compared to Lekki phase I, emphasizing higher impact of flooding on sales and rental value reduction in Oniru.

Correlation Analysis of Flooding Occurrence and Value of Landed Property in the Study Areas

Relationship between occurrence of flooding and landed property value is examined with Pearson Product- Moment Correlation and the result is given on table 4.

Table 4: Correlation Analysis of Flooding Occurrence and Value of Landed Property in the Study Areas

	Water Corporation Road ONIRU			Admiralty Way LEKKI		
	Land Value/m ²	Residential Building (rent/m ²)	Office Building (rent/m ²)	Land Value/m ²	Residential Building (rent/m ²)	Office Building (rent/m ²)
r	-0.343*	-0.290	-0.053	-0.403**	-0.479**	0.004
p-value	0.030	0.070	0.747	0.010	0.002	0.982
Remark	Relationship exists	No Relationship	No Relationship	Relationship exists	Relationship exists	No Relationship
		p	p			p

From the result, the p-value indicates statistical significance of correlation coefficient between flooding and land value in Oniru; $r = -0.343$, $p < 0.05$, implying a relationship between the two variables. Meanwhile, the p-value indicates statistical significance of correlation coefficient between flooding and land value in the two location, and residential building rental value in Lekki; $r = -0.403$, $p < 0.05$ and $r = -0.479$, $p < 0.05$, respectively. For each of these findings, a negative relationship exists, meaning that the less frequent is flooding the higher the value of landed property and vice versa. It therefore implies that while flooding is related to land value in Oniru, there is no such relationship for residential and office rental values in Oniru. We equally found no relationship between office rental value and flooding in Lekki Phase I.

DISCUSSION OF FINDINGS AND CONCLUSION

Findings of this study have shown that impact of flooding on land price and rental value of properties appear to be a reaction to flood events rather than the perceived risk of flooding, damage to buildings and cost of remediation (repairs). Although about 75% of the respondents

acclaimed seriousness of flood occurrence in the study location, the depth has not exceeded between ground level and up to 1 meter deep. However, during incidence of flooding, water remained on land for 1 to 24 hours before receding.

The study further showed the effect of flooding on traffic, buildings, on-going construction open land and household items with mean of 4.54, 4.13, 3.77, 3.32 and 3.26 respectively. The effect of flood on traffic was considered very high compared to the effect on building which was considered high. However with effect on open land, on-going construction and household items, respondents were indifferent. The occurrence of flooding showed a reduced demand on land and building averagely between 1-20%. 11-20% in Oniru while Lekki phase 1 only recorded between 1-10% reduction in respect of demand of land and building. Oniru further recorded high impact of flooding on market value than Lekki phase 1. At Oniru, the degree of effect on the market value of land varies averagely between 5-25% discounts while in Lekki phase 1, below 1-10% discount. In fact some respondents ascribed no effect on market value of land in lekki. This emphasizes a higher degree of flood impact in Oniru than lekki Phase 1.

This further corroborates studies that flood risk results in discount in land value. For instance, Fukozono and Ikeda (2003) ascribed a discount of between 1.27 and 4.7% to land values in Japan, Bin and Polasky (2003) ascribed 5 and 8% discount in North Carolina, Lambley and Cordery affirmed between 4 and 12% discounts in Australia while Lamond (2008) ascribed a discount of between 15 and 35% to land values in the UK.

In testing for the relationship between occurrence of flooding and landed property values, the study establishes that a negative relationship exists between land in Oniru, Lekki Phase1 and residential buildings in Lekki which implies that less frequent flooding will result in higher property value and vice versa. However, there is no such effect on rental value of residential and office building in Oniru and office building in Lekki which implies that flooding has no implication in determining rental values of this class of buildings in the study location. This could be attributed to the other factors that affect property performance other than occurrence of flooding or flood risk as the result further showed that location is the major determinant of land and property values as it ranked first in the study location. This further affirms Meldrum (2011) and Lamond (2008) statement that flood risk is subjective in nature, hence often times there are no discount in property values in flood plain areas.

This study therefore concludes that the occurrence of flooding significantly affects the sales price of land in both Oniru and Lekki Phase1 than it does on rental values of office and residential buildings in the study location. Therefore, there is need to improve on the drainage systems to aid quick flow of excess water in less than an hour to reduce the physical impact on traffic and implementation of building code. Furthermore there is need to improve on the embankments on shore lines to reduce water waves and over flooding of land and buildings in the study location.

REFERENCES

- Aderogba, K. (2012). Global Warming and Challenges of floods in Lagos Metropolis, Nigeria. *Journal of Accademic Research International*. Vol. 2, No. 1. Retrieved from www.journal.savap.org.pk 23rd April, 2013.
- Adetunji, M., and Oyeleye O. (2013). Evaluation of the Causes and Effects of Flood in Apete, Ido Local Government Area, Oyo State Nigeria. *Civil and Environment Research Journal* Volume 3, Number 7, Pp19-27. Retrieved from <http://www.iiste.org/journals-volume> 7th September, 2013.

- Becker, H. S. (1963). "Outsiders: studies in the Sociology of Deviance" Free Press, New York page 46 retrieved 26th March, 2013
- Beacker, Karte and Dennis W. (1993). "Recovery after disaster: Achieve Sustainable development, Mitigation & Equity. *Disaster Journal* Retrieved 23rd April, 2013.
- Bin O., and Polasky S. (2003). Effects of Flood Hazard on Property Value: Evidence before and after hurricane Floyd. Retrieval from citeseerxist psu.edu/view doc/download d? doi, 10.1.1-198.596 & rep 1 & type = pdf – 25th August 2013.
- Bramley, G., Munro, M., & Pawson, H. (2004). *Key Issues in housing Policies and markets on 21st Century Britain*, Palgrave Macmillan.
- Bryman, A. (2008). "Social Research Methods" 3rd ed. Oxford University press, UK page 31
- Damianos, D., and Shabman L.A. (2010). Land Prices in Flood Hazard Areas: Applying methods of land value Analysis Retrieved <http://www.share.net/ctlachu/floods-8957078#btnNext>, 25th August, 2013.
- Douglas, I., Alam, K., Maghenda, M., McDonnell, Y., Mclean L., and Jack, C. (2008). Unjust Waters: climate change, flooding and the urban poor in Africa, *Environment and Urbanization Journal*, 2008 20: 187. DOI: 10.1177/0956247808089156
- Gayelord, N. (2008). The Effect of Flood on Everyday Life. Retrieved <http://www.content4reprint.com/home/the-effects-of-flood-damage-on-everyday-life.htm>
- Green, C. (2004). The evaluation of vulnerability to flooding. *Disaster prevention and management Journal*, Vol. 13(4), Pp323-329.
- Green, C., Van derveen, A., Wierstra, E., & Penningrowsell, E. (1994). Vulnerability refined: analysing full flood impacts in Penningrowsell, E., & Fordham, M., (Eds.) *Floods across Europe*. London, Middlesex University Press.
- Grima, D., Deguara, J., and Jones, M. (2011). Flooding: World Overview. Retrieved From <http://www.slide share.net/geography students/flooding>, 25th August, 2013.
- Han, D. (2012). Concise Environmental Engineering, PHD and ventus publishing APS Downloaded from ebookboon.com, October 28th, 2012.
- Kellens, W., zaalbery, R., Neuten, T., Vanneuville, W., and De Maeyer, P. (UD). An Analysis of the public perception of flood Risk on the Belgian Coast Assessed 28th October, 2013 from www.researchgate.net/...perception-of-risk../d912f50a3b56b364
- Kropp, S. (2012). The Influence of Flooding on the Value of Real Estate. FIG Working Week 2012 Conference held in Roma, Italy, May 6-10, 2012 Retried from www.fig.net/pub/fig2012/papers/tso6H-kropp-5.729.PDF?page=1&2room=084
- Kousky, Carolyn (2010). Learning from Extreme Events: Risk Perceptions after the Flood. *Journal of Land Economics*, Volume 86 (3), Pp 395-422. Assessed 4th November from www.rff.org/Documents/publications/RFF_pubs/kousky-2010Learning from extreme events.
- Lakshmanan, C.T. (2011). Floods. Retieved from <http://www.slide share.net/ctlachu/floods-8957078#btnNext>, 25th August, 2013.
- Lambley, D., & Cordery, I. (2013). 'The Effects of Disclosure of Food-Liability on Residential Property Values' *Australian Journal of Emergency Management*, 20(12), 15–19. Retrieved 25th August, 2013.
- Lamond, J. (2008). The Impact of Flooding on the Value of Residential Property Price in the UK: A PhD thesis submitted to the University of Wolverhampton. Retrieved from Wlv.opnrepository.com/wv/bitstream/2436/31427/1/Lamond-PhDthesis, Retrieved 27th March, 2013.
- Lancaster, J., Preene, M., and Marshal, C. (2004). Development and flood risk - *Guidance for the Construction Industry*. CP/102 Funders Report *Construction Industry Research and Information Association*.

- Meldrum, James (2011). Using Rental Properties to Better Understand the Subjective Risks to Flooding. Assessed 28th October, 2013 from www.spot.colorado.edu-meldrumj/papers/meldrum-2011-AESS-abstract.pdf
- Munoyerro, J. (2011). Flood Risk Management in Spain: Flood Control in Trans Boundary Rivers: Being a workshop paper on flood management in a Trans boundary context, Zagreb, 13th -14th November, 2011 Retrieved from http://www.slide/share.net/GWP/mediteranean/workshop_on_flood-management_in_a_trans_boundary_context_131412011_justo_morra. 25th August, 2013.
- Nyarko, K. (2002). Application of a rational model in GIS for flood risk assessment in Accra Ghana. *Journal of spatial Hydrology*. Vol. 2, pp 1-2
- Odunuga, S., Oyebande, L., and Omojola A. S. (2012). Social Economic Indicators and Public Perception on Urban Flooding in Lagos Nigeria. *Journal of the Nigeria Association of Hydrological Sciences*, 2012 Retrieved from <http://www.unaab.edu.ng> 27th August, 2013.
- Omirin, M. M. (2013). Economic Challenges of the Emerging Lagos Megacity. Being paper presented at the MCPD programme organized by NIESV Lagos State Branch at Airport Hotel, Ikeja, Lagos.
- Omojola, A. (2009). Framework for City Climate Risk Assessment. *Fifth Urban Research Symposium*, 2009
- Pryce, G., Chen Y., and Galster, G. (2011). The impact of floods on house prices: An imperfect information approach with myopia and amnesia, *Housing Studies Journal*, Vol. 26, No 2, pp 259-279 DoI:10.1080/02673037.2011.542086 Retrieved from <http://dx.doi.org/DoI:10.1080/02673037.2011.542086>.
- Slovic, P. (1987). Perception of Risk. *Journal of Science*, 236(4799), 280-286.
- Stone, B. (2009). Land Use as Climate Change Mitigation. *International Journal of Environment Science & Technology*, Atlanta Georgia, Volume 43, Pg. 9052-9056. Retrieved from lu_cc_mitigation_stone 09. January, 28th, 2013.
- The World Bank International Development Association Report, (2009). Managing Natural Hazards, Reducing Risks to Development. *Journal of CRED Crunch*, Issue 16, April 2009. Retrieved 23rd February, 2013. <http://www.worldbank.org/ida>
- The United States Geological Survey Website Maps.com Retrieved 24th February, 2013, <http://www.maps.com>
- United States Department of State. (2010, January). *Indonesia (01/10)*. Retrieved from <http://www.state.gov/r/pa/ei/bgn/2748.htm>
- Turnbull G., Herbert V., and Mothorper C. (UD). flooding and liquidity On the Bayou: The Capitalization of Flood Risk into House Value and Ease-of –Sale. Assessed 28th October, 2013 from Lema.seal.psu.edu/risk/...turbull-et-al-flooding-on-the_bayou-psu-2...
- UNEP (2007) “Global Environment outlook GEO4: Environment for Development” United Nations Environment Programme Nairobi, Kenya Retrieved from http://www.unep.org/IK/PDF/Indigeneous_Booklet.pdf
- Vanguard Newspaper, June 30th, 2012. www.vanguardngrnews
- World Bank – UNDP Framework report: (2013). Disaster Risk Management Programs for priority countries, Africa Retrieved 26th March 2013 from www.Google_Scholars
- World disaster Report (2002). “Focus on Reducing Risk” retrieved from <http://www.itrc.org/publicat/wdr2002/> Accessed 26th March, 2013.
- Yeo, Stephen (UD). Effects of Disclosure of Flood-Liability on Residential Property Values. Risk Frontiers – N H R C Macquaries Unversity Assessed 28th October, 2013 from www.riskfrontiers.com/yeo_property_values/Report3.doc

ENVIRONMENTAL CHARACTERISTICS OF COMMUNITY PARK AND USERS' HEALTH: A CASE STUDY OF ROWE PARK, YABA, LAGOS

Orelaja Olabode

Department of Urban and Regional Planning,
University of Lagos
olabodeorelaja@gmail.com

ABSTRACT

Well-designed public park that encourages physical activity is a community asset that could potentially contribute to the health of local residents. Parks are potential venue for increasing physical activities and it is one of the most important predictors of physical activity. This paper investigated the influence of park features, condition, access, aesthetics, safety and policies on users' health in the study area. It addressed the health and wellness needs of people. It examined the influence of physical and environmental characteristics of parks in enhancing or limiting the opportunities people have to be active.

Using System for Observing Play and Recreation in Communities (SOPARC) tool, data for the study was gathered through the use of questionnaires, checklist, oral interview and observation. A baseline data gathered from a 7day pre-survey of users was used. It included an average total of 368users from 8 different activities who were randomly selected from each activity. Available facilities and its conditions were documented, users' socio-economic characteristics were studied and distance of the park from users was examined. The association between access to park and physical activity was examined. Also, park's policies on usage, attitude to leisure, safety and security measures were studied.

It was gathered from the survey that 63.1% of the respondents use the park for physical activity and 44.3% of the respondents live in less than 1km from the park. Findings revealed that distance reduces the frequency of patronage of the park by users. It was also reported that 67.2% of the respondents use the park because of its attractive and environmental features.

Proximity to attractive park is associated with higher levels of thoughtful design that create increase walking. Attractive park with facilities that encourage active use by multiple users (e.g., walkers, sports participants, picnickers) enhances community health.

Keywords: Park, Physical activity, Environmental features, Health

INTRODUCTION

Physical inactivity is widely recognized as a significant public health concern, and many attributes of the physical environment, including parks, influence the opportunities people have to be active (Kaczynski & Havitz, 2010). Urban public services and facilities, such as public parks and open spaces, are vital to the quality of life of city dwellers. Besenyi (2011) noted that parks are valuable community resources that can play an important role in the battle against rising rates of obesity and chronic disease in youth across the country. Better understanding the ways in which these settings are associated with physical activity among children can inform future research and environmental and policy changes that can promote the health and well-being of generations to come. It, therefore, becomes imperative that the provision of urban parks and open spaces is accompanied by a fundamental need for ensuring adequate access to such facilities.

Contemporary provision of urban parks rests largely on professional assumptions about its significance in the lives of residents. Jacquelin, Carolyn & Melaine (2012) showed that the most highly valued parks are those which enhance the positive qualities of urban life: variety of opportunities and physical settings; sociability and cultural diversity. These improve the social

aspects of life that enhance people's satisfaction, experiences and perceptions of the quality of their everyday environments (Mahdavinejad & Abedi, 2011).

The negligence of adequate planning and development of urban parks affects cities from achieving maximum utilization of their social, economic and environmental sectors (Officha, Onwuemesi, Enete & Nzeamalu, 2013). Also, managerial problems in maintaining the few available urban parks have led to its gradual decay and loss. Inefficient use and loss of urban parks had invariably reduces its comfort, aesthetic view, relaxation, recreation, communal interaction and preservation of natural system (Officha, Onwuemesi & Akanwa, 2012). Hence, there is an existence of urban sprawl which is characterized by waste of prime agricultural land, lack of aesthetics and uneconomic pattern of development.

Urban park is a promising means to satisfy current physical activity requirements of users. Its use can greatly be influenced by access, physical dimensions and perceptions of difference. Genuine consideration of users in the planning and management of urban parks establishes interest in relationships among the environment, exercise and health. Barriers to exploration and fuller engagement in physical activities (real or perceived) have impact on the environment and health (Ayamba and Rotherham, 2010). The impact can be measured psychologically, socio-culturally and economically. Against this background, this paper examined the influence of physical and environmental characteristics of parks in enhancing or limiting the opportunities people have to be active. It provides information on available recreational facilities for healthy living and also alerts the park managers on the need to ensure supply of users' needs in the study area.

METHODS

This descriptive study explored the potential for public parks and recreation centers as intervention sites for promoting physical activity, which enhances health among residents. Investigation through checklist, informant interviews with relevant stakeholders and through a comprehensive survey of questionnaire administration were employed for the study. A baseline data gathered from a 7day pre-survey of users was used. It included an average total of 368users from 8 different activities who were randomly selected from each activity. Available facilities and its conditions were documented, users' socio-economic characteristics were studied and distance of the park from users was examined. The association between access to park and physical activity was examined. Also, park's policies on usage, attitude to leisure, safety and security measures were studied.

FINDINGS AND DISCUSSION

Rowe park is a community recreational centre located at Alagomeji area of Yaba, Lagos for the purpose of relaxation (leisure), educational, health and economic. The centre is dominated by active type of recreational activities. This study identified various sporting activities that are actively engaged-in by users. These activities can be broadly classified into indoor and outdoor games. The indoor games include 6numbers table tennis court, 3numbers badminton court and the indoor hall is used for other sporting activities like boxing, judo and karate. Also, the outdoor activities include the basketball court, handball court, lawn tennis court and volleyball court (also used for abula games). Other recreational activities that take place within the study area are relaxation spots where users can get refreshed and cycling within available paved spaces in park. Rowe park has an administrative building, registration centre, offices, and a block of retail shops. Two car park spaces are available and functioning efficiently at both entrances to the park. It is well landscaped with trees for aesthetics.

Findings on park policies showed that there is no restriction to use of available facilities, provided the prospective user is competent to play the game. There is safety and security measures being put in place to ensure the safety of those using the park as well as the facilities. Security services are provided by the Lagos State vigilante group, assisted by the police. The

availability of a standard clinic ensures quick response to any injured participants. The attitude to leisure can be rated high as there are so many people at different sporting facility which is efficiently and effectively put to use.

Generally, the park is in good condition as the environment is characterized by the standard that is fit for organized sports competition; good drainage system for surface water run-off, parking lots and the placement of the adjoining facilities and structures. Every point within the park is easily accessible and easy connected to different game centres. In terms of the beautification and design of the park, it is generally fair because the park lacks adequate landscaping and greenery both within and outside except for the trees planted along the parking lots.

Findings showed that the park is mostly used during the weekend and holidays. Users during weekdays are mostly those preparing for sporting events. It was gathered from the survey that 63.1% of the respondents use the park for physical activity while others use for relaxation. 44.3% of the respondents live in less than 1km from the park. This implies that over 50% of the users come from distance of more than 1km to the park. Findings revealed that distance reduces the frequency of patronage of the park by users as 21.8% of the respondents visit the park daily and 56.7% of the respondents are occasional visitors. 61.4% of the respondents reported that they make use other parks in the city as Rowe park lacks sensorial elements that enhances psychological balance. Also, other respondents reported the use of other parks in the city because there is no track for athletes and pitch for footballers. It was also reported that 67.2% of the respondents use the park because of its safety and security measures, attractive and environmental features.

LITERATURE REVIEW

Recreational concept of open spaces describes open spaces as publicly accessible open spaces designed and built for human activity and enjoyment (Lynch, 1981). These include parks, neighbourhood playgrounds, community gardens, downtown plazas, streets and malls.

Gehl (2007) described open space from users' point of view as being an arena that allows for different types of activities encompassing necessary, optional and social activities. Necessary activities are compulsory activities that take place independent on physical environment. This implies that the design and management of physical environment have an impact on the opportunities that arise for such social activities.

Kaczynski & Havitz (2010) examined the relationship between proximal park features and residents physical activity in neighbourhood parks. The study was conducted in 1km radius around 33 municipal parks within the four neighbourhoods. The Environmental Assessment for Public Recreation Spaces (EAPRS) instrument was found to be a valuable tool for examining the park features that may be related to physical activity. Data from participants showed that having five facilities (unpaved trail, meadow, water area, basketball court, and soccer field) and six amenities (restroom, historical/educational feature, landscaping, bike rack, parking lot, and a roadway through the park) within a nearby park was significantly related to an increased likelihood of using neighbourhood parks for physical activity. One other nearby facility, a ball diamond, was related to significantly lower odds of engaging in at least some physical activity in neighbourhood parks. Parks with a variety of built and natural facilities and amenities can support a range of physical activity behaviours.

Lee & Maheswaran (2011) reviewed the evidence of health benefits of urban green spaces. They gathered that there is weak evidence for the links between physical, mental health and well-being, and urban green space but environmental factors such as the quality and accessibility of green space affects its use for physical activity. User determinants, such as age, gender, ethnicity and the perception of safety, are also important.

Tilt (2010) explored demographic, environmental factors and preferences for adults with children in the household in walking trips to parks within the city of Seattle, Washington and surrounding suburbs. Using postal survey, the study measured walking trip frequency, preferences for walking environments and demographic information. Association between variables were analysed using Analysis of Variance and Multiple Linear Regressions statistical tools while chi-square and qualitative content analysis were used to understand preferences for walking environments. It was gathered from the survey that demographic and environmental factors influence walking trips, particularly perceived level of neighbourhood vegetation and individual preferences. Adult respondents with children living at home walked most frequently to parks compared to other destinations. Owning a dog, living within close proximity to a variety of destinations, perceptions of ample neighbourhood vegetation, and preference for natural-looking environments were factors positively associated with these walking trips.

Crawford et al (2007) examined the relations between neighbourhood and socio-economic status and features of public open spaces (POS) in Melbourne, Australia. Variability of public open spaces features identified within 800m radius of each participant's home was examined across quintiles of neighbourhood Socio-Economic Index for Areas (SEIFA). They gathered that POS in the highest socioeconomic neighbourhoods had more amenities (e.g. picnic tables and drink fountains) and were more likely to have trees that provided shade, a water feature (e.g. pond, creek), walking and cycling paths, lighting, signage regarding dog access and signage restricting other activities. There were no differences across neighbourhoods in the number of playgrounds or the number of recreation facilities (e.g. number of sports catered for on courts and ovals, the presence of other facilities such as athletics tracks, skateboarding facility and swimming pool). This study suggests that POS in high socioeconomic neighbourhoods possess more features that are likely to promote physical activity amongst children.

Besenyi (2011) examined association of park proximity and park features with nearby youth achieving recommended levels of physical activity in Kansas City, Missouri. While detailed park characteristic information for all parks within 1 mile of the youth was obtained via observational audits, binary logistic regression analyses were used to examine the relationship between each park proximity and park characteristic variable and the likelihood of youth meeting physical activity recommendations, while controlling individual and neighbourhood level covariates. It was gathered from the survey that all youth and female youth who had a park within one-half mile of home were more likely to achieve physical activity recommendations than those with no parks nearby. Likewise, all youth and male youth with three or more parks within 1 mile were significantly more likely to achieve physical activity recommendations than those with only 1 park. Further, youth that had a park with a playground within one-half mile or a baseball field within 1 mile of their home were more likely to achieve physical activity recommendations.

Concepts of Urban Public Park

Urban public park is often appreciated for the recreational opportunities it provides. Recreation in urban open space includes active recreation (such as organized sports and individual exercise) or passive recreation, which may simply entail being in the open space. Time spent in an urban park for recreation offers a reprieve from the urban environment. For example, lack of community and public access to safe open and green space is a critical area of concern for urban residents in New England (USEPA, 2006). Urban park provides recreational areas for residents and also helps to enhance the beauty and environmental quality of neighbourhoods. Broad range of recreational sites equally broad brought with it range of environmental issues. Just as in any other land uses, the way parks are managed can have good or bad environmental impacts, from

pesticide runoff, siltation from overused hiking and logging trails, and destruction of habitat (USEPA, 2006).

Nature encourages the use of outdoor spaces, increases social integration and interaction among neighbours (Coley et al., 1997). The presence of trees and grass in outdoors common spaces may promote the development of social ties (Kuo et al., 1998). They also found out that greenery helps people to relax and renew, reducing aggression. Natural environments can also be seen as a domain of active experience providing a sense of challenge, privacy and intimacy, aesthetic and historical continuity. Beside the social and psychological benefits mentioned above, the functions of urban nature can provide economic benefits for both municipalities and citizens. CABESpace (2009) gathered in London that a high-quality public environment has a significant impact on the economic life of urban centres, and is therefore an essential part of any successful regeneration strategy. Hence, the presence of good parks, squares, gardens and other public spaces become a vital business and marketing tool as it increases the attractiveness of the city and promote it as tourist destination, thus generating employment and revenues.

Public recreation parks are multi-use, but recent advances in best practices have prompted many cities to move away from old-fashioned and biologically impoverished "urban savannah" designs, to mosaic environments, which allow full recreational use but maintain higher levels of biodiversity and hence deliver greater benefits to human well-being (Thwaites, Helleur & Simkins, 2005). A recent study in Sheffield, United Kingdom, found that the psychological benefits gained by visitors to urban green spaces increased with their biodiversity (Fuller, Irvine, Devine-Wright, Warren & Gaston, 2007), indicating that 'green' alone is not sufficient; the quality of that green is important in delivering the health benefits. In spite of the benefits of urban open space, some studies have identified crime and drug use problems in urban open spaces.

Urban Parks in Lagos State

Urban parks in Lagos State are inadequate and suffer neglect. Neglect of urban open space development in Lagos metropolis, which is characterized by clusters of many towns with indigenous core, is historical. This is because various conglomerates of cities and towns that make up the metropolis grew without a plan except for the European Quarters now known as Government Reservation Areas. Inadequacy of public recreation open spaces in Lagos State was a testimony to the little attention successive governments gave to this urban sector (Falade, 1998).. A base line study of Oshodi/Isolo Local Government revealed the lack of public recreational facilities forcing the residents especially children and adolescents to convert any available space including unbuilt residential plots, streets and school sports ground for active leisure activities.

So much lip service had been paid to the development of public park system since 1960 (Falade, 1998). Less than 10% of the 72 hectares of open spaces identified for development by the Ministry Youths Sports and Social Development in 1986 remained by 2002 (Ashiyanbi, 2002). Until recently, Rowe park and other recreation centers like Evans square - Ebute Metta, Onikan open space, Ajele playground and Orija lane playground Ikeja were in a state of total disrepair. In achieving this development, Lagos State government established Lagos State Parks and Gardens Agency (LASPARK) in accordance with the Lagos State Parks and Gardens vide law13, 2011. The agency is to implement the greening policy of the State government towards the restoration of the lost glory of old Lagos noted for her green ambience and also re-awaken the consciousness of the indigenes to the importance of green environment.

REFERENCES

- Ashiyambi Associates (2002) *Lagos State Regional Plan Review*. Lagos. Ashiyambi Associates. Lagos.
- Ayamba M.A. & Rotherham (2010) *Inclusion and Access to Open Spaces: Perceptions of the Outdoors by Black and Ethnic Minorities with a case study from England*. Tourism Leisure and Environmental Change Research Unit, Sheffield Hallam University, United Kingdom.
- Besenyi G.M. (2011) *Park environments and youth physical activity: exploring the influence of proximity and features across Kansas City, Missouri*. Master of Public Health Thesis, Kansas State University, Missouri. Retrieved from www.k-state.edu on the 3rd of September, 2014.
- CABESpace (2009). *Open Space Strategies: Best Practice Guidance*. London: Commission for Architecture and the Built Environment and the Greater London Authority.
- Coley, R., Kuo, F., Sullivan, W., (1997) *Where does community grow? The social context created by nature in urban public housing*. *Environmental Behaviour*, 29, 468–494.
- Crawford et al (2007) *Do Features of Public Open Spaces vary according to Neighbourhood Socio-Economic Status?* *Health and Place*, 14(4): 889-893.
- Falade J. (1998) *Public Acquisition of Land for Landscaping and Open Space Management*. *Journal of Nigerian Institute of Town Planners*. 6(1).
- Fuller, R., Irvine, K., Devine-Wright P., Warren, P. & Gaston, K. (2007) *Psychological benefits of Green space increase with Biodiversity*. *Biology Letters*, 3, 390–394.
- Gehl, J., (2007) Public spaces for a changing public life, in Thompson C.& Travlou P. (eds) *Open space: People Space*, Taylor and Francis, Abingdon, Oxon, pp. 3-10.
- Jacquelin B., Carolyn M. & Melaine L. (2012) *People, Parks and the Urban Green: A Study of Popular Meanings and Values for Open Spaces in the City*. *Urban studies*, 25(6): 455-473
- Kaczynski A. T. & Havitz M. E (2009) *Examining the Relationship between Proximal Park Features and Residents Physical Activity in Neighborhood Parks*. *Journal of Park and Recreation Administration*, 27(3).
- Kuo, F., Bacaioaca M. and Sullivan W. (1998) *Transforming Inner City Landscapes: Trees, Sense of Safety, and Preferences*. *Environmental Behaviour*, 1 (30), 28–59.
- Lee A.C. K. & Matheswaran (2011) *The Benefits of Urban Green Spaces: A Review of Evidence*. *Journal of Public Health*, 33(2): 212-222.
- Lynch, K. (1981). *The Image of the City*. M.I.T. Press Cambridge, Massachusetts.
- Mahdavinejada, M., Abedia, M., (2011). *Community-oriented landscape design for sustainability in architecture and planning*. *Procedia Engineering* 21:337–344.
- Officha M. C., Onwuemesi F. E., Enete I. C. & Nzeamalu I. C. (2013) *Assessing the Need for Developing and Managing Recreational Facilities in Nigeria*. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 3(1), 26-29. Retrieved from iosrjournals.org on 4th April, 2014.
- Officha M.C., Omwuemesi F.E. & Akanwa A.O. (2012) *Problems and Prospect of Open Space Management in Nigeria: The Way Forward*. *World Journal of Environmental Biosciences*, 2(1): 7-12.
- Thwaites, K., Helleur, E. & Simkins, I. (2005) *Restorative Urban Open Space: Exploring The Spatial Configuration of Human Emotional Fulfilment in Urban Open Space*. *Landscape Research*, 30, 525–547.
- Tilt J. H. (2010) *Walking Trips to Parks: Exploring Demographic, Environmental Factors and Preferences for Adults with Children in the Household*. *Preventive Medicine*, 50: 569-573.
- USEPA (2006) Urban Environmental Program in New England.

FACTORS AFFECTING MAINTENANCE COST OF INSTITUTIONAL BUILDINGS

Olajide Faremi, Olumide Adenuga, Martin Dada & Beauty John

Department of Building, Faculty of Environmental Sciences,
University of Lagos, Akoka, Lagos, Nigeria

ABSTRACT

Building maintenance management in institutions and organisations with sizeable building assets is a complex and multi-faceted process that involves planning, directing, controlling and organizing resources for the sustenance of the building's physical, functional and operational performance. The purpose of this research work is to propose ways of optimizing maintenance expenditure of institutional buildings in Nigeria. Based on review of literatures, factors impacting maintenance costs were categorized into four categories comprising of; building characteristics, political factors, technical and administrative factors respectively. A questionnaire survey of maintenance departments' staff of tertiary institutions in Lagos State was conducted and the data were analyzed using the statistical packages for social science (SPSS). The study reveals the predominant factors affecting maintenance costs of institution buildings to include; age, floor area and vertical spread of buildings, poor building designs, improper coordination of incorporated building services and deferred maintenance. The study recommends a review of maintenance policies for institutional buildings with a view to equipping the maintenance organisations with competent hands and skilled personnel to handle maintenance activities of critical systems and services in institution buildings.

Keywords: Costs, Maintenance, Factors, Institutional-Buildings, Strategy

INTRODUCTION

Maintenance of existing building stock is by no means a small responsibility for organizations and government institutions as significant expenditures are incurred annually on maintenance related activities. Generally, the totality of maintenance cost is expected to comprise the cost of materials, labour, site overheads, equipment/plant cost, head office cost and profit. In most part of the world including Nigeria however, experience and historical data has shown that there are other costs for which provision should be made following the unprecedented development of maintenance need. It is not surprising that Chanter and Swallow (2007) posit that the cost of maintenance work is usually higher than the cost of new construction work.

Maintenance cost is the total cost or budget set aside to keep, restore or improve a building. Maintenance cost differs in various places owing to some peculiarities such as building location, availability of resources, lack of funds, non-availability of building materials, inadequate transportation and many others. Mbachu and Nkado (2004) express that high maintenance costs have negative implications on key stakeholders in particular, and the industry in general. To the client, high maintenance cost implies added costs over and above those initially agreed upon at the onset, resulting in less returns on investment. To the end user, the added maintenance costs are passed on as higher rental / lease costs or prices. To the consultants, it means inability to deliver value for money and could tarnish their reputation and result in loss of confidence reposed in them by clients. To the contractor, it implies loss of profit through penalties for noncompletion, and negative word of mouth that could jeopardize his/her chances of winning further jobs, if at fault.

Hence this study will investigate the factors affecting maintenance cost of institutional buildings in Lagos state with a view to sensitizing maintenance managers and stakeholders in the

maintenance management of institution buildings on measures at optimizing maintenance expenditures.

Statement of the Problem

The wealth of many nations is determined by the level of their infrastructures while a nation's standard of living is also based on the quality of housing for the public in such a nation (El-haram and Horner, 2002). Nigeria as a developing nation is struggling with infrastructural deficit due low budgetary provisions for new infrastructure by government and extremely challenging economic climate on the part of private investors who are constraint by stringent monetary policies. In spite of this, defects in both private and public sector facilities are highly visible; most public facilities are in a state of disrepair. Quest for effective maintenance management of physical assets in tertiary institutions are by no means the least of the challenges facing management and stakeholders in the education sector. This study therefore sets to investigate the factors that impact on the costs of maintenance of buildings in tertiary institutions in Nigeria.

Aim of the Study

The aim of the study is to assess factors that affect maintenance cost of buildings in tertiary institutions in Nigeria.

Objectives of the Study

- (i) To assess the operational state of institutional buildings in Lagos state.
- (ii) To examine the factors affecting cost of maintenance of the institutional buildings in Lagos state.
- (iii) To assess maintenance management strategies adopted in maintenance of institutional building.

Research Hypothesis

- There is no significant difference in factors affecting maintenance cost of federal institution buildings and state institution buildings.

LITERATURE REVIEW

Effective building maintenance can contribute immensely to reducing the lifecycle cost (LCC) of a building through optimal maintenance execution at the operation and maintenance phase of a building's lifecycle. Moreover, the reduction of building maintenance cost can be achieved through deep understanding of building maintenance cost concepts. Al-arjani (2002) asserts that governments of developing countries all over the world commit considerable expenditure to maintenance and operations of buildings but according to chanter and swallows (2007), the backlog of repair and maintenance work are depriving these country's building stock from attaining minimum acceptable maintenance level consequently, the deterioration of these building stock are growing at an unacceptable rate.

Francis, Yik and Lee. (2002) posit that building maintenance management is an operation that involves interaction or combination of technical, social, legal and fiscal determinants that govern and manage the use of buildings. For instant, the state of facilities in an academic institution may impact the quality of academic service delivery. In other words, the assets of tertiary institutions must be in optimum operable performing state at all times in order to deliver quality education. Institutions asset comprises funds, technology, human capital, equipment, plants and buildings. Although, human capital is institution's most significant resource, because tertiary educations are labour intensive, building is the most valuable asset of the institutions. Specifically, institutional buildings are procured to create a suitable, conducive, and adequate environment to support,

stimulate and encourage learning, teaching, innovations and researches (Olanrewaju, Khamidi and Idrus, 2010). The cost of maintaining buildings consumes a great portion of the limited resources available for running organisations and institutions.

According to El-haram and horner (2002) and Ali (2009) factors that affect maintenance cost of buildings can be divided into four groups of variables comprising building characteristics, political factors, technical and administrative.

Building characteristics parameters comprises; the building size, building age, function, height of building, type of structure, finishes, building materials and building components. Sonthya (2006) opine that building characteristics are different in terms of the building amenities provided in the building as well as facilities and services available.

El-Haram and Horner (2002) identified technical and administrative factors which affects maintenance costs of buildings as poor workmanship and poor quality of spare parts and materials, poor maintenance management, budget constraints, failure to execute maintenance at the right time and poor budgetary control. The selection of the maintenance management team and staff is closely related to the maintenance factors that affect the housing maintenance cost.

Besides, the factors that have been stated, there are other factors that affect the building maintenance cost such as third-party vandalism and poor or lack of training (El-Haram and Horner, 2002). These factors can impact building maintenance cost Due to the inflexibility of buildings, institutions, organisations and occupiers need to have clear strategies to manage, control and develop buildings profitably (Zulkarnain, Zawawi, Rahman, Mustafa, 2011).

METHODS

A structured questionnaire was designed and used as the principal instrument for obtaining data for this study. The questionnaires were targeted at maintenance resource persons in the maintenance departments of the surveyed tertiary institutions in Lagos State. Selection of respondents for this study was by simple random sampling method.

A total of 80 questionnaires were administered to the targeted respondents, of the 80 administered questionnaires a total of 50 questionnaires were retrieved and duly completed representing 63% response rate. The returned questionnaires were scrutinized for errors, omissions, completeness and inconsistencies and were found to be adequately completed and therefore suitable for analysis. The data collected was processed and analysed with the aid of Statistical Package for Social Sciences (SPSS). Frequency tables, bar charts and mean score were used for the descriptive statistic while the spearman's rank correlation and Chi-square were used to test the hypothetical statement formulated for this study.

RESULTS

Table 1 shows the demographic details of respondents; the table shows that more of the respondents were male with a percentage of 74% while the female respondents amount to 26%. This implies that greater number of the workforce of the maintenance department of the various institutions were men.

The table further shows that majority of the respondents' are learned hence their ability to comprehend the questions articulated in the questionnaire and to respond accordingly.

The buildings in the various institutions are used for different purposes and are classified accordingly as shown in table 2. 48% of the respondents expressed that the buildings they manage in the institutions are essentially multi-purpose in nature while 18% of the respondents reported that the buildings within the scope of their operations as maintenance personnel are basically used for academic purposes. Such building comprises; auditoriums, lecture theatre halls, workshops among others.

Table 3 shows the maintenance strategy adopted by the maintenance departments of the various institutions in addressing maintenance issues. Respondents were asked to assess the frequency at which the three articulated maintenance strategies are used in their maintenance operations using 5 point likert scale of; Always, Often, Sometimes, Rarely, and Never in descending order of 5 to 1 respectively. The analysis shows that corrective maintenance was the most frequently adopted strategy for maintenance works executed by the maintenance departments, which implies that most of the maintenance work done were undertaking after a failure or breakdown had been reported. Preventive maintenance ranks second inferring that on some occasions, maintenance work are carried out based on a routine schedule for maintenance activities. The table also shows that Conditioned-based maintenance is rarely used as a strategy for maintaining systems and equipment in the surveyed buildings.

From the analysis, the age, size of buildings, vandalism by users, faulty design and poor incorporation of building services are the top five dominant factors that impact the costs of maintenance of tertiary institution buildings. The impacts of these factors were rated high on maintenance costs. The result implies that as a building age, the costs of maintenance increases. Also, the frequency and volume of replacement of parts and spares in and old building is likely to be more than in new buildings as systems wear and tear due to use; pipe corrodes and joints leaks, roof leaks and paints fades while a number of defects grow with the building age.

The result also shows that damage arising from poor handling of systems and services in the buildings by users contribute immensely to the increased cost of maintenance in tertiary institution buildings. Errors attributable to poor designs in the architecture, services and specifications of buildings at the pre-construction phase of a building are seen to impact the costs that are eventually incurred on maintenance throughout the life of a building. Furthermore, poor integration of building services ranked as the fifth factor that affects maintenance cost as embedded services without adequate provision for maintenance access would result in breaking of walls, floors and related surfaces before maintenance activities can be carried out on underneath services.

Test of Research Hypothesis

- H₀- There is no significant difference in the factors affecting maintenance cost of Federal owned and State owned tertiary institution buildings
- H₁- There is significant difference in the factors affecting maintenance cost of Federal owned and State owned tertiary institution buildings

The analysis of variance was used to test the formulated hypothesis and the results is as shown in table 5. At 5 percent, level of significance when P – value is <0.05, majority of the variables (factors) have significant difference between the data that is being compared or tested. Analysis of variance result in respect of testing the above perception of respondents' as regards factors affecting maintenance cost of institutional buildings indicated that the calculated F-value for vandalism by users ($F_{cal.} = 9.808$) is higher than the tabulated F-value ($F_{tab} = 9.78$) at a 5% level of significance, hence null hypothesis is to be accepted which infers that there is no significant

difference in the factors affecting maintenance cost of federal and state institutional buildings. Majority of the other factors identified are also accepted at 1% to 5% significance level with the exception of delay and failure in reporting maintenance problems, building services, poor budgetary control, and third party vandalism having the calculated F-value been less than the tabulated F-value, therefore, allowing for the alternative hypothesis been accepted that is H_1 .

Conclusively from Table 5, the high ranked factors indicated an calculated F-value which is greater than the tabulated F-value; hence the results suggest that the null hypothesis be accepted inferring that there is no significant difference in the factors affecting maintenance cost of Federal owned and State owned institutional buildings.

DISCUSSION

From the analysis, building age ranked top as the factor that affects tertiary institution buildings' maintenance cost. This justifies the position of Lateef (2008) that one of the essential factors that need to be measured in the allocation of maintenance budgets is the building age. This is probably due to the need of additional maintenance works to be carried out in older buildings. For example, major refurbishment and retrofitting of building equipment or elements need to be implemented when a building has reached its economic life span (Ali, 2009). Following the building age as a top ranked factor is the Building area or size, this factor determines the amount an organization or institution allocate towards maintenance activities. According to MCB UP Ltd (1987), building services and maintenance accounts are relatively high, covering 20-45% of the total building running costs, even at the lowest estimate. This statement is justified by the findings of this research work, whereby the poor integration of building services and faulty design ranked within the first five factors that affect building maintenance cost. Hence, the timely maintenance of building services is necessary to avert premature and frequent breakdown of building systems and service failure. Adequate attention should also be given to the scrutiny of building services design at the pre-construction stage of new buildings with a view to identify errors or poor design proposal at an early stage of the building life.

Also, the type of building materials used for the construction of buildings was ranked as the sixth factor affecting maintenance cost of institutional buildings. According to Hanim (2008), the price of building materials has been on the increase because of the escalating cost of raw material and high operational costs incurred at the production of construction materials. Consequently, maintenance cost has increases significantly overtime especially when there is need for significant replacement or upgrade in the buildings arising from deteriorations or prolong defects. This finding aligns with the findings of Nor Haniza et al. (2007) and Cheung and Kyle (1996) that improper or poor material selection is one of the dominant factors affecting housing maintenance cost over the life of a facility or building component.

Furthermore, this study reveals that failure to execute maintenance as at when due may result in an increased in the costs of such maintenance activity when the activity is eventually carried out. This concurs with the position of Narayan (2003), stating that failure or delay to execute maintenance tasks at the right time may cause further deteriorating impacts and further burden the overall cost of executing the repair or replacement work. This also agrees with the findings of Suttell (2006) that maintenance is not expensive when compared to what might need to be spent if the system is allowed to degrade and fail ultimately.

CONCLUSION

Building age, building size, vandalism, faulty designs, poorly integrated building services, substandard building materials, and failure to execute maintenance at the right time were seen to

high degree of influence as factors responsible for high cost of maintenance in institutional buildings, this study therefore recommends that annual audit of buildings in tertiary institution be consistently conducted by skilled maintenance personnel to afford the maintenance organizations the opportunity of tracking changes or otherwise in the performance of building elements, systems, and services in the buildings as they age. The procedure for such an audit should be expressly defined and documented within the maintenance organization policy with a view to ensure that such audit fulfills the purpose for which it is conducted. Competent personnel should be resourced and included in the audit team so that all critical systems in the buildings can be properly examined in the course of the audit. Also, routine maintenance and repair works should be timely to avoid further deterioration. Building designs should be critically reviewed at the preconstruction stage from maintenance perspective by experienced maintenance personnel with a view to achieving ease of maintenance at the operation and maintenance phase of the building.

REFERENCES

- Abdul Lateef Olanrewaju, Arazi Idrus, Mohd Faris Khamidi, (2011) "Investigating building maintenance practices in Malaysia: a case study", *Structural Survey*, Vol. 29 Iss: 5, pp.397 – 410.
- Al-Arjani, A.H. (1995), "Impact of cultural issues on the scheduling of housing maintenance in a Saudi Arabian urban project", *International Journal of Project Management*, Vol. 13No. 6, pp. 373-82.
- Ali, A.S. (2009), "Cost decision making in building maintenance practice in Malaysia", *Journal of Facilities Management*, Vol. 7 No. 4, pp. 298-306.
- Chan, K. T., Lee, R.H.K., Burnett, J.(2003). "Maintenance Practices and Energy Performance of Hotel Buildings", *Strategic Planning for Energy and the Environment*, 23(1) 6-28.
- Chanter, B. and Swallow, P. (2007), *Building Maintenance Management*, 2nd ed., *Blackwell Science*, Oxford.
- Cheung, M.S. and Kyle, B.R. (1996), "Service life prediction of concrete structures by reliability analysis", *Construction and Building Materials*, Vol. 10 No. 1, pp. 45-55.
- Coetzee, Jasper (1999). A holistic approach to the maintenance "problem". *Journal of quality in maintenance engineering* 5:3, pp 276-280.
- El-Haram, M.A. and Horner, M.W. (2002), "Factors affecting housing maintenance cost", *Journal of Quality in Maintenance Engineering*, Vol. 8 No. 2, pp. 115-23.
- Francis W.H. Yik, W.L. Lee, C.K. Ng, (2002) "Building energy efficiency and the remuneration of operation and maintenance personnel", *Facilities*, Vol. 20 No. 13/14, pp.406 – 413.
- Horner, R.M., El-Haram, M.A. and Munns, A. (1997), "Building maintenance strategy: a new management approach", *International Journal of Quality in Maintenance*, Vol. 3 No. 4, pp. 273-80.
- Lateef, O.A. (2008), "Building maintenance management in Malaysia", *Journal of Building Appraisal*, Vol. 4 No. 3, pp. 207-14.
- Lee, R. and Wordsworth, P. (2001), *Lee's Building Maintenance Management*, 4th ed., *Blackwell Science*, Oxford.
- Loosemore, M, and Hsin, YY (2001), "Customer-focused benchmarking for facilities management", *Facilities*, Nov/Dec 2001, Vol. 19, Issue 13/14.
- Mbachu J.I.C. and R.N. Nkado. (2004) "Reducing Building Construction Costs; the Views of Consultants and Contractors". *COBRA*.
- MCB UP Ltd (1987), "Planned maintenance for building services", *Facilities*, Vol. 5 No. 10, pp. 9-13.
- Mendelson, S. and Greenfield, H. (1996): Taking value engineering into the twenty- first century. *International Journal of Cost Estimation, Cost/Schedule Control and Project Management*, 37 (8).

- Narayan, V. (2003), "Effective Maintenance Management: Risk and Reliability Strategies for Optimizing Performance", *Industrial Press*, New York, NY.
- Nor Haniza, I., Chohan, A.F. and Ahmad, R. (2007), "Implications of design deficiency on building maintenance at post-occupational stage", *Journal of Building Appraisal*, Vol. 3 No. 2, pp. 115-24.
- Shen, Q. P. and Lo, K. K. (1999), "Priority setting in maintenance management - An analytic approach", *Hong Kong Polytechnic University*, 62.
- Sonthya, V. (2006), "Relationship between building characteristics and rental to support serviced apartment investment", paper presented at the Pacific Rim Real Estate Society (PRRES) Conference.
- Suttell, R. (2006), "Preventive HVAC maintenance is a good investment", *The Source for Facilities Decision-maker: Buildings*, UNICCO, Newton.
- Tse Peter W., (2002) "Maintenance practices in Honk Kong and the use of the intelligent scheduler, *Journal of quality in maintenance engineering* 8:4, 369-380.
- Zulkarnain, S.H., Zawawi, E. M. A., Rahman, M. Y. A., Mustafa, N. K. F. (2011), "A Review of Critical Success Factor in Building Maintenance Management Practice for University Sector", *World Academy of Science, Engineering and Technology*, Vol. 5.

APPENDIX

Table 1: Demographic Details of Respondent

Demographic Data	Frequency	Percentage
Gender		
Female	13	26
Male	37	74
Total	50	100
Academic Qualification		
OND	11	22
HND/B.Sc./B.Tech	23	46
M.Sc./M.Tech	12	24
PhD	4	8
Total	50	100

Table 2: Building Classification

Building classification	Frequency	Percentage
Administrative Block	7	14
Academic Block	9	18
Recreational Block	1	2
Utility Block	9	18
Multi-purpose	24	48
Total	50	100

Table 3: Maintenance Management Strategy Adopted by the Department

Maintenance Management Strategy	N	Mean	Rank
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Corrective Maintenance	50	4.54	1
Preventive Maintenance	50	2.96	2
Condition-based Maintenance	50	2.30	3

Table 4: Factors Affecting Maintenance Cost of Institutional Buildings

Factors affecting maintenance cost	N	Std deviation	Mean	Rank
Building age	50	0.639	4.40	1
Building area or size	50	0.607	4.28	2
Vandalism by users	50	0.536	4.28	2
Faulty design	50	0.771	4.24	4
Building services	50	0.591	4.24	4
Building materials	50	0.872	4.12	6
Deferred maintenance	50	0.746	4.12	6
Poor maintenance tracking	50	0.807	4.04	8
Budget constraint	50	0.845	4.02	9
Poor quality of spare parts	50	0.892	4.02	9
Low concern for future maintenance	50	0.869	3.98	11
Lack of quality control	50	0.781	3.96	12
Delay and failure in reporting maintenance problem	50	0.778	3.92	13
Poor workmanship	50	0.839	3.90	14
Poor budgetary control	50	0.918	3.88	15
Third party vandalism	50	0.800	3.82	16
Poor or lack of training	50	0.847	3.76	17
Non standardized components/materials	50	0.967	3.62	18

Table 5: Analysis of variance for research hypothesis

Variables		Sum of Squares	df	Mean Square	F	Sig.	Remark
Vandalism by users	Between Groups	11.579	3	3.86	9.808	0.000	Accept H ₀
	Within Groups	18.101	46	0.394			
	Total	29.68	49				
Building area or size	Between Groups	12.414	3	4.138	12.213	0.000	Accept H ₀
	Within Groups	15.586	46	0.339			
	Total	28	49				
Delay and failure in reporting	Between Groups	7.173	3	2.391	5.276	0.003	Accept H ₁
	Within Groups	20.847	46	0.453			
	Total	28.02	49				
Building services	Between Groups	8.683	3	2.894	7.724	0.000	Accept H ₁
	Within Groups	17.237	46	0.375			
	Total	25.92	49				

Variables		Sum of Squares	df	Mean Square	F	Sig.	Remark
Building materials	Between Groups	8.296	3	2.765	4.646	0.006	Accept H ₀
	Within Groups	27.384	46	0.595			
	Total	35.68	49				
Non standardized components/ materials	Between Groups	5.434	3	1.811	2.377	0.082	Accept H ₀
	Within Groups	35.046	46	0.762			
	Total	40.48	49				
Poor workmanship	Between Groups	10.037	3	3.346	4.616	0.007	Accept H ₀
	Within Groups	33.343	46	0.725			
	Total	43.38	49				
Poor quality of spare parts	Between Groups	13.051	3	4.35	6.908	0.001	Accept H ₀
	Within Groups	28.969	46	0.63			
	Total	42.02	49				
Poor maintenance tracking	Between Groups	6.821	3	2.274	4.038	0.012	Accept H ₀
	Within Groups	25.899	46	0.563			
	Total	32.72	49				
Budget constraint	Between Groups	5.374	3	1.791	3.013	0.039	Accept H ₀
	Within Groups	27.346	46	0.594			
	Total	32.72	49				
Deferred maintenance	Between Groups	5.96	3	1.987	2.534	0.068	Accept H ₀
	Within Groups	36.06	46	0.784			
	Total	42.02	49				
Poor budgetary control	Between Groups	1.676	3	0.559	0.557	0.646	Accept H ₁
	Within Groups	46.104	46	1.002			
	Total	47.78	49				
Faulty design	Between Groups	14.951	3	4.984	5.325	0.003	Accept H ₀
	Within Groups	43.049	46	0.936			
	Total	58	49				
Low concern to future maintenance	Between Groups	10.443	3	3.481	4.199	0.010	Accept H ₀
	Within Groups	38.137	46	0.829			
	Total	48.58	49				
Third party vandalism	Between Groups	2.91	3	0.97	1.129	0.347	Accept H ₁
	Within Groups	39.51	46	0.859			
	Total	42.42	49				
Poor or lack of training	Between Groups	6.513	3	2.171	2.378	0.082	Accept H ₀
	Within Groups	41.987	46	0.913			
	Total	48.5	49				

THE IMPACT OF HOUSING QUALITY ON HEALTH IN LAGOS STATE, NIGERIA

Timothy G. Nubi, Afe Yetunde & Austin C. Otegbulu

*Department of Estate Management,
University of Lagos, Akoka*

ABSTRACT

Housing constitute an important determinant of the health status and health expenditure of residents. Correlating housing quality indicated by the rent paid in two residential areas of urban Lagos Nigeria with health expenses incurred within these neighborhoods revealed that the quality of housing can affect health inversely. The study found that in Gowon Estate, an area with relatively better housing, better surface drainage, centralized sewage system and less occupancy ratios, health expenditures on common health problems were much lower compared to Makoko area where the housing and living conditions were much worse. Hence, improving living conditions through standard housing lessens predisposition to common ailments like malaria, typhoid, diarrhea and as well as provide an efficient option for reducing health expenses.

Keyword: Housing, health, Environmental Valuation,

INTRODUCTION

The influence of housing on the diverse areas of man's existence fittingly makes housing a basic human need. Housing as a complex concept is multidimensional and cannot be precisely defined. Moreover, issues in housing are dynamic evolving in different forms and magnitudes because all levels of the society: individuals, families, organisations and government are concerned about housing.

The United Nations, in Article 25 of the Universal Declaration of Human Rights states that, "everyone has the right to a standard of living adequate for the health and well being of himself and of his family including food, clothing, housing and medical care".

Human needs are neither independent of each other nor mutually exclusive but rather highly dependent; hence, housing cannot be described in isolation. Health, like housing, has been identified as a fundamental human right under the Universal Declaration of Human Right earlier stated. The World Health Organisation defined health as "a state of complete physical, mental and social wellbeing and not merely the absence of disease or infirmity

One area of concern which housing affects is health. Hence, how does housing affect health?

Worldwide, housing disparity is a pronounced feature that reflects variation in cost, quality, rental value, location, environmental facilities, housing needs and demands. Houses make up the environment and when the necessary facilities are lacking, the environment becomes unsafe for human habitation. Irrespective of the shape, size and design, a standard house which intends to provide the basic need of shelter should have water and other social services like electricity, sanitary and waste disposal facilities to mention but a few. The bulk of the housing stock in Nigeria is characterised by impoverished surroundings with few local amenities. These physical and social characteristics of housing are obvious determinants of good health.

Housing and health are important socio-economic indicators of the wellbeing of a nation's population. In addition both sectors require huge capital sums to function efficiently.

Significance of Study

Rigorous effort towards health service improvement and housing delivery by the Government does not reflect any awareness of the relationship between housing and health. Over the years, health expenditure has been on the increase. There is no gain saying about the vital role living conditions play in the prevention and control of malaria. However considering the deteriorating

housing condition of Nigerians, spending huge sums will obviously not curb the malaria scourge if the present living conditions are ignored. Reasoning along this path reflects the depth of connection between housing and health within the context of the national economy. The study therefore aims to establish the link between housing and health and subsequently show that the provision of suitable housing can enhance healthy living.

The costs and benefits of housing and health sector are most times assessed in economic terms. Assessing costs and benefits in quantitative terms precludes the intangible costs and benefits applicable to housing and health. For these reasons, environmental valuation techniques which take account of social values and have proved useful in related studies would be considered as a means of assessing the value of tangible and intangible impacts of poor housing quality on health.

Furthermore, the influence of housing on health can be considered as a basis for improving the value of the housing sector. The health benefits derived from housing facilities and environmental condition can be used to assess the value of rent paid, value of investment in housing and the efficient use of resources as a whole. Also, the health outcome of housing can help to improve the housing market through the regeneration of various avenues of funding.

LITERATURE REVIEW

Awareness of the health effects of housing is visibly low and the dearth of substantial research materials in this field have further contributed to the poor recognition of its relevance within the society. However, historical account lends credence to the conceptual relationship between housing and health and the attention it attracted back then which made it an issue of public debate. In recent years, advocating (on the basis of rational ideas) that housing affects health presents no sufficient proof to justify the public regulation of housing. It has been observed that if housing is poorly built, too crowded, located in unsafe areas or inadequately serviced with water and sanitation it can lead to increased incidence of sickness and death; conversely good housing can lead to better health and higher rate of labour participation (Mayo et al, 1993). Therefore, limited research evidence linking housing and health (Acevedo et al, 2004) has made the hypothetical reasoning that bad housing result in ill-health a subject of widespread criticism. For so many years, the World Health Organisation (WHO) has advocated the health benefits of housing and identified nine features of the housing environment that have, important direct and indirect effect on the health of the occupants. These include: the structure of the shelter, including the extent to which it protects the health of the occupants from the elements; provision of adequate water supplies; provision of proper sanitation and waste disposal; the quality of housing sites; overcrowding which can lead to household accidents and increased transmission of airborne infections such as acute respiratory infections diseases, pneumonia and tuberculosis; the presence of indoor air pollution associated with fuels used for cooking and heating; food safety standards including adequate provision for storing food to protect it against spoilage and contamination; vectors and host of diseases associated with the domestic and peri-domestic environment; and the home as a workplace-where the use and storage of toxic and hazardous chemicals and unsafe equipment may present health hazards (WHO,1998).

Housing and mental health

Mental well-being involves an integration of social, cultural and individual realities (Bonney et al, 2004). It signifies a stable state of the body, mind and soul and its deficiencies are manifested in the situation of stress, depression, anxiety, vandalism, insomnia, paranoid feeling and the like. Indoor exposure to toxic substances (e.g. heavy metal solvents) may lead to neuropsychiatry disorders. A survey by Bonney et al (2004) concluded that people are significantly more depressed and more anxious when they live in a dwelling that does not offer sufficient protection against external aggressions, noise, vibrations, dampness ,moulds, droughts, colds in winter;

does not allow space to isolate oneself (overcrowding or poor architectural design) or to feel free in one's home; lack light and /or does not offer a nice view on the outside environment; does not facilitate socialization (absence of parks and garden) and is prone to vandalism

Health effects of mouldy/damp houses

Houses with excess moisture trapped within the building fabrics due to negligence during construction or poor maintenance like neglect of plumbing faults or lack of disposal facilities for waste water encourages dampness within the building and subsequently leads to mould growth in and around the house. Damp and mouldy homes have been associated with allergic rhinitis, asthma, fatigue, diarrhoea, cough, wheezing, breathlessness, phlegm, meningococcal infection irritation of the throat and eyes Arthritis, depression and particularly respiratory infections (Shaw et al, 1999; Dunn et al, 2003; Bonnefoy et al, 2004).

Internal and surrounding housing conditions and Health

Overcrowding, either in terms of spatial arrangement of housing units or the number of persons occupying a dwelling unit have important bearing on health. Burns, Scalds as well as infectious diseases like cholera, tuberculosis, and hepatitis e.t.c. are features of overcrowded housing. Overcrowding has been acknowledged as an indirect cause of childhood death, stomach cancers, respiratory problems and heart diseases (Environmental Epidemiology, 1999)

Housing services/ utilities and health

Facilities like safe and regular water supply, effective waste disposal services, adequate sanitation services and functional drainage doubtlessly promote good health. Typhoid, cholera, infective hepatitis, scabies etc. are water-borne diseases transmitted through faecal-oral routes and inadequate water supply while stagnant water aids the breeding of Schistosomiasis and malaria (Gilles & Brown, 1997). Poor housing features like scarcity and pollution of water, poor sanitation and lack of appropriate sewage disposal is a major cause of diarrhoea, (Esibike & Moses, 2004).

Sick building syndrome (SBS)

Defects in the building structure and internal environment can cause discomfort, unease or illness (Iyagba, 2005). Combustion pollutants carbon monoxide (CO), nitrogen dioxide (NO₂) and sulphur dioxide (SO₂); biological air pollutants (dander moulds, mites) volatile organic compounds (VOCs), emitted gases, solids and liquids, heavy metals, mechanical ventilation of building, inadequate illumination, noise, rat, cockroach infestations, sanitary conditions are all major contributors to SBS. Five key symptoms of SBS include: mucus membrane irritation that affects the eyes and throat; neuropsychiatry disturbances such as fatigue, headache, convulsion and dizziness; skin disorders such as itchiness, dryness and rashes; asthma –like symptoms such as tight chest and breathing difficulties and unpleasant odour and taste sensation (Iyagba, 2005).

METHODS

Housing and Health variables extracted from the questionnaires administered were analysed to determine the type and strength of relationships. Details of housing qualities and health outcomes of about 280 residents of various housing types ranging from tenement to duplex were obtained for analysis. Housing variables used in analysis included rent, house type (flat, bungalow etc), occupancy ratio, water supply (drinking and domestic activities), quantity and quality of lavatory services, waste disposal services. Health impacts were measured considering hospital charges for treatment of malaria, typhoid fever while cost of self-medication were considered in cases of ailments like cough, malaria, dysentery, catarrh, feverish feeling, and the frequency of the use of multi-vitamin supplements. The cost of maintaining good health was obtained using cost

incurred in buying water for domestic and drinking purposes, the cost incurred by residents who have no toilets at home and have to pay for such service and the cost of disposing refuse.

The cost of illness method discussed in a 1998 World Bank environmental assessment source book involves the cost of treating illness resulting from environmental impacts or prospective projects in comparison with the cost of measures adopted to reduce or prevent such health problems (World Bank, 1998). In a similar vein, housing can be considered as a means of preventing or reducing housing related health problems. In this way the rent represents the cost of accommodation. The preventive /defensive expenditure method takes account of money spent on appropriate preventive/mitigating measures to prevent losses arising from environmental problems or to mitigate adverse environmental effect (Dharmanrantne & Strand, 1999).

Prevailing hospital charges for the treatment of malaria and typhoid accounted for the cost of illness where hospital visits were acknowledged. For respondents who suffered from malaria but have no record of hospital visit the minimum cost of medication for treatment were used. Cost of treating catarrh, cough, dysentery, feverish feeling and rate of use of anti-malaria drugs were based on the cost of self-medication. Since most multivitamin contain 30 tablets with a recommendation of one tablet per dose the amount spent on multivitamin in a year was calculated according to frequency of use. The average amount spent on buying water for drinking and domestic use per capita per day was used. Commercial use of toilet and refuse disposal expenses were also accounted for.

The rent paid by each respondent and the corresponding expenses incurred on health in the year was analysed by Product Moment Correlation to ascertain the strength of the relationship between the two variables.

The study area

Gowon Estate is a Federal Housing Authority (FHA) Residential Scheme situated at Egbeda. It is a medium density, well-planned residential neighbourhood with different types of prototype houses of standard accommodation which consist of bungalows, blocks of flats and duplexes with well ventilated, beautiful surroundings with central sewage system, good water supply and functional waste disposal system.

Makoko, is a high density, poorly planned residential area that can be practically described as a slum. Refuse often litter the roads, constituting nuisance, creating offensive odour and polluting the environmental ambience. Majority of the houses here are tenement buildings, mainly bungalows and storey buildings of varying number of floors, with no adequate setbacks and airspaces. This area is also characterised with inadequate/total lack of basic facilities; non-serviceable sanitary facilities, inadequate water supply, overfilled/seeping septic tanks, uninhabitable rooms and a very noisy environment.

RESULTS

Graphical analysis of rent and health expenditure

The differences observed in housing and health are expressed in monetary terms as rent and health expenditure respectively. The distribution of rent in the two areas is presented in figures A and B, while that of health expenditure is presented in figures C and D.

The rent distribution in Gowon Estate appears to be fairly symmetrical indicating a minimum rent of ₦150,000 and a rental value as high as ₦400,000 per annum. This reveals a prevalence of varying pattern of rental values in the neighborhood. A 2/3 bedroom in a block of flat cost between ₦150,000-₦200,000 per annum, the bungalows cost between ₦200,000- ₦300,000 per annum while a typical duplex goes for a minimum of ₦350,000 per annum. In Makoko, the most prevalent type of houses are tenement houses with rental value of between ₦8,000 – ₦18,000 per annum per room. More than 50% of the respondents paid the minimum rent of ₦10,000 per

annum while only few respondents pay rent of between ₦ 10,000- ₦ 20,000. The distribution of the rent is positively skewed with a clear modal rental value of ₦10,000 per annum.

Health expenditures also differ significantly in the two areas as shown in figures C and D.

The amount expended on health by individual respondents consisted of the cost of illness which included an aggregate of the cost of the number of times each respondent treated malaria and typhoid at the hospital, used anti-malaria drug , treateddiarrhoea, catarrh and cough. The cost of maintaining good health which include cost of multi-vitamins taken and the amount spent on buying water, toilet , and disposing refuse is added to the cost of health. All these annual costs made up the health expenditure of each respondent.

Figure C shows that health expenditure in Gowon Estate were positively skewed with a high percentage of the respondents spending below ₦10,000 and 80% of the respondents spending between ₦1000 and ₦3000 on health. On the other hand, figure D shows that the respondents in Makoko spent between ₦10,000 and more than ₦20,000 on health during the year .

Analysis of housing and health variables using the cost of illness approach

Under the Cost of Illness Approach, the observed housing and health variables are valued as rent and health expenditure respectively. The rent per annum represents the cost paid to enjoy the benefit of housing. Health expenditure represents the cost incurred on health due to housing deficiency during the year by the resident. The difference between them (rent and health expenditure) translates into a net benefit if there is a surplus and a loss if a negative answer results. The rent and health expenses incurred are then correlated to see if a linear relationship exist between them and the significance of 'r' value obtained is established to test the stated hypotheses

Correlation of rent and health expenditure in Gowon estate and Makoko

Hypotheses:

H₀: Housing quality (rent) has no effect health of residents

H₁: Housing quality (rent) can affect health of residents.

For Gowon Estate, the Table 2 shows a correlation coefficient 'r' of -0.316 at a significant level of 0.01 with a coefficient of determination of about 10%. This result indicates a negative/inverse but low degree of relationship between the cost of accommodation (rent) and health expenditure.

Decision: Since the correlation coefficient is significant at 0.01 level the Ho (Null Hypotheses) is rejected. This implies that the cost of accommodation (rent) can affect health expenditure; the higher the rent, the lower the health expenses. The decision to reject Ho considering that the 'r' value of -0.316 which indicates a weak correlation and significant at 0.01 level shows that the observed relationship between cost of accommodation (rent) and health expenditure is not due to chance. This means that an increase in the rent produced a little reduction in health expenditure. Also the coefficient of determination 'r²' of approximately 10% further confirms the decision taken because it shows that 10% of any variation in health expenditure is caused by a change in rent. Hence a factor effect of 10% on a variable cannot be discarded as irrelevant.

With respect to the correlation of rent and health expenditure in Makoko as outlined in Table 2, a correlation coefficient of 'r' -0.121 with no significant level at either 0.05 or 0.01 but with a coefficient of determination 'r²' of 1.5% was obtained. The 'r' value obtained indicates that there is little or no correlation between cost of accommodation and health expenditure

Decision: Since the 'r' value assumes no significance at the conventional level of 0.05 and 0.01 then Ho is rejected. This implies that housing quality (rent) can affect health expenditure. The decision to reject Ho stems from the fact that the correlation coefficient of -0.121 which indicates a negligible or zero relationship between cost of accommodation and health expenditure is not significant. Since the correlation coefficient is not significant it is NOT reliable and must have

occurred by chance. Hence, this means that a relationship must have existed between them in the study area; though negative as shown by the sign of the 'r' value and this suggest that a nonlinear relationship could present a clearer explanation

Comparing the 'r' values of Gowon and Makoko which are -0.316 and -0.121 respectively it shows that the cost of accommodation in Gowon had a significant effect on health expenditure while in Makoko the 'r' value indicating a negligible or zero effect of rent on health expenditure is not significant showing that this degree of relationship indicated may have occurred by chance. Thus the quality of housing in Makoko considering the rent has an effect on the health of the residents. This analysis suggests that a non-linear relationship between these variables will present a stronger affinity.

DISCUSSION

Collectively, the correlation results of both study areas show that the quality of housing can affect health inversely. This implies that as the quality of housing improves there is a little but significant reduction in health expenses.

The varying health bills incurred by respondents who paid the same amount of rent may help to explain the weak relationship observed between the rent and health expenditure showing that the differences in housing quality will have a weak effect on health as shown by the correlation coefficient. However it was observed that 77% of respondents in Gowon Estate who paid a minimum rent of ₦160, 000 per annum incurred health expenses within the range of ₦0 - ₦5,000 while about 83% of those in Makoko who pay rent within the range of ₦ 7,200 - ₦ 50,000 per annum incurred health expenses ranging from ₦ 10,000-₦ 20,000 in the year. This shows that the sharp disparity in the environmental condition between the two study areas explains the wide gap in the health expenses incurred and that the state of the environment dictates the health status. Furthermore it was observed that environmental condition is an underlying factor that determines the trend of health expenditure. For instance differences in housing quality presented little differences in health expenses.

The health outcome of residents in Makoko irrespective of the type of house they lived in presented no significant difference. Hence if houses were exchanged between the study areas, then the new residents of Makoko would pay a slightly lower rent than the rent paid presently in Gowon Estate but would incur extremely higher health expenses. This may be a little lower than the present health expenses obtainable in Makoko due to the poor state of the environment even though the quality of each housing unit has improved. The change in quality would also result in higher rental value than the present rent obtainable in Makoko. It was also observed that majority of Makoko residents paid a minimum of 83% of their rent on health while about 70% of the health expense was spent on water which the rent was expected to cover.

The wide gap in health expenditure between these two areas indicates that when housing with the basics amenities are situated in a well organised environment with standard and functional facilities, there is reduction in health problems. This shows that the influence housing quality has on the health of the inhabitants is complemented by the setting of the environment. Thus, a good house in a bad environment does not guarantee good health.

SUMMARY OF FINDINGS

In this study, the findings revealed that the condition of the residence and the environment around it affects the health of the residents. However the above assertion appears to be one sided with greater emphasis laid on the health impact of poor and substandard dwellings. This is because the health benefit of decent housing can be more readily assessed than the health outcome of residents of poor dwellings. Besides, even standard dwellings can also pose health threat through in-house activities, occupancy ratio, building materials, design and lack of

maintenance to mention but a few. Recently sophistication in housing has also been found to affect health. However the health features of poor housing are highly pronounced.

Issues of tenure, absence of maintenance and regulations in the housing sector and affordability have also encouraged poor housing. The qualities of the houses in Makoko is at wide variance to those in Gowon Estate as are the rent charges paid. The study also reveals that the correlation of rent and health expenditure though linear is weak and indirect. The correlation result also showed that an upward review in rent would result in a little reduction in health expenditure.

CONCLUSION AND RECOMMENDATIONS

The link between housing and health cannot be described as a direct or straight forward relationship. Housing is neither a disease-causing organism nor a drug that cures ailment but can act as barrier or a catalyst of disease. A standard housing facility should include amongst other things water, sanitary facilities and sewage. The rent paid for accommodation is expected to cover the provision of these services. When these facilities are missing or unserviceable, their impact can be measured in health terms. The knowledge that better housing quality and environmental condition can effectively cut down health expenditure will help to improve housing quality. This will make housing policy not only effective but realistic, ensuring regulation of housing stock, encouraging maintenance and repairs of housing facilities and attracting more investment into housing. Thus, this type of study is capable of motivating policy makers to pay earnest attention to housing matters. All these will enhance the value of real estate sector and therefore requires the attention of real estate professionals.

REFERENCES

- Acevedo-Garcia, D., Osypuk, T.L., Werbel, R.E., Meara, E.R., Cutler, D.M., & Berkman, L. F., (2004). Does housing mobility policy improve health? *Housing Policy Debate*, 15, 49- 98.
- Bonnefoy, X. R., Annesi-Maesano, I., Aznar, L.M., Braubach, M., Craxford, B., Davidson, M., Ezratly, V., Fredouille, J., Gonzalez-Gross, M., Kamp, I. V., Maschke, C., Mesbah, M., Moissonier, B., Monolbaev, K., Moore, R., Nicol, S., Niemann, H., Nygren, C., Ormandy, D., Robbel, N., & Rudnai, P. (2004, June 23-25). Review of evidence on housing And Health. Paper Presented At “Fourth Ministerial Conference On Environment And Health Organized By World Health Organisation” Budapest Hungary
- Dharmarantne, G. S. & Strand, I. (1999, October). *Approach and methodology for natural resources and environmental valuation*. Barbados: Author.
- Dunn, R.J., Hayes, M., Hulchanski, D., Hwang, S. & Potvin, L. (2003). *Housing as a socio-economic determinant of health*. Canada: Canadian Institutes Of Health Research.
- Garb, M. (2003, September). Health morality and housing: the “tenement problem” in Chicago (Review Of The Book Public Health Then And Now). *American Journal Of Public Health*, 93 (9), 1420-1430
- Iyagba, O. A. (2005). *The menace of sick buildings: a challenge to all for its prevention and treatment*. Lagos: University Of Lagos Press.
- Markandya, A. (2000). *The valuation of health impacts in developing countries*. U.K: University of Bath, Department Of Economics And International Development
- Mayo, S.K., Angel, S., & Heller, M. (1993). *Housing enabling markets to work with technical supplements*. Washington D.C.: The International Bank For Reconstruction And Development/ The World Bank (A World Bank Policy Paper).
- The Global Housing Crisis: Is There A Solution? (2005, September 22). *Awake!* pp.3-12.
- The World Bank (Environmental Department), (1998, April). *Economic analysis and environmental assessment. Environmental assessment sourcebook update*, (23)
- Williams, P. (1995). The United Kingdom housing context. *Housing policy debate*, 6 (3), 759-783.

World Health Organisation (1987, December). *Housing and health an agenda for action*. England: Birkenhead Press.

World Health Organisation (2000, July 12-13). *Integrated approach in to housing and health*. Copenhagen: Author.

World Health Organisation (2005) *Housing and health*. (On-Line). Retrieved September 21, 2005 From The World Wide Web: <http://www.euro.who.int/housing>

APPENDIX

Table1: Housing Characteristics in Gowon Estate and Makoko areas of Lagos State, Nigeria

Housing Quality & Condition	Gowon Estate		Makoko	
	Frequency	Percentage	Frequency	Percentage
With WC toilet	108	100	41	37.96
With pit toilet	0	0	44	40.74
No toilet	0	0	23	21.30
With water	95	87.96	5	4.63
No water	13	12.04	103	95.37
>2persons /room	12	11.11	88	81.48
Very bad	0	0	15	13.89
Bad	0	0	61	56.48
Fair	25	23.15	18	16.67
Good	56	51.85	0	0
Very good	27	25	0	0

Source: Field Survey 2006

Table 2: Relationship between the Cost of Accommodation (Rent) and Health Expenditure.

Areas	Variables	N	Mean	Standard Deviation	Correlation Coefficient(R)	Significant Level	Coefficient of Determination
Gowon	Rent	108	284,305.56	83,412.774	-0.316	0.01	0.0999(9.99%)
	Health	108	3,918.2870	3,332.6987			
Makoko	Rent	108	18,794.44	17,311.321	-0.121	0.01	0.01464(1.5%)
	Health	108	16,614.907	14,413.365			

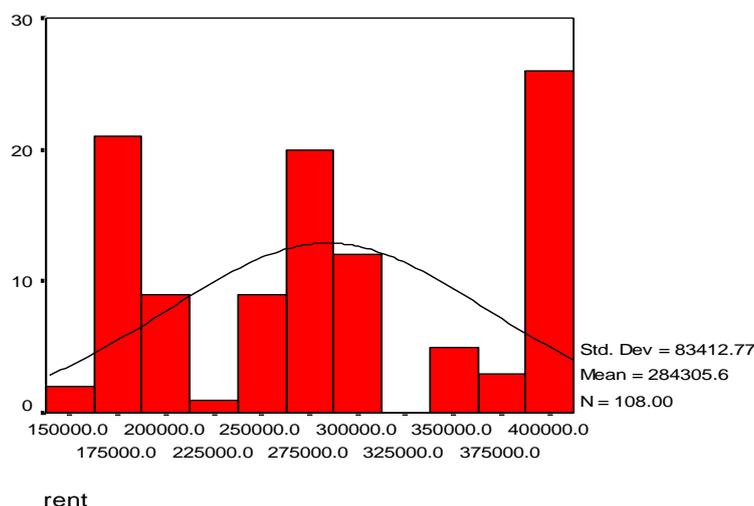


Fig.1: Distribution of Annual Rent Expenditure in Gowon Estate

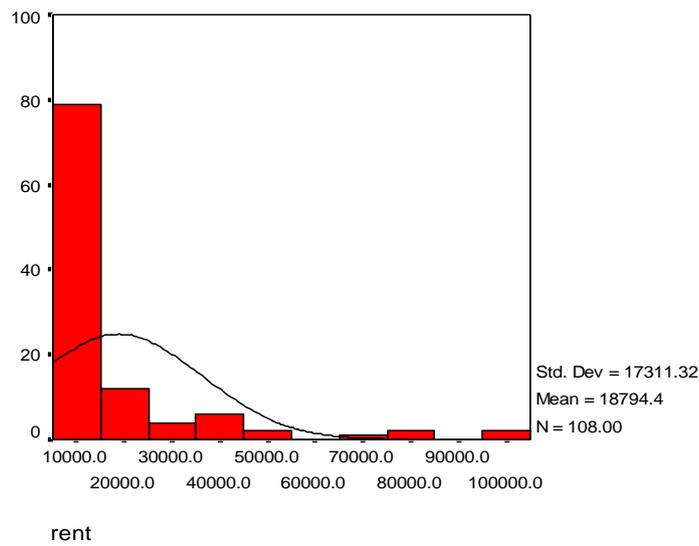


Fig. 2: Distribution of Annual Rent Expenditure in Makoko

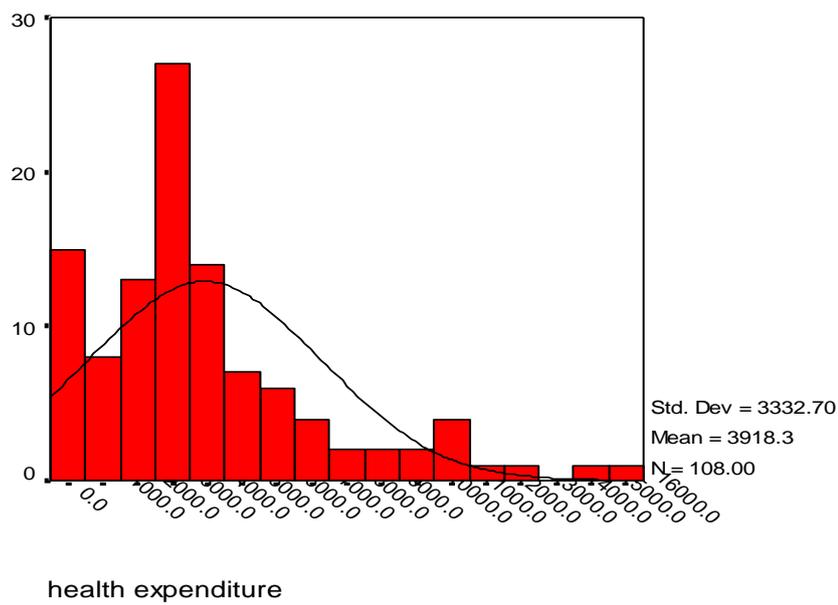


Fig. 3: Distribution of Health Expenditure in Gowon Estate

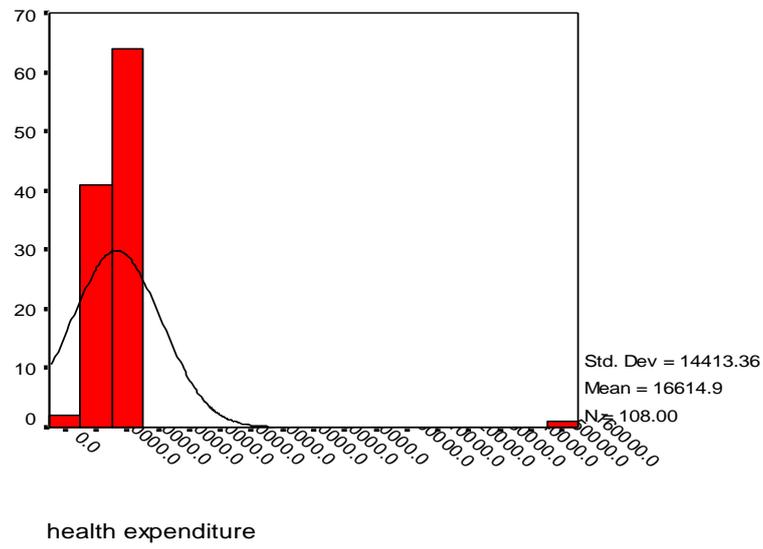


Fig 4: Distribution of Health Expenditure in Makoko

AN EXAMINATION OF THE USE OF INFORMATION TECHNOLOGY (IT) FOR PROPERTY VALUATION IN LAGOS METROPOLIS

O.B.A. Idowu & G.K. Babawale

Department of Estate Management, University of Lagos,
Akoka, Lagos, Nigeria
obaidowu@yahoo.com, oidowu@unilag.edu.ng, gkbabs@yahoo.com.

ABSTRACT

Values submitted by estate surveyors and valuers depend to a great extent on its acceptability by the clients and other end users. However, this is dependent on the reliability of the figures contained in the valuation report. This study was carried out to investigate the extent of the use of Information Technology (IT) for property valuation in Lagos metropolis with a view to reducing error associated with conventional methods of valuation. Methods involved the use of primary data obtained via structured questionnaire to elicit information from practising estate surveyors and valuers using simple random sampling technique cum secondary materials. SPSS statistical tool was used for the analysis. The study identified among other things the IT facilities available in the estate firms, factors responsible for the present level of IT usage and the scope of IT usage for property valuation. The study propounds a conceptual framework which should be mandatory for certification and accreditation of all estate firms by both the Nigerian Institution of Estate Surveyors and Valuers (NIESV) and Estate Surveyors and Valuers Registration Board of Nigeria (ESVARBON).

Keywords: *Information Technology, Property Valuation, Lagos*

INTRODUCTION

Property valuation is the act of determining the worth of rights and interests in landed properties. This exercise is carried out for various purposes which include mortgage, compensation, sale, purchase, etc. It is also defined as the art and science of estimating the open market value or the prediction of the most likely selling price of interest in land (Abbott 2000, in Daly, Gronow, Jenkins & Plimmer, 2003).

However, in recent times there has been growing concern on the challenges facing the profession of estate surveying and valuation. Prominent among these challenges is the issue of the determination of property values. This has generated so much debate among the various practitioners in the built environment, to the extent that other professionals have openly challenged property valuation being the exclusive responsibility of estate surveyors and valuers. For instance, while quantity surveyors have argued that they should carry out cost method of valuation; engineers have gone further to open a faculty to undertake plant and assets valuation. Aluko (2004) noted that the Bureau of Public Enterprise (BPE) lent their support that quantity surveyors are better equipped to give assets value on specialised buildings in Nigeria.

This should be a concern for the profession more so, that Decree 24, of 1975 now CAP111 of the Laws of the Federation of Nigeria 1990 as amended, exclusively empowers the estate surveyors and valuers to carry out property valuation. This is borne out of their response to changing trends which have affected the expectations of users of valuation report. Despite this, it appears that estate surveyors and valuers still remain docile. It is therefore imperative that with the sophistications and unassuming paradigm shift something critical must be done to make them relevant to carry out valuation exercise. This goes to show the need for standardisation of valuation by the professional bodies regulating valuation. While efforts are in place to

incorporate valuation standards in Nigeria it is important to incorporate the place of IT, hence the need for this study to be able to appreciate the areas that will need to be addressed.

Ukabam (2005) citing Bloom and Harrison (1978), Okoye (1985) and Odudu (1989) observed that the cost and investment method are associated with substantial error and that the methods are unrealistic and unreasonable. However, Aluko (1998) and Ogunba (2002) in Ukabam (2005) took a different position by recommending multiple regression analysis (MRA) for property valuation. What this implies is that with MRA as a modern valuation technique the errors will be minimised if not totally eliminated. Despite this assertion, it appears that there has not been any significant change as valuation methodology still remains as usual. This is because the issue of valuation challenges continue to feature in literature (Ajibola, Oloyede & Atere)

Though, extant studies have been undertaken to address the myriads of problems confronting the traditional areas of estate profession only few directly address the issue of IT and property valuation. In fact, the literature is replete with issues that border on valuation inaccuracy, reliability, valuers behaviour (Babawale, 2011, Ayedun 2009) among others.

Specifically, the empirical study seeks to explore the extent of adoption and use patterns of IT among estate surveyors and valuers in Lagos. It also identifies the types of IT facilities used for valuation and IT usage employed by estate surveyors and valuers, the type of IT/Valuation software used for property valuation and the factors responsible for the present level of IT compliance among estate surveyors in Lagos metropolis.

LITERATURE REVIEW

Value signifies ability to satisfy a need or want, it also denotes utility. Value concepts of properties depend on the purpose and the context of valuation. Hence, a property has different values for different purposes to different people at the same time (Ifediora, 2005, Opara, n.d)

Generally, property values are multi-faceted depending on the purposes for which valuations are required. These various property values had earlier in the introductory section of this study been enumerated. The valuer's assignment is limited to the scope of their instruction which in most cases is the determination of the open market value. This has been extensively discussed in past studies (IVSC 2003, Aluko, 2004).

Surprisingly, studies have revealed that the discrepancies noted in values have been so significant that some clients doubted its usefulness. Some of the challenges of valuation arise from the client, the surveyor and his personal interest. Despite these, all advised values should be within an acceptable range. The differences are attributable to the rudimentary and traditional methods of valuation.

Valuation exercise begins with accepting instruction to physical inspection, actual valuation and ends with report writing. All these stages are to be transparent. At the stage of inspection, the physical attributes of the properties like the design; accommodation standard external and internal finishes and other factors as availability of substitutes, tastes and preferences as well as location of the property are taken into consideration. Often, clients' information is unreliable. Thus, further enquiry in form of physical inspection is necessary to authenticate information contained in the land survey, title document and plans. Presently, most of these activities are undertaken manually.

Estate surveyors and valuers carry out physical inspection using facilities such as measuring tapes, note pads, calculators as well as rely on their memory. Information obtained during inspection sometime gets missing en route the office. Record keeping in books, cabinets, shelves is not only outdated but occupy space. Such data are prone to loss due to fire, thefts, flooding, mutilation etc. Thus, they are only useful in the short term. This accounts for why valuations are fraught with errors. This is the reason the Nigerian Institution of Estate Surveyors and Valuers created a data bank using Information Technology (IT).

Lunt, Ekstrom, Gorka, Hislop, Kamali, Lawson, LeBlanc, Miller and Reichgelt (2008) noted that IT is an integrative discipline that pulls together data bases, human-computer interaction, networking, programming and website consultation. It is used to solve all types of computing and information problems regardless of their origin.

Using IT facilities during physical inspection such as digital tapes and camera, IPAD, Blackberries and Tablets instead of manual tools will not only reduce inspection time but will also minimise error. They easily capture electronically all physical attributes and accommodation details. IT is also useful for valuation exercise such as reconnaissance survey, site inspection, and market survey. Thus, IT facilities enhance accuracy.

Valuation reports can be safely kept as soft copies for a longer period and are easily retrieved when needed. This has been made possible with the use of IT facilities such as flash, external drives and other hardware, internet facilities like clouds etc. Networking is facilitated among estate surveyors as information is easily shared unlike in the past.

There are several processes that have been identified as essential in the determination of property values in different countries. These include the definition of the assignment, preliminary analysis, data selection and collection, land value estimate, application of valuation approaches, reconciliation of value indications and final value estimate and preparation of report of defined value (IVSC 2003, Babawale 2009). In all these, there have been challenges which resulted in unacceptable or contestable valuation results in Nigeria.

Although this may seem to have worked in Europe e.g UK, France, Sweden, Netherlands, Portugal and Italy they appeared not to conform to the Nigerian environment given the level of controversies that have emerged as a result of valuations.

In carrying out valuation exercise, the cost method, sales comparison approach and the income capitalisation approach are the conventional methods hitherto used by the estate surveyor and valuers in Nigeria (Abbott (2000) in Daly, Gronow, Jenkins & Plimmer 2003). These methods seem to work for identical properties. They are often amenable by subjective opinion and often ignore the effect of competition (Britton, Davies & Johnson, 1980, Ifediora 2005). These methods are fraught with errors due to their limitation in carrying out more complex valuation.

With the advent of IT, it has been observed in literature that there are many advanced and statistically available valuation methods which can be used to carry out more complex valuation. These include multiple regression technique, Hedonic pricing model and spatial methods, Spatial Analysis method (SAM), Artificial Neural Methods, Fuzzy logic (FL), Rough Set Method (RSM), Autoregressive Integrated Moving Average method (ARIMA), Monte Carlo Simulation technique. Dyna, Argus, Circle and Cougar, PM Fox i.e. Micro property and Valuation Package, Automatic Valuation Model, 360 Value, Caprate Calculator and Narrative Complete. These techniques and methods have the capacity to tackle variability due to local regions and preferences, and solving mathematical equations (Bulut, Allahverdi, Kahraman and Yalpir, 2011, Wardman, Bristow & Arsenio, 2005; Kauka 2007, Sirmans, Sirmans & Benjamin 1989; Ibrahim, Cheng & Eng, 2005). These methods have proved to be consistent, accurate and transparent in North America, Europe, USA, UK, Australia and South East Asia. Valentine (1999) and Fabozzi (1998) in Ibrahim et al. (2005) observed that the accuracy associated with AVM is within the range of 6-12% while costs savings are in the region of 20-75 % of traditional valuation.

Succinctly put, to successfully carry out valuation using IT there is a need for the estate surveyor to be specially skilful and knowledgeable. However, this is lacking among the estate surveyors and valuers (Oloyede et al. 2011). What this implies is that he has to seek the service of experts to undertake valuation.

METHODS

The population of Lagos is estimated at 9,014,534 (2006, National Population census) while a parallel census conducted at the same time by Lagos state put the figure at 17,552,942. Lagos state is divided into twenty local government areas occupying actual area of 3577.28 sq metres. The population is projected to reach 23,305,971 by 2015 at an annual growth rate of 3.2%.

However, this study is limited to Lagos metropolis. Lagos state is said to be the smallest in land size among the 36 states in Nigeria. Babawale (2011) described Lagos as the hub of Nigeria's commercial and industrial activities while Ayedun (2009) reiterated the fact that the city is the most important commercial city in Nigeria which provides a sufficiently vibrant economy base capable of providing a rigorous and robust study as well as its being the largest city in Africa. NIESV Directory (2009) showed that most Estate Surveyors and Valuers in Nigeria are found in Lagos metropolis. 267(46%) of estate firms are based in Lagos metropolis with sixteen (16) out of the twenty (20) Local Government Council Areas in Lagos state falling within the metropolis (Ajibola, Oloyede and Atere, 2011). Using Lagos for this study is considered appropriate particularly that almost half the estate surveyors and valuers in Nigeria are based in the city. Thus, the outcome of the study will be a true representative of the entire country.

Simple random sampling technique was adopted to gather data from the practising estate surveyors and valuers across the Lagos metropolis. The sample frame is the directory of registered estate surveyors and valuers consisting of 415 members. This is dependent on the formulae contained in Otte (2006) adopted from Ayedun (2009).

However, in Nigeria, as seen in the conceptual frame work below we are proposing the mandatory use of IT for all practising estate firms.

INSERT FIG (A)

The above picture presents the model which depicts the applicability of Information Technology to property valuation. In the model IT influences physical inspection when carrying out activities like reconnaissance survey, actual measurement of properties, data capture- video/picture. The outcome of this affects property value. In the same manner its accuracy or quality influences actual valuation. Some of the modern valuation methods in vogue cannot be used without IT e.g.fuzzy logic, 360 Value, Multiple Regression Analysis Automated Valuation Method etc. Consequently, good report writing which is the summary of all inspection and actual valuation is dependent on IT. These translate to the property values. Moreover, the challenges of valuation influence property values negatively. To overcome this IT will be useful to consequently turn the challenges to impact positively on the property values.

Some inhibiting factors of IT usage include high procurement costs, ignorance, poverty, lack IT skills, qualified personnel and network infrastructure, security and trust factors, uncertainty of payment methods and legal framework. (OECD 2004)

RESULTS

Information Technology Usage

Up to 85.7% of the study sample size claimed to use IT in their respective offices, while just 14.3% decline such claim. It implies that, on a general note, large number of estate firms used IT for office work.

INSERT FIG (B)

The study is expanded to cover the type of IT available in the estate firms. The findings as reported in Table1 show twelve different types of IT facilities available for usage. From the Table1, desktops, printers, digital camera and internet with 90.2, 96.3, 89 and 93.9 percent respectively, are the common IT facilities available across the industry. A total of 54,

approximately 68 percent claimed to have website, implying that up to 32 percent of the estate firms in the study location operate without a company website. More shocking, is the scanty figure of those who used extranet; 9 cases representing only 12.5 percent of all the respondents.

INSERT TABLE 1

The study obtains the scope of IT usage in valuation practice by examining areas where the technology has been deployed. The findings which are reported in Table 2 below noted four valuation areas with considerable level of IT deployment. The first, as indicated by 87.5 percent of the respondents is in the preparation of valuation brief/proposal, the second area is production of drawing, with 86.3 percent. On a much higher response are preparation of valuation report with 93.1 percent and data storage with 86.3 percent. Conversely, the use of IT in many other areas is limited and these include physical inspection (30.6 percent), actual valuation practice (33.8 percent) and holding meeting (38.9 percent).

INSERT TABLE 2

Factors limiting deployment of IT Facilities

INSERT FIG (C)

Examining the frequency in response, the indicated factors are higher, thus most of the factors are impactful

SPECIFIC IT FACILITIES IN USE

Table 3 gives the outcome of the IT facilities available and in use among Estate Surveyors. The IT facilities in use examined are thirteen in number as indicated and ranked in the table below. The findings primarily show that Dyna model, Cougar, Circle, Narrative complete and Pm fox with score little above 1, are rarely used.

INSERT TABLE 3

CONCLUSIONS AND RECOMMENDATIONS

The empirical study was an examination of the use of IT for property valuation in Lagos, Nigeria. The result revealed that most Nigerian valuers are conversant with IT usage with a considerable number having IT facilities within their organisation and 68% claimed to have installed website although scanty figure used extranet. Furthermore, Most of these firms claimed to have IT experts in their organisation while 30.9% did not. Interestingly, this has not affected valuation results and performances in the study areas. However, it appears the expertise the valuers claimed to have in their organisations have been applied in the area of administration e.g obtaining brief, preparation of proposal, valuation reports preparation or data storage. It is recommended that a study be conducted in future to ascertain the depth in terms of figures of IT facilities to valuation. Although, they all claimed to use various categories of IT software. Spread sheet ranked first in terms of usage while others as contained in table 3 above, rarely feature.

Findings also revealed that Estate Surveyors' firms in Lagos are automated. However, It is suggested that these firms should effectively use IT facilities to improve valuations in their respective organisations both in Lagos and across Nigeria. For instance, awareness of valuation software or modern valuation techniques are not sufficient it must be seen in the quality of valuation and the output of Estate Surveyors and Valuers. Several studies still emphasise the existence of inaccuracies in valuations in Nigeria. This seems to be a paradox giving the result of the study. May be, there is need for time to determine the effect of the outcome on the organisational performance. Obviously, due to the paradigm shift errors associated with conventional methods will be minimised among the Lagos valuers. To achieve these, efforts

should be directed to optimally use the various IT facilities for property valuation. IT usage for property valuation will unearth the latent benefits that have hitherto eluded the Nigerian valuers. It is further recommended that the Nigerian Institution of Estate Surveyors and Valuers (NIESV) and Estate Surveyors and Valuers Registration Board of Nigeria (ESVARBON) should establish a faculty for IT as well as introduce continuous accreditation of estate firms with a view to standardising their practice. Also, IT usage and compliance must form part of the requirements for recertification of all estate firms. Also the professional bodies should begin to accredit estate firms while using the framework propounded in the study.

Notwithstanding the above, the use of IT is beset with some problems emanating from the estate surveyors and valuers themselves and their personnel, the Government and the society at large. To overcome this, there is a need for concerted efforts of the Government, the professional bodies on IT training and the practitioners themselves in terms of improving the power supply and enactment of enabling legislation on Information technology.

REFERENCES

- Ajibola, M. O., Oloyede, S. A. & Atere, O. O. (2011). Estate surveyors and valuers perception and methods of wetland valuation in Lagos metropolis. *Journal of Research in International Business Management*, 1(4), 85-95.
- Aluko, B.T. (2004) Privatisation of public enterprises in Nigeria: Issues and problems. *Journal of Business Economics and Management*, 5(4), 193-203.
- Ayedun, C.A. (2009) *Reliability and consistency of the Investment method of Valuation: A study of Lagos metropolis*. Unpublished doctoral dissertation. Covenant University, Ota, Nigeria.
- Babawale, G.K. (2011). *An evaluation of factors influencing inaccuracy in residential property valuation in Lagos metropolis*. Unpublished doctoral dissertation, University of Lagos, Nigeria.
- Britton, W., Davies, K. & Johnson, T. (1980). *Modern methods of valuation of land, houses and buildings*, (seventh edition), London: The Estate Gazette Ltd.
- Bulut, B., Allerverdi, N, Kahramanli, H, & Yalpir S. (2011). A residential real estate valuation model with reduced attributes. *International Journal of mathematical models and methods in Applied Sciences* 3(5), 586-593.
- Daly, J., Gronow, S., Jenkins, D. & Plimmer, F.(2003). Consumer behaviour in the valuation of residential property: A comparative study in the UK, Ireland and Australia *Property Management*, 21(5), 295- 314.
- Ibrahim, M.F., Cheng, F.J. & Eng, K.H.(2005). Automated valuation model: An application to public housing resale market in Singapore. *Property Management*, 23 (5), 357-373.
- Ifediora, B.U.(2005). *Valuation mathematics for valuers and other financial & Investment Analysts*, Enugu: Immaculate Publications Ltd.
- Kauko, T. (2007). Advances in mass appraisal methodology: An international perspective. International conference, 25-28 June, Sustainable urban Area (Rotterdam)
- Lunt, B.M, Ekstrom, J.J., Gorka, S., Hislop, G., Kamali, R., Lawson, E., LeBlanc, R., Miller, J & Reichgelt, (2008). Information Technology. Curriculum Guidelines for undergraduates' degree programme in information technology. Retrieved on 22nd May, 2013, pgs 5- 139 from <http://www.acm.org/education/curricula.html>.
- OECD (2004). Recommendation of the Council on Broadband Development; OECD Statement by the OECD Committee for Information, Computer and Communications Policy, Broadband Driving Growth Policy Responses. Retrieved from internet on 25th June, 2012.
- Ogunba, O.A and Ajayi, C.A. (2007). The response of Nigerian Valuers to increasing sophistication in investors requirements *Journal of property Investment & Finance*, 25(1),43-61

Opara, U. E. (nd). *A comprehensive valuation for tertiary Institutions and practitioners*, Awka: De emeralds Printing & Publishing Company.

Parker, D.,& Robinson, J. (2002). Property valuation software packages: An evaluation. Paper presented at the conference of the Pacific Rim Real Estate Society, Christchurch, 20-22 January, 2002 & Robinson.

Sirmans, G. S., Sirmans, C.F. & Benjamin J.D (1989). Determining apartment rent: The value of amenities, services and external factors. *The Journal of Real Estate Research*, 4(2),33-43.

Ukabam, T.A (2005) An overview of Automated Valuation Using Direct Comparison Method. *Journal of the Nigerian Institution of Estate Surveyors and Valuers*, 28(2), 24-26.

Wardman, M., Bristow, A & Arsenio E.(2005) Applying stated preference methods to the valuation of noise: Some lessons to date . Environmental Noise Control. The 2005 Congress and Exposition on Noise Control Engineering. 07-10 August 2005 –Rio de Janeiro- Brazil

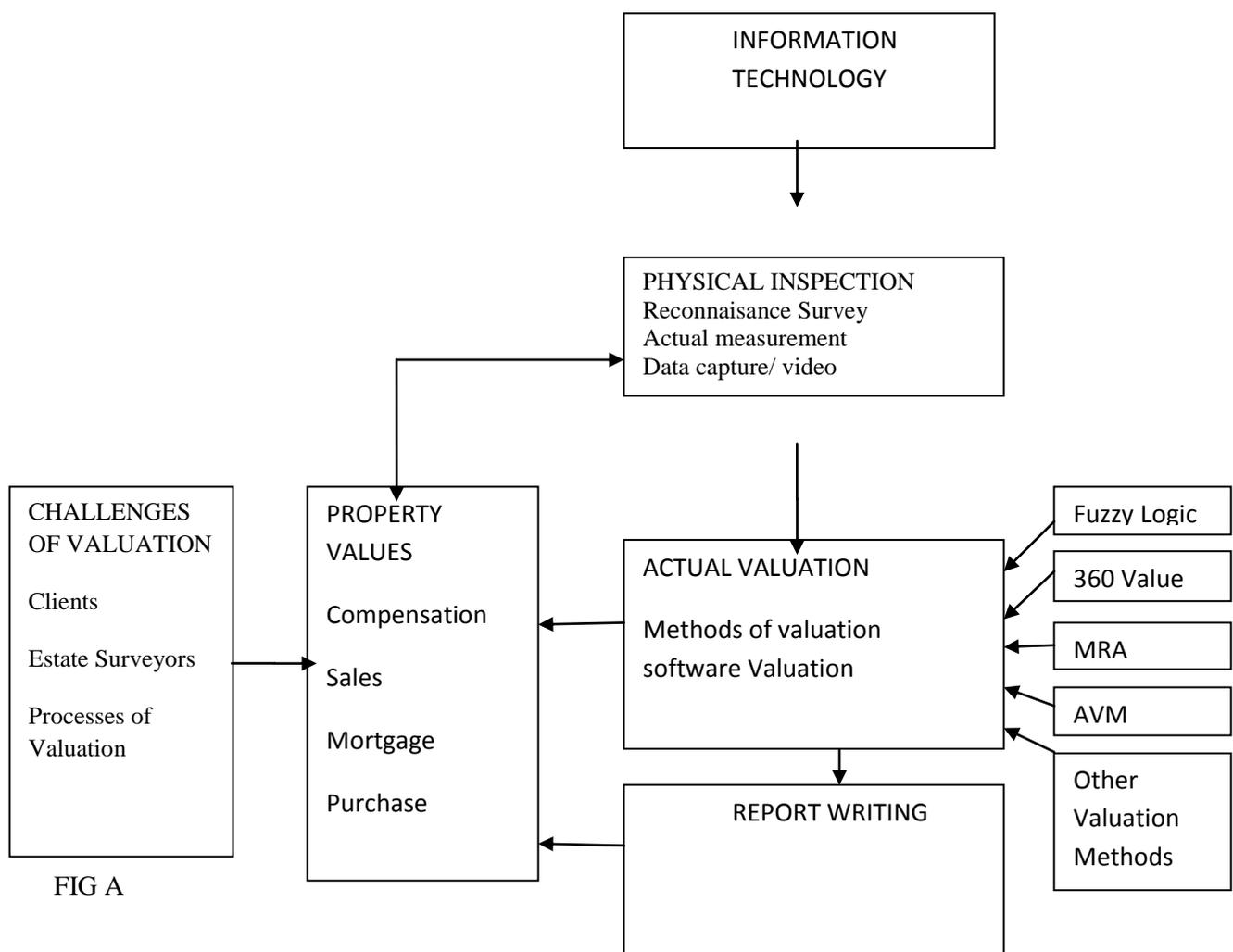
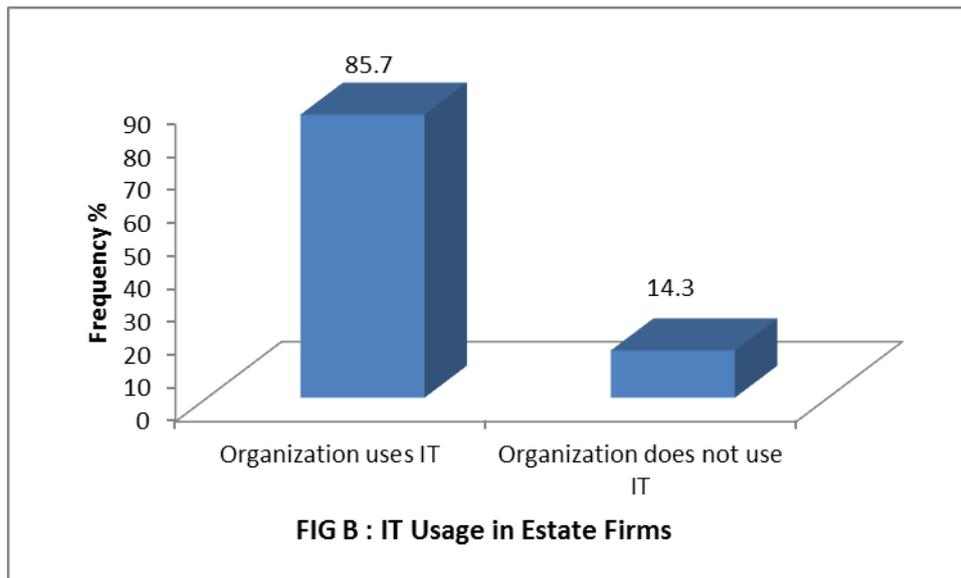


FIG A

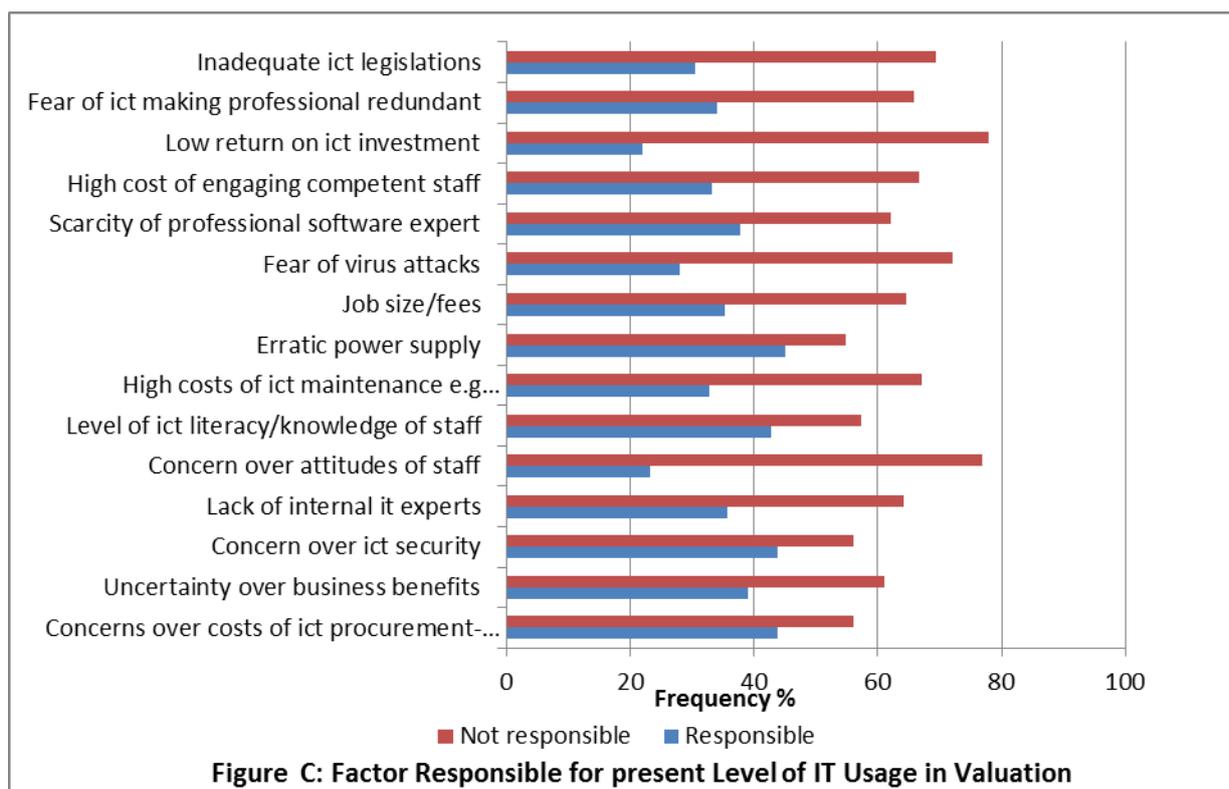
Author's Conceptual Framework**Table 1: Type of IT Facilities Available in the Organization**

	Engaged in		Not engaged in	
	Freq.	%	Freq.	%
Desktops	74	90.2	8	9.8
Laptops	69	85.2	12	14.8
Modems for staff	53	65.4	28	34.6
Printers	79	96.3	3	3.7
External disk, cds etc	53	68.8	24	31.2
Internet	77	93.9	5	6.1
Extranet	9	12.5	63	87.5
Mobile phones	69	84.1	13	15.9
Company own website	54	67.5	26	32.5
Latest operating systems	39	50	39	50
Anti-virus	69	84.1	13	15.9
Digital camera	73	89	9	11

Source: Field Survey,2013

Table 2: Area of Valuation where IT is used

	Engaged in		Not engage in	
	Freq.	%	Freq.	%
Preparation of valuation brief/proposal	63	87.5	9	12.5
Obtaining valuation brief	46	63.0	27	37.0
Digital measuring tape for physical inspection	22	30.6	50	69.4
Production of drawing e.g. use of autocad	63	86.3	10	13.7
Consultation with clients	48	65.8	25	34.2
Carrying out actual valuation i.e. use of valuation software	24	33.8	47	66.2
Preparation of valuation report	67	93.1	5	6.9
Submission of valuation report	37	52.1	34	47.9
Making & receiving payment	45	61.6	28	38.4
Data storage	63	86.3	10	13.7
Holding meeting e.g. conference meetings via mobile phones use of tapes to record proceedings in meetingsmp4	28	38.9	44	61.1



Source: Field Survey, 2013

Table 3: IT facilities in Use

	N	Mean	Ranking
Spreadsheet	81	1.79	1
Investment analyst	81	1.22	2
Enterprise software	81	1.19	3
Argus valuation model	81	1.16	4
AVM model	81	1.15	5
360 value	81	1.14	6
Caprate calculator	81	1.11	7
Sage management software	81	1.11	7
Pm fox	81	1.06	9
Narrative complete	81	1.06	9
Circle	81	1.05	11
Cougar	81	1.02	12
Dyna model	81	1.02	12

Source: Field Survey,2013

**CHECKING SECURITY IN RESIDENTIAL HOUSES AND BANKS, USING CCTV IN
LAGOS METROPOLIS
A CASE OF LEKKI PENINSULA, ETI-OSA L.G.A.**

Ademola Farinmade, Oluwole Soyinka & Olubukola Osazuwa

Department of Urban and Regional Planning
Faculty of Environmental Sciences
University of Lagos, Nigeria
afarinmade@unilag.edu.ng, soyinkaoluwole@gmail.com

ABSTRACT

Checking safety and security are critical issues in achieving sustainable standards of living globally. This paper examines the effectiveness of using electronic security system in both residential houses and banks with focus on Lekki Peninsular as the study area. The research aim is to examine the effectiveness of electronic security system in reducing criminal activities in residential areas and banks. The objectives were: to examine the socio-economic characteristics of the respondents, examine the existing security structure of the study area; assess the criminal activities in the study area and also examine the level of awareness on the use of CCTV in the study area. The research adopts descriptive statistic and participant observation methods to measure the effectiveness of electronic security device in the study area. The sample frame for the study is a total of two thousand (2000) households and eight (8) banks in Lekki Peninsula. Sample size of 10% was adopted from the sample frame, with Two hundred (200) questionnaire administered in housing area, 2 questionnaire administered in each of the eight (8) banks to make a total of two hundred and sixteen (216) questionnaires. The study reveals that CCTV is a very essential tool for apprehending criminals in banks, while the same could not be categorically stated with residential houses. The study reveals that both residential houses and banks have suffered adverse security issues, anti-social menace and the installation of CCTV cameral would improve the situation drastically. This study represents a major advancement in knowledge of CCTV in urban planning and achieving sustainable development. Appropriate recommendations were made for government agencies and co-operate entities to curb crime and insecurity in the area.

Keywords: Banks, Checking safety, Residential houses and Security,

INTRODUCTION

Safety and security is a global phenomenon that has increased drastically in Nigeria over time. In recent times the crime rate in Nigeria and Lagos Metropolis has risen to the level of unanimous outcry of the public and private individuals for urgent solution. The issue of cybercrime, economic fraud, theft and robbery are increasing by the day. Government has adopted various security policies (National Defense Policy 2006, ECOWAS Conflict Prevention Framework and Human Right Act among others) to secure the lives and properties of its citizens, but none of these policies has actually yielded positive results (Ecoma. 2011). Human abduction, armed robbery, terrorism, bomb attacks and lots more have been the order of the day in the country. In the light of this, the governments and private individuals have come up with the introduction of computer –based closed circuit to television (CCTV) cameras in public places to monitor and record images of what is taking place in specific locations. Many developed countries have used CCTV to reduce the crime rate in their respective countries. Besides CCTV is relatively not new in Nigeria, but it still not clear how effective it is in detecting or reducing crime in Nigeria (Salau, and Lawanson, 2010).

The CCTV is a potent and intelligent security management system which can take footage of activities and crime as it is being committed. It is a system that has been practiced in the United

Kingdom for as long as eighteenth century (Aldridge, 1994). It is a system that has made the job of the police easy and court disputes settled in record time. In contrast to broadcast TV, a CCTV security camera doesn't transmit the signal openly. The foremost quality of CCTV is that it is employed for surveillance, and thus CCTV security cameras are presumably positioned in crowded places or places where security service is a must, such as; airports, banks, ATMs, casinos, etc. A CCTV camera is placed in extraordinary corner of a location or activity station for protection of their customers and services. CCTV cameras are not just restricted to watching airports and banks, they are additionally installed in environments that are comfortable for individuals, or with the aim to record a process that is observed and controlled from a control room (Bennet, and Gelsthorpe, 1996).

However, CCTV being one of the effective information technologies for private, local and national security gave respondents good indicators in supporting the usage of CCTV in provision implementation and achieving safety and security. Closed circuit television (CCTV) plays a significant role in protecting the public and assisting the police in the investigation of crime. Considering the function and the increase need of promoting safety and security in Nigerian cities and Lagos Metropolis, this paper examines the effectiveness of CCTV in respect to crime reduction and disorder in the residential neighborhood of Lekki and some banks in its environs. Consequently, community perceptions were sought to know the effectiveness and acceptability of the tool in houses and public places (Bennet, and Gelsthorpe .1996).

LITERATURE REVIEW

Farrington (1997), Security is the situation that exists as a result of the protection measures put in place for the protection of personnel, information and property against hostile persons, influences and actions. Security can also be defined as any measure taken with a view to protecting anything of interest to an individual, organization or government.

The threats to Nigeria security according to Ekblom (1992), epitomize the virtually unstoppable rural-urban drift, the fierce competition for the control of State power (especially at the federal level), the manipulation of ethnic and religious identities and sensibilities as a major factor in safety and security issues. The clamor for resource centres, conference control and convocation of a sovereign National conference (SNC) is also seen as indicators of the failure of growth and development of security. The list of criminal act is endless with: assassinations, kidnapping, arson, armed robbery, vandalization, ritual acts, financial crimes, fraudulent acts, impersonation, economic sabotage, political brigandage in the general society, prostitution and women trafficking, drug abuse, cultism, examination malpractices, bullying, raping and assault amongst youths and students.

The overwhelming success of CCTV coverage in parts of Europe has prompted most African cities to look seriously at adopting their own public video surveillance systems. Considering the developed cities where CCTV cameras have been properly employed, the universal experiences are dramatic reduction in crime and victimization (Brown, 1995).

Literatures from: Clarke & Felson 1993, Brown 1995, Chainey 1999, Burrows (2009), Cook & Campbell 2000 and other arguments for and against in the use of CCTV in public and private places in the researches reviewed only emphasize the important off CCTV as the source of crime reduction and the wiliness of the people to give their privacy to achieve maximum security. The following concepts were also identified for the determination of effectiveness and further strategy in promoting it sustainability:

Crime Prevention Concept

Crime prevention concept is a term describing techniques used for reducing victimization as well as deterring crime and criminals. It is a strategy applied specifically to efforts made by government to reduce crime, enforce the law, and maintain criminal justice. Obviously, crime prevention is including any initiative or policy which reduces or eliminates the aggregate level of victimization or the risk of individual criminal participation. It includes government and community based programmes to reduce the incidents of risk factors correlated with criminal participation, the rate of victimization as well as efforts to reduce perception and fear of crime (Deismann 2003).

CCTV System and Security Concept

Ditton and Short (2009), present CCTV system and security concept as a valuable management and security tool for maintaining safety and security. The concept presents the installation of a CCTV system as part of a series of security recommendations generally intended to prevent or detect crime. CCTV can be very effective in maintaining security; video evidence can help with security enquiries or investigations and assist in securing criminal convictions. The visual recording of incidents, for evidential or investigative purposes, has many benefits and with a competitive customer given market is no longer cost prohibitive. CCTV systems will vary in size and complexity depending on their purpose and the defined security operational requirements. However, the basic purpose of any system will be to observe a scene and the activities that occur within it. The observation may be:

- i) Covert - the camera is concealed.
- ii) Discreet - the presence of the camera will be known to some people, but its appearance will not automatically suggest its purpose.
- iii) Overt - the appearance of the camera will be designed to clearly indicate its function and maximize the deterrent effect. For crime prevention, overt CCTV systems are usually more suitable whereas discreet or covert systems are more appropriate for crime detection and prosecution.

The concept presents the different forms and strategies of using the CCTV for the process of achieving safety and security in the neighborhood. The concept presents the strategy as covert, discreet and overt approach in observation and checking of security.

Study Area

The Lekki Sub-Region comprises of a naturally formed peninsula on the Atlantic Ocean East of Lagos City and on Lagos Lagoon. The peninsula is approximately 70 to 80 km long, stretching from Victoria Island in the west to Refuge Island in the east, with an average width of 10 km. The Lekki Sub-Region includes several Estates, farmlands, areas allocated for a Free Trade Zone (FTZ), an airport, and a sea port. The proposed land use master plan for the Lekki Sub-region envisages the Lekki Peninsula as a Blue-Green Environment City.

Lekki neighborhood is one of the highbrow residential neighborhoods in Lagos metropolis. The neighborhood is fast becoming a beehive of activities as commercial and light industrial activities are springing up there. Residential buildings are fast being converted to other land uses. Also, people from other areas of Lagos and Nigeria are buying properties in this area which is making the population rise. Lekki is experiencing urbanization and these phenomenon accompanied with its challenges are the increased crime rate. As a consequence of the rapid urbanization in Lekki, criminals see the neighborhood as a veritable location to perpetrate heinous crime such as burglary, bank robbery, car snatching, kidnapping, rape, even murder, to mention a few. Despite several attempts to curb crime in the neighborhood by Nigerian police and private guards, it has remained unabated. Some crimes are committed by residents who take advantage of the security lapses of another, such kind of crime can hardly be detected except

there is a “fixed eye” watching around 24 hours and seven days a week, hence the Close Circuit Television (CCTV) is required in this location.

METHODS

Both primary and secondary sources of information were used in this study. Primary data was obtained through a number of processes: At first stage, a pre-survey of the study area was carried out with the aid of secondary data obtained from the neighborhood management authority to take account of existing area where the CCTV camera is installed, the population characteristics and land use. The second stage was visiting the field (Lekki Peninsula neighborhood) and checking what is on ground as against the secondary data. The third step was the use of structured questionnaire to obtain information from the population. Sample of two hundred housing units were drawn from the sampling frame representing 10% of all the residential buildings in the area. Sixteen questionnaires were administered in eight banks in the study area. In all, 216 questionnaires were administered to both households and banks in Lekki Peninsula. A sample of random sampling method was adopted in which only house owners were administered questionnaire. The questions were fixed to value their perception of the purpose, capabilities and public concern in respect of CCTV implementation. The questionnaires were analyzed using simple descriptive statistics.

DISCUSSION

The findings and discussion of this research will be directed towards the most relevant data and findings of this study and recommendations will be made accordingly so as to achieve the aim of this research.

Socio-Economic Characteristics:

The summary of socio-economic characteristic of the study area reveals 52% are female while 48% are male. The age range of reveals that with 51.6% are 30-40 years, 30.56% are 41-50years while 17.8%. are above 50 . More than half of the respondents were self-employed (50.56%), lastly the table deduced that most of the respondents (40%) were graduates with only B.Sc. and those with MSc., PhD., HND, and WAEC qualifications are 21.11%, 18.33%, 14.44% and 6% respectively.

Table 1: Socio-Economic Characteristic of Respondents

Variables		Freq.	%	Variables		Freq.	%
Gender	Male		48%	Age	30-40years		51.6%
	Female		52%		41-50years		30.56%
	Missing		0		Above 50		17.8%
	Total	216	100%		Total	216	100%
Variables		Freq.	%	Variables		Freq.	%
Educational Level	WAEC		6%	Occupation	Self-employed		50.56%
	OND/HND		14.4%		Civil servant		20.55%
	B.Sc.		40%		Retired		10.55%
	M.Sc.		21.11%		Others		13.34%
	PhD		18.33%		Missing		0
	Total	216	100%		Total	216	100

Source: Authors Field Work 2012.

The table and the analysis of the data collected reflects that the study area is a settlement of average standard of living with educated and a more active age group with a settlement of rapidly increasing economic features that can induce or attract crime and insecurity.

CCTV: Level of Awareness, Its Purpose, Effectiveness and Efficiency

Level of Awareness: When provided with a list of possible locations, almost all respondents reported seeing CCTV in a number of other places. However there was a marked difference in the awareness of CCTV in these different locations such as; Shops, Car Parks, City Street, Housing Estates and Banks. Banks were quoted most frequently with 97% being aware of CCTV in their location while City streets was the 2nd highest with a frequency of 34% claiming to have seen CCTV on city streets, followed by shops with 17% claiming to have seen CCTV in shops. Housing estates and car parks had the lowest frequency with both 7% claiming to have seen CCTV in houses and car parks.

Table 2: CCTV Level of Awareness

Variables				Variables			
		Freq.	%			Freq.	%
Bank Awareness	Yes		97%	Housing Awareness	Yes		14%
	No		3%		No		45%
	Don't Know	0	0		Don't Know		41%
	Total	16	100%		Total	216	100%

Source: Authors Field Work 2012.

Its Purpose: When asked about the purpose of CCTV, some of the respondents (67%) see CCTV as a safe tool (17.1%), (15.7%) see it as a spy tool CCTV while 15.2% regard it as tool for scaring people from committing crime. 15.1% consider CCTV as a tool to stop trouble from breaking out, (14.8%) regard it as a tool for crime apprehension while in the opinion of (13.4%) of the respondents it is for public checkup and the rest (8.3%) were of the opinion that it is for crime reduction.

Purpose of CCTV Installation

Variables		Freq.	%
Its purpose	CCTV as a safe tool	37	17.1%
	CCTV as a Spy tool	34	15.7
	CCTV as tool for scaring people from crime	33	15.2
	CCTV as tool for stopping trouble	32.7	15.1
	CCTV as tool for crime apprehension	32	14.8
	CCTV as tool of public check up	29	13.4
	CCTV as tool for crime reduction	18	8.3
	Total	216	100%

Source: Authors Field Work 2012.

Effectiveness: The summary of respondents perceptions of CCTV in a general survey with regard to its effectiveness as a safe tool, crime detection and crime prevention in the study area shows that; majority of the respondents (54.4%) believed that CCTV has been very effective in crime reduction, 24.4% rated it as fairly effective while 9.4% rated it as not effective. The rest 11.6% were indifferent.

Table 4: CCTV; Effectiveness

Variables		Freq.	%
Its purpose	Effective in crime reduction		54.4%
	Fairly effective		24.4%
	Not effective		9.4%
	Don't Know		11.6%
	Total	216	100%

Source: Authors Field Work 2012.

The research further gathered data on who should be allowed to make decisions about installing CCTV. The data analysis indicates that individual households and estate management should

make the most decision on installing CCTV while the Federal Government, the police and the local government should be the least in making decisions regarding the installation of CCTV. Majority of the respondents also preferred the CCTV that has picture TV taped on video in their choice of CCTV cameras. They were of the opinion that the CCTV should be watched by the bank manager. The bank manager should watch the CCTV tapes for the banks while the local neighborhood watch groups and estate management should watch the CCTV tapes for the houses, in order to enhance security.

RECOMMENDATIONS

Network Availability: The success of an IP-CCTV system depends on the network to guarantee timely, fast and affordable delivery of high volume, robust and accurate images. The capture of evidential quality images depends on this. To this end, the capacity of our local area networks will have to increase and fast LANs running at 1 Gigabit per second and above will be required. This increase in capacity greatly reduces the threat of LANs being swamped by CCTV image traffic. Further the bandwidth requirements for CCTV images are decreasing. This is partly through improvements in compression technologies and partly because installers and system managers are making better use of controls that exist to segment and prioritize CCTV traffic to reduce its impact on traffic levels. The implementation of traffic management techniques will be more widely spread as IP knowledge and experience grows in the installer industry. However this needs to be balanced by measures that protect the evidential integrity of the recorded image. The advent of wireless LANs (54Mbps) and (11Mbps) provides a cable free method of connecting devices over IP. Wireless LANs are becoming common place across industry and commerce are starting to be deployed for the purpose of CCTV communications.

IP and the Future of CCTV (Recommend CCTV Model for the Government and Cooperate Entities)

This is a Local Area Network that interconnects computers in a limited area such as a home, school, computer library, or office building using network. They are usually higher data-transfer rates.. Although IP is growing steadily, it hasn't yet transformed the industry. CCTV is still dominated by the traditional analogue devices and transmission, and even when, for instance, DVRs overtake VCRs in annual sales, it will still be some time before IP dominates the scene. The key to understanding the future of IP in CCTV is to recognize its essentially evolutionary nature and its growth will be determined as much by the evolution of the technology as by the eagerness of the industry to embrace it. Above all the CCTV industry is price driven and it is increasing affordability that will eventually determine the success of IP-CCTV.

Responsibility to Ensure CCTV System Is Maintained and Operational: The operator's standard operating procedures should detail a schedule for the checking of recording equipment to ensure the equipment is in good working order. A library of tapes, compact discs should be maintained, sufficient for the operator's operating purposes.

Past Investments: Existing CCTV installations have invested heavily in analogue systems and cabling networks. There is no cost justification at present for the wholesale replacement of existing analogue infrastructures in the vast majority of instances. Instead the industry will see the growth of hybrid networks that link analogue systems to IP networks via codec devices (that convert analogue streams to IP) to facilitate a link between the old and new worlds. Hybrid networks offer the functional benefits of IP without requiring high capital investments. IP-CCTV adoption will therefore take place in stages. Initially many analogue CCTV systems will interface with digital video recorders that allow the transmission of images on demand or on alarm over an existing IP network. New IP-CCTV installs or very major upgrades in existing IP-

rich environments will piggyback on existing LANs. However ultimately we will see the wholesale replacement of analogue local networks on upgrade replaced with LAN communications.

Control Rooms: Personnel assigned to monitoring and operating CCTV systems from a control room must not utilize the systems in an inappropriate manner. If evidence is provided that an individual or individuals are using the system inappropriately, the operator should take appropriate measures to eliminate or minimize the risk of reoccurrence. The CCTV system should only be operated within applicable law and only for which it was established. These purposes include:

- i. Assisting in the protection of residents, visitors, workers and passengers
- ii. Providing a level of security for staff with face to face public contact.
- iii. Monitoring passenger and driver behaviors within the streets.
- iv. Deterring vandalism, property incidents, assaults, robbery and other criminal or anti-social behavior.
- v. Providing enhanced security of assets, including vehicles and equipment.

Contact with Police: The operator's standard operation procedures should also detail a protocol covering the release of images to the law enforcement agencies. The release of images should be supported by adequate documentation detailing the reasons for the release.

System Integration: Finally, demand for IP is being partly driven by end users who desire to integrate all security applications; CCTV, Access Control, and Fire into a single system running over the same network and under the same management. The benefits that IP brings to CCTV; □ Ease of communication way beyond limits of a dedicated network, □ The management flexibility, □ The functional benefits of being software controlled, and □ The immediate and long term cost advantages of being part of the huge IT industry. All apply equally to other technologies. The decision to bring these diverse applications together on the IP network is straightforward common sense, especially where a company's LAN and WAN already carry other communications traffic, voice telephony as well as data.

CONCLUSION

The growth of IP-CCTV adoption depends upon a succession of technological evolutions creating a strong business proposition in its favor. The industry faces a tremendous educational challenge to ensure that the installers have the knowledge and skillsets required to meet users' needs. And without doubt the nature of the installer community itself is changing as system integrators and others, already well-established in the IT industry, spot the commercial opportunities opening up before them. The technical challenges that remain formidable are network availability which is essential to ensure the image is recorded and the quality of the camera and recording system that needs to be of an evidential quality.

Currently CCTV has a broadly positive perception from members of the general public. Levels of concern are not high. CCTV is assumed to be fairly effective in crime control. However public acceptance is based on limited and partly inaccurate knowledge of the functions and capabilities of CCTV in public places. There may need to be guidelines that will make possible an informed public acceptance of CCTV through fuller consultation and the provision of information. There is also a need to encourage operational procedures that will maximize the effectiveness of CCTV and minimize any threat to civil liberties which may arise from either sloppy practices or the deliberate misuse of such systems. As systems become more complex and become capable of achieving more, it is vitally important that all those involved are trained to meet the challenges ahead. Government agencies, The Police, Security organizations and all those involved in the

criminal justice system, need to be brought up to date with the technical changes and the new opportunities that are generated so as to prepare the ground

It is easy with hindsight, to state that the effectiveness of CCTV will be compromised if: the wrong cameras are fitted, if they do not work well and are placed in wrong locations. The most in-appropriate use of its purpose is when its management is weak, if the operators are not trained or (and) not familiar with the layout of the area and if the police are not supportive among others. All these must be addressed by the government and all the stakeholders to promote the use of CCTV so as to maximize the benefits derived from it.

REFERENCES

- Aldridge, J. (1994). *Who Will First To Test Your CCTV Security or Safety Team? CCTV Operational Requirements Manual*, Police Scientific Development Branch, no. 17.
- Armstrong, G. and Giulianotti, R. (1998). *From Another Angle: Police Surveillance and Football Supporters*, in C. Norris, J. Morgan, and G. Armstrong (eds): *Surveillance, Closed Circuit Television and Social control*, Aldershot: Ashgate.
- Bennett, T. and Gelsthorpe, I. (1996). *Public Attitudes towards CCTV in Public Places Studies on Crime and Crime Prevention*, 5/1: 72-90.
- Brand, S. and Price, R. (2000). *The Economic and Social Costs of Crime*. Home Office Research Study no. 217. London Home Office.
- Brown, B. (1995). *CCTV in Town Centres: Three Case Studies, Crime Prevention and Detection Series, no. 73*. London: HMSO.93
- Burrows, J. (2009). *The Impact of Closed Circuit Television on Crime on The London Underground*, in P. mayhew, R. Clarke, J. burrow, M. Hough and S. Winchester: *Crime in Public View*, Home Office Research Study, no. 49, London : HMSO.
- Chainey, S. (1999). *Crime Mapping Case Studies Volume 2: Successes in the Field, United States Institutes of Justice*. Washington DC.
- Clarke, R. and Felson, M. (1993). *Routine Activity and Rational Choice*. New York: Transaction publications.
- Cook, T. and Campbell, D. (2000). *The design and Conduct of Quasi-Experiments and True Experiments in Field Settings*. In M. D Dunnette (ed): *Handbook of Industrial and Organizational Psychology*, New York.
- Deismann, W. (2003). *CCTV Literature Review and Bibliography, Research and Evaluation*. Branch, Ottawa: Royal Canadian Mounted Police.94
- Ditton J. and Short, E. (1999). *Yes, It Works, No It Doesn't: Comparing The Effects of Open Street CCTV in Two Adjacent Scottish Town Centers*", in K. Painter and Tilley,(eds.) *Surveillance of Public Space: CCTV, Street Lighting and Crime Prevention*, Monsey, NY: Criminal Justice Press.
- Ditton, J., Short, E., Phillips, S., Norris, C. and Armstrong, G (1999). *The Effect of Closed Circuit Television on Recorded Crime Rates, and On the Fear of Crime in Glasgow, Edinburgh*: Central Research Unit, Scottish Office.
- Ditton, J. (2000). *Crime and the City: Public Attitudes to CCTV in Glasgow*. *British Journal of Criminology*, 40, 692-709. Ditton J., Levine M. and McCauley R. (forthcoming): *Street Drinking Legislation, CCTV and Public Space: Exploring Attitudes towards Public Order Measures*, London HMSO.
- Drummond, M. (1997). *Methods for the Economic Evaluation of Health Care Programmes*, Second Edition, Oxford University Press.
- Ecoma, A. (2011). *Gender and Security Policy in West Africa*. Online Published by Friedrich-Ebert-Stiftung, Regional Office Abuja. www.fes-westafrica.org.

- Egger, M, Davey, Smith G, and Altman D. (1995). *Systematic Reviews in Health Care: Meta-Analysis in context*. London: BMJ Publishing. 95
- Eklblom, P. (1992). *The Safer Cities Programme Impact Evaluation: Problem and Progress Studies on Crime and Crime Prevention, 1:1*.
- Evet, C. and Wood, J. (2004). *Designing a Control Room, CCTV image*, spring, pp 24-25.
- Farrall, S. Bannister, J. Ditton, J. and Gilchrist, E. (2000). *Social Psychology and the Fear of Crime: Re-examining a Speculative Model*, British Journal of Criminology, 40, 399-413.
- Farrington, D. (1997). *Evaluating a Community Crime Prevention Programme" Evaluation, Neighbourhood Watch in England and Wales. A Locational Analysis*. Sohain Husain. 1988. V+63pp. (0 86252 314 1).
- Salau, T. & Lawanson T. (2010). *Security Consciousness in City Planning: The Case Study of Lagos Megacity*. Retrieved from http://www.google.com/physical_planning/urban_security.pdf

EFFECTS OF PROJECT MANAGEMENT ON ABANDONMENT OF BUILDING PROJECTS IN LAGOS STATE, NIGERIA

Dosumu, Oluwaseun Sunday & Akinsiku, Emmanuel Olusegun

Department of Building, Faculty of Environmental Sciences, University of Lagos,
Lagos, Nigeria

Oluwaseundosumu97@gmail.com, eoakinsiku@yahoo.com

ABSTRACT

The study was conducted to investigate the roles of project management on building projects in Lagos, Nigeria. The objectives of the study are to determine the project management factors responsible for project abandonment, effects of poor project management on construction projects and the ways of reducing project abandonments in Lagos state. The study made use of 66 questionnaires out of the 80 that were administered on project managers within Lagos metropolis. The project managers of selected public and private abandoned projects were used for the study and the results of the study were analyzed with SPSS software using percentages and mean scores. The results of the study show that 15 project management factors lead to project abandonments to a high extent while another 15 lead to project abandonments to an average extent. The effects of poor project management on construction project abandonments and stakeholders include conflicts, loss of economic value and reduced standard of living. Project abandonment could be reduced by adequate planning, use of competent professionals and standard project management procedure. The conclusion of the study is that poor project management is key to construction project abandonments and to prevent project abandonment, the study recommends that project managers must engage in adequate planning, cost control and resource management.

Keywords: Abandonment, Building project, Lagos, Project manager, Project management

INTRODUCTION

The influence of project management on building project abandonment in Nigeria cannot be underestimated as it has grave consequences on the stakeholders (clients, consultants, contractors and users) and the nation at large. The menace of missed project objectives such as schedule and cost target overrun with distressing regularity and backlog of projects waiting to be tackled have largely characterized the Nigerian construction industry. These occur as a result of many unidentified factors (including poor project management) which eventually lead to building projects being abandoned. Unless the factors influencing project abandonments in Nigeria are identified, the statistics of failed projects will likely continue to be on the increase.

While project management was described to involve an array of carefully planned, interrelated and organized effort directed towards the accomplishment of project objectives (Young, 2006), Project abandonment was explained as the decision of management, for whatever reason to temporarily or permanently discontinue a project under development or currently in operation (Ewusi-Mensah & Przasnyski, 1991). Henachor (2012) explained that abandonment is an act of giving up on something completely, with no certain intention of when to resume. It was noted in Olusegun and Michael (2011) that there are about four thousand (4000) uncompleted or abandoned projects which belong to the Federal Government of Nigeria with an estimated cost of over N300 billion which will also take thirty (30) years to complete at the current execution capacity of the government.

Many factors have been traced to abandonment of construction projects. Yeo (2002) discovered that hostile company culture, political pressure, improper reporting structure, influences, vested interest and inappropriate level of management commitment are the organizational and managerial causes of project abandonment. Ewusi-mensah and przasnyski (1991) highlighted staffing, managerial and communication aspect of project management as the causes of project abandonment. Keider (1984), in his study concluded that although some projects are abandoned as a result of technology or design problems, the main reason behind project abandonment is a lack of understanding of the influence of project management on construction projects thereby leading to project abandonment. Other causes of project abandonment include – lack of social analysis of a project, project imposition, improper financial analysis, under bidding of project and lack of technical analysis (Henachor, 2012). Aluko (2012) asserted that contractors' bankruptcy, variation of project scope and incompetent project managers are responsible for project abandonment in Nigeria.

Abandonment of construction projects as a result of these factors has had devastating effects on both the projects and its stakeholders. Olusegun and Michael (2011) declared that project abandonment leads to the disappointment of the populace, low standard of living, wastage of resources, reduction in employment opportunities, decrease in economic activities, decrease in revenue accruing to government, difficulties in attracting foreign loans and increase in final cost of the project. Carrero, Malvarez, Navas and Tejada (2009) described the impacts of an abandoned project as both socio-economic and environmental. Henachor (2012) opines that project abandonment has its effect on individual, community and the government.

Since project abandonment has been attributed to poor project management (Al-Ahmed, Al-fagih, khanfar, Alsamara, Abulal Abu-Salam, 2009), it is important to work towards preventing its occurrence by identifying the project management factors responsible for project abandonment, the effects of project abandonment in the construction industry and the strategies that can be used to avoid project abandonment. Against this background therefore, the study intends to investigate the project management factors responsible for project abandonment, determine the effects of poor project management on construction projects and examine ways of preventing project abandonments caused by poor project management.

From the literature used for this study, it can be observed that there are many factors that are responsible for abandonment of construction projects and project management related factors are on all the lists. Therefore, if the project management related factors could be eliminated, project abandonment related factors could be eliminated; project abandonment will be reduced to a bearable minimum. El-Eman and Koru (2008) claimed that project abandonments are not always bad as they can lead to substantial learning and produce artifacts that are applicable to future projects. This notion was supported by Ewusi-Mensah and Przarnyski (1991) when it was stated that project abandonment in itself may be a good and acceptable management practice because it may prevent further investment of scarce organization resources in a non-productive venture. On the other hand however, El-Elam and Koru (2008) stated that project abandonment was corporate resources and is often difficult to deal with because it requires special management skills and critical business decisions.

Various effects have been highlighted by authors as a result of poor project management and abandonment of project. Carrero, Malvarez, Navas and Tejada (2009) established that project abandonments have both socio-economic and environmental impacts.

The effects identified by Olusegun and Michael (2011) are disappointed of the populace, reduced standard of living, wastage/under utilization of resources, reduction of employment

opportunities, decrease in tempo of economic activities, decrease in revenue accruing to government and difficulties in attracting foreign loans. Henachor (2012) noted that the effects of poor project management are felt by the individuals, community and government.

Many of the authors that worked on the factors and effects of project management and abandonment of projects actually suggested solution to the problems. This is evident in the works of Lemon, Liebowitz, Burn and Hackney (2002) when they suggested that project abandonments can be cured by extension of project schedule, better project management procedures, addition of more people, increased funding, increasing pressure on suppliers, reduced scope of project, request for outside help, better development methods, changed technology and performing some other functions.

The solutions of Olusegun and Michael (2011) are adequate planning inception, making fund available, engage competent construction professional, production of economic designs, project scope should not be varied, prompt payment to contractor, partnering, risk appointment, risk review, clear communications, root cause analysis, maintaining morale and right culture and keeping register of uncertainty, government should reduce inflation, previously started jobs should not be abandoned for new idea and strong financial based contractors should be employed. Henachor (2012) took a multi-dimensional approach by suggesting social analysis, institutional analysis, financial analysis, economic analysis and technical analysis to solve the problem of project abandonment.

In addition, Boehm (2001) suggested that project abandonment can be avoided by conducting user satisfaction and needs survey, holding internal technology fairs, ensuring sustained user involvement in product definition, project reviews and studying clearing that unanticipated changes might make it advisable to terminate or redirect the project.

METHODS

This study is both survey and descriptive in nature and involves the assessment of selected abandoned projects through the use of structured questionnaire and interview for data collection. Since construction projects fall into different categories such as building, civil and heavy engineering amongst others, the study focuses on building (residential, industrial, institutional and recreational) projects within the Lagos metropolis. Any construction related professional such as Architect, Builder, Estate Surveyor and Valuer, Quantity Surveyor or Engineer would make a good project manager provided there is requisite knowledge, experience of the industry and ability to lead and co-ordinate (Oduami, Omirin & Iyagba, 2003). Hence, the population of this study consists of abandoned projects (public & private) that are carried out by construction related project managers.

The sample for this study consists of public and private abandoned building projects within Lagos metropolis. The projects used for the study were selected through convenience sampling (Non-probabilistic) technique. The construction project managers that worked on the selected public and private abandoned building projects within Ikeja local government area are the subjects for this study.

Project management experts were interviewed in order to shed more light on the subject of the study. The project managers have a minimum of fifteen years work experience and have been engaged on an array of building projects which include residential, institutional, recreational and religious buildings. The academic background of the professionals involved in the interview is basically M.Sc but some of them still hold Bachelor's degree. The responses of the interviewees were tape recorded and replayed after the interviews have been completed to extract important

comments that are useable for results and analysis. Tape recorder was used to prevent the interviewer from asking the interviewees to retake some statements, thereby disturbing the flow of information within the interview session.

Furthermore, the questionnaire for the study was initially administered on ten respondents in order to discover the weaknesses in it and make necessary corrections, additions and subtractions that are noted by respondents. However, the responses from the pilot study (10 respondents) was combined with those from the main respondents (51 respondents) during data analysis because the corrections made to the questionnaire were in the area of creating open ends for contributions from respondents rather than the contents of the questionnaire and correcting some spelling errors. Furthermore, the respondents for the pilot study were part of the sample for the study. The main statistical method employed for this study is the mean item score.

The project management factors that are responsible for abandonment of building projects are depicted in table 2. These factors which include lack of good project planning (4.35), inadequate cost control (4.30), poor resource management (4.15), wrong estimation (4.15), improper financial analysis (3.97), construction not following specifications (3.88), poor communication among project participants (3.76), improper documentation (3.73), improper definition of roles and responsibilities (3.65), poor risk management (3.53), misunderstanding of user requirements (3.47), lack of clear project goals and value (3.45), differences between management and client (3.45) and lack of commitment to project (3.45) are responsible for project abandonment to a high extent.

Also, insufficient management (3.42), lack of effective project management technique (3.42), lack of contingency plans (3.39), faulty designs (3.39), assignment of resources to a higher priority project (3.38), inadequate task definition (3.36), lack of management judgement (3.30), lack of training and over dependence on consultants (3.30), mis-used project management technique (3.27), over scheduling of experts (3.24), lack of user involvement (3.14), incomplete requirements (3.14), technology illiteracy (3.08), number of organizations involved in project (2.91) and lack of IT management (2.86) lead to project abandonment only to an average extent. Table 3 indicates the extent of the effects of building projects abandonment on construction projects and stakeholders in Nigeria. To that extent, wastage/underutilization of resources (3.85), conflicts (3.65), loss of economic value (3.62), visual effects (3.52) and marginalization of population (3.50) are the effects of poor project management that are experienced in Nigeria to a high extent.

Furthermore, reduced standard of living (3.41), pollution (3.39), decreased biodiversity (3.39), erosion (3.29), unemployment (3.29), landscape modification (3.17), disappointment of the populace (3.14) and difficulty in attracting loans (3.02) are effects of building projects abandonment that are experienced to an average extent in Nigeria.

Table 4 reveals the various ways that were suggested by respondents for preventing the occurrence of building projects abandonment in Nigeria. Thus, adequate planning at inception (4.58) and engaging competent construction professional (4.48) are very highly agreed to by the respondents as ways of reducing construction project abandonment in Nigeria. Also, standard project management procedure (4.29), clear communications (4.15), good development technique (4.06), increased funding (4.00), employment of strong financial base contractors (3.98), production of economic designs (3.97), economic and financial analysis (3.94), risk apportionment (3.91) and unvaried project scope were highly agreed to as ways of reducing abandonment of building projects in the Nigerian construction industry.

In addition, change of technology (3.88), risk review (3.82), root cause analysis (3.79), keep register of uncertainties (3.76), ensure sustained user involvement (3.76), conduct user satisfaction and need survey (3.73), maintaining good morale and right culture (3.71), extension of project schedule (3.68), previously started jobs should not be abandoned for new ideas (3.64), government should reduce inflation (3.52) and increasing pressure on suppliers (3.50) were highly agreed to by the respondents as ways of preventing project abandonment.

The effects of building projects abandonment from the interview conducted are basically:

(1) capital loss, (2) material waste, (3) promotion of illegal activities, (4) adverse effects on the community, (5) aesthetics, (6) decrease in the tempo of economic activities and the proffered solutions in addition to the existing ones are (1) inculcation of operational, strategic, personal, technological, marketing and environmental strategies to prevent financial predicament, (2) mandatory use of duly registered professionals and project management professionals, (3) constant training of organizations' staff involved in capital projects and (4) compulsory adoption of Building Information Modeling (BIM) for construction projects, (5) fairness, (6) accountability on the part of constructor, (7) honesty and integrity, (8) transparency, (9) establishment of National bank for the construction industry so that lending rates can be affordable.

DISCUSSION OF FINDINGS

Many factors could lead to abandonment of building projects but the ones that are related to project management have been highlighted and rated in the order of their importance by the respondents of this study. The respondents believe that to a high extent, lack of good project planning, inadequate cost control, poor resource management, wrong estimation, improper financial analysis, construction not following specifications, poor communication among project participants, improper documentation, improper definition of roles and responsibilities, poor risk management, misunderstanding of user requirements, lack of clear project goals and value, differences between management and client and lack of commitment to project are responsible for abandonment of building projects in Nigeria. These factors are consistent with literatures in the area of lack of good project planning (Akindoyeni, 1989; Olusegun & Michael, 2011; Alfaadel, et al, ND; Lemon, et al, 2002), inadequate cost control, wrong estimation and improper documentation (Olusegun & Michael, 2011; McManus & Wood-Harper, 2007).

The study of Olusegun and Michael (2011) is also consistent with the findings of this study in the area of incompetent project manager and unqualified/experienced consultants while the poor management mentioned by Zairu and Rahinah (ND) is equally in consonance with the findings of this study. The results of Ewusi-Musah and Przasnyski (1991), Munns and Bjeirmi (1996), Liebowitz and Hackney (2002), El-Eman and Koru are in agreement with this study in the area of unsupportive top management, managerial and communication aspect of project management, wrong person as project manager and senior management not sufficiently involved in construction process. The mention of poor stakeholder's communication, poor competencies, poor risk management, lack of management support (McManus & Wood-Harper, 2007; Boehm, 2001), lack of clear project goal and value (Alfaadel, et al, ND), misunderstanding of user requirement and improper definition of roles and responsibilities (Schmidt, et al, 2001) are also findings that are consistent with the finding of this study.

However, the findings of Boehm (2001), Alfaadel, et al (ND), Schmidt, et al (2001), Lemon, et al (2002), El-Eman and Koru (2008) in the area of lack of user involvement, lack of IT management, technology illiteracy, complete and stable requirements, lack of training and critical quality problems with software as factors that can highly lead to project abandonment are

not very consistent with the findings of this study because they are rated only to an average extent as factors that can lead to project abandonment. Factors bothering on information technology, software and users' consent may not be of much weight in the Nigerian construction sector because most project managers appear to have ICT training and the lack of sufficient housing facilities may leave users with a few choices on the decency of accommodation even if they are not pleased with them.

Concerning the effects of project abandonment on construction projects and stakeholders, the findings of this study are very consistent with that of Carrero, et al (2009) in the area of wastage/underutilization of resources, conflicts, loss of economic value, visual impacts and marginalization of population as having high effect on project abandonments in Nigeria. Other effects such as reduced standard of living, pollution, erosion, unemployment and disappointment of the populace only have average effect on construction project abandonment in Nigeria.

Thus, according to this study, just as lack of planning is the most rated factor responsible for construction project abandonment, adequate planning at inception and engagement of competent construction professionals are rated highest as the ways of preventing construction project abandonment in Nigeria. In addition, standard project management procedure, clear communications, good development technique, increased funding, economic designs, risk management, user satisfaction survey and so on were also rated high as solutions to construction project abandonment in Nigeria. However, at the bottom of the list of solutions to construction project abandonment in Nigeria are partnering, holding internal technology fairs, requesting for external assistance, adding more people to projects and reducing scope of projects.

CONCLUSION

The study concludes that apart from the non or poor execution of project managers roles, project management factors such as poor planning, inadequate cost control, poor resource management, wrong estimation, improper documentation and poor communication can also lead to construction project abandonment.

Based on this conclusion, the study recommends that project abandonment should be prevented by planning at inception, cost control, resource management, wrong estimation, financial analysis, constructing according to specifications, competent project manager, communications, proper documentation, risk management, understanding user requirement, clear project goal and value and commitment to project.

REFERENCES

- Akindoyeni A. (1989). The management of abandoned project. *Journal of the Nigerian Institute of Building*, 1 (2) 22-31
- Al-Ahmad, W., Alfagih, K., Khanfar, K. Alsamara, K., Abuleil, S. and Abu-Salem, H. (2009) A taxonomy of an IT project failure: Root causes. *International Management Review*, 5 (1) 93-99
- Alfaadel, F., Alawairdhi, M. and Al-Zyoud, M. (ND) Success and failure of IT projects: A study in Saudi Arabia. *Recent Researches in Applied Computers and Computational Science*, 77-82
- Aluko, O. (2012) Impact of poverty on housing condition in Nigeria: A case study of Mushin Local Government Area of Lagos State. *Journal of African Studies and Development*, 4 (3) 81-89
- Boehm, B. (2001) Project termination doesn't equal project failure. *Software management*, 94-96

- Carrero, R., Malvarez, G., Navas, F. and Tejada, M. (2009). Negative impacts of abandoned urbanization projects in the Spanish coast and its regulation in the law. *Journal of Coastal Research, special issue 56*
- El-Eman, K. and Koru, A.G. (2008) A replicated survey of IT software project failures. *IEEE software*, 84-90
- Ewusi-Mensah, K. and Przasnyski, Z.H. (1991) On information system project abandonment: An exploratory study of organizational practices. *MIS Quarterly*, 67-86
- Henachor, M.E. (2012) Community development project abandonment in Nigeria: causes and effects. *Journal of Education and Practice*, 3 (6) 33-36
- Kaplan, L.A., McKeeman, R. and Zhang, L. (2006) Early warning signs of IT project failure: the dominant dozen. *Information Systems Management*, 31-36
- Keider, S.P. (1984) Why systems development projects fail. *Information Systems Management*, 1 (3) 33-38
- Lemon, W.F., Liebowitz, J., Burn, J. and Hackney, R. (2002) Information system project failure: a comparative study of two countries. *Global Information Management*, 10 (2) 28-39
- McManus, J and Wood-Harper, T. (2007). Understanding the sources of information systems project failure. *Management Services*, 38-43
- Munns, A.K. and Bjeirmi, B.F. (1996) The role of project management in achieving project success. *International Journal of Project Management*, 14 (2) 81-87
- Odusami, K. T., Iyagba, R. O. and Omirin, M. M. (2003). The relationship between project leadership, team composition and project performance in Nigeria. *International Journal of Project Management*, 21 (7), 519-527.
- Olusegun, A.E. and Michael, A.O. (2011). Abandonment of construction projects in Nigeria: causes and Effects. *Journal of Emerging Trends in Economics and Management Sciences*, 2 (2) 142-145
- Schmidt, R., Lyytinen, K., Keil, M. and Cule, P. (2001) Identifying software project risks: an international delphi study. *Management Information Systems*, 17 (4) 5-36
- Yeo, K.T. (2002) Critical failure factors in information system projects. *International Journal of Project Management*, 20, 241-246
- Young, S. (2006) *Using POMDPs for dialog management*. IEEE/ACL workshop on spoken language technology
- Zairu, M. and Rahinah, I. (2008). *Abandoned housing projects in Malaysia: proposal for promoting the BTS concept for Malaysian housing development*. Obtained on 12th June, 2013 from www.academia.edu

APPENDIX**Table 1: Project management factors responsible for abandonment of building projects**

Project management related factors	Mean	Extent of effect	Rank
Lack of good project planning	4.35	High extent	1
Inadequate cost control	4.30	High extent	2
Poor resource management	4.15	High extent	3
Wrong estimation	4.15	High extent	4
Improper financial analysis	3.97	High extent	5
Construction not following specifications	3.88	High extent	6
Incompetent project manager	3.88	High extent	7
Poor communication among project participants	3.76	High extent	8
Improper documentation	3.73	High extent	9
Improper definition of roles and responsibilities	3.65	High extent	10
Poor risk management	3.53	High extent	11
Misunderstanding of user requirement	3.47	High extent	12
Lack of clear project goals and value	3.45	High extent	13
Differences between management and client	3.45	High extent	14
Lack of commitment to project	3.45	High extent	15

5 = Very High Extent (VHE), 4 = High Extent (HE), 3 = Average Extent (AE), 2 = Low Extent (LE), 1 = Very Low Extent (VLE)

Table 2: Effects of project management on construction project

Effects	Mean	Extent of effect	Rank
Wastage/underutilization of resources	3.85	High extent	1
Conflicts	3.65	High extent	2
Loss of economic value	3.62	High extent	3
Visual effects	3.52	High extent	4
Marginalization of population	3.50	High extent	5
Reduced standard of living	3.41	Average extent	6
Pollution	3.39	Average extent	7
Decreased biodiversity	3.39	Average extent	8
Erosion	3.29	Average extent	9
Unemployment	3.29	Average extent	10

5 = Very High Extent (VHE), 4 = High Extent (HE), 3 = Average Extent (AE), 2 = Low Extent (LE), 1 = Very Low Extent (VLE)

Table 3: Ways of preventing project abandonments

Solutions	Mean	Level of agreement	Rank
Adequate planning at inception	4.58	Very high agreement	1
Engage competent construction professional	4.48	Very high agreement	2
Standard project management procedure	4.29	high agreement	3
Clear communications	4.15	high agreement	4
Good development technique	4.06	high agreement	5
Increased funding	4.00	high agreement	6
Strong financial base contractors should be employed	3.98	high agreement	7
Production of economic designs	3.97	high agreement	8
Social, institutional, financial, economic and technical analysis	3.94	high agreement	9
Risk apportionment	3.91	high agreement	10

5 = Very Highly agreed (VHA), 4 = Highly agreed (HA), 3 = Averagely agreed (AA), 2 = Low agreement (LA), 1 = Very Low agreement (VLA)

EVALUATION OF WATER AND TOILET SANITATION INFRASTRUCTURE FOR HEALTHY LEARNING ENVIRONMENT AT PRIMARY SCHOOLS IN LAGOS STATE, NIGERIA

Anyakora, M.I., Osagie, J.U. & Prof. Nubi, T.G

Department of Estate Management, University of Lagos, Nigeria.

anyakoramike@yahoo.com, manyakora@unilag.edu.ng

ABSTRACT

The study is a cross sectional descriptive survey that examined the availability of water and toilet sanitation facilities in public primary schools within Lagos state, Nigeria. The study covered thirteen local government areas (LGAs) out of the twenty LGAs in the state. Objectives of the study were: to ascertain the sources of portable water available in the schools, to determine accessibility and uses of water in the schools, to ascertain availability, types and condition of toilet facilities in the schools, to assess the arrangement made in the schools for regular hand washing hygiene by the pupils, and finally, to discover water and toilet sanitation challenges which may be threatening the learning environment of the schools. Multi – stage randomly sampling technique was used to select 261 schools out of 751 primary schools in the LGAs for the survey. Results of the study reveal that 83.0% of the schools have water supplies within the premises, while 15.3% of the schools neither have water source nor storage tanks. Over half of the schools 58.5% rely on borehole water source, many of the schools in this category do not have ancillary water treatment plant to go with the borehole. Drinking and hand washing water buckets are lacking in 34.1% and 27.5% schools respectively. In addition, the local government education management authorities need to liaise with the state government in the provision of toilets in schools where none presently exists. Also there is the need for both tiers of government to partner in repair and maintenance of toilets in primary school, provide soap and bacteria sanitizers as a means of raising health standards in learning environments in primary schools in the state.

***Keywords:** Healthy learning environment, Water, Sanitation, Primary Schools, and Lagos.*

INTRODUCTION

Interplay of cohesive force seems to exist between water, toilet sanitation, and healthy learning environment in schools. On one hand, availability of water strongly correlates with health and general sanitation condition (UNICEF, 2007; USAID, 2008; Brown, Cairaross, & Ensink, 2013). While on the other hand, healthy learning environment in schools may be difficult to achieve without adequate provision for water and toilet sanitation facilities. UNICEF (2007) reported that adequate provision of water and sanitation facilities in schools have positive impact on child health as it provides safer environment and reduces outbreak of diseases. Lack of abundance of water supply in schools makes it difficult for good hygiene and sanitation practices to be observed (Olukanni, 2013; & Ukpanukpong et al, 2014).

Healthy learning environment is a sub set of school environment, and school environment includes: the classrooms, libraries, technical workshops, laboratories, teachers' quality, school management, teaching methods, peers, in addition to water, sanitation and waste handling facilities. Existing studies have shown that the above listed variables are capable of affecting students' academic achievement (Ajayi, 2001; Oluchukwu, 2000) cited in Omotere (2013). Healthy, safe, and orderly learning environment significantly relate to students' academic

performance (Glassman, 1994; Marsden, 2005, and Williams, Persaud, & Turner, 2008) cited in Omotere (2013).

The study is aware of different aspects of sanitation such as collection, treatment and disposal of wastes, but those are not covered in this investigation. Use of toilet as a healthy means of getting rid of human excreta is the sanitation aspect focused upon in this study.

Sanitation in schools is very important particularly in the context of recent outbreak of Ebola Viral Disease (EVD) in many countries including Nigeria. The implication of the relationship between water availability and sanitation for primary schools in Lagos state is that addressing water problems will help improve sanitation and promote healthy learning environment. Brown, Caimaross, & Ensink, (2013, p.1) argued that “water, sanitation, and hygiene measures remain critically important to global public health, especially among children in low income countries, who are at greatest risk from enteric infections.....”. Ofovwé and Ofili (2007) identified Nigeria among the developing countries with high infant mortality rate due to poor sanitation.

All the issues discussed above and the useful findings documented in previous studies as highlighted above strongly indicate the need for intensive academic evaluation of water and toilet sanitation infrastructures in schools generally particularly the public primary schools. The study is topical and timely as findings will contribute to government efforts to stem down the outbreak of EVD and other infectious diseases among school children and members of the society in general

Aim and Objectives of the Study

The study aims to assess availability of water and sanitation resources of primary schools in Lagos state in order to gather vital information which will be useful in the planning and strengthening of healthy learning environment in Lagos state.

Objectives of the study include: to ascertain the sources of portable water available in the schools, to determine accessibility and uses of water in the schools, to ascertain availability, types and condition of toilet facilities in the schools, to examine the arrangement made in the schools for regular hand washing hygiene by the pupils, and finally, to discover water and toilet sanitation challenges which may be threatening the learning environment of the schools.

Conceptual Framework of the Study

Conceptual model was developed to guide the logic of this study. The issues involved in achieving healthy learning environment in primary schools consist of two major closely interrelated components namely: (1) Availability of water, and (2) Toilet infrastructures. The conceptual framework of this study is weaved around water and toilet sanitation main variables while each of them is measured using five distinct sub variables as illustrated in fig.1 below.

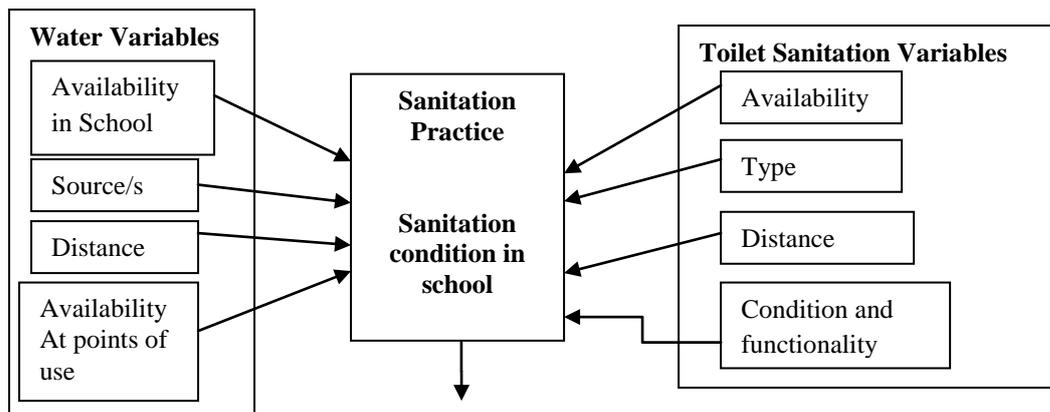


Fig. 1 Conceptual Framework of the Systemic Interplay of Availability of Water in School premises, Source/Type, Distance, Condition and Functionality of Water and Toilet Infrastructures and School Sanitation condition in the formation of Healthy Learning Environment in Primary Schools.
Source: Authors, 2014.

In Figure 1: The conceptual framework perceives the learning environment of a school as a mini ecosystem in which the interactions between human beings (pupils, teachers and other staff), water and toilet infrastructures come together to inform the sanitation practice. While the nature of sanitation practice under the prevailing water and toilet sub variables determine general sanitation condition in the school premises. The quality of the sanitation condition finally becomes classified as healthy or unhealthy learning environment. Basically, the process observed in the conceptual framework appears to follow known argument that regular supply of water and availability of toilet promote sanitation and curtail diseases (UNICEF, 2007; USAID, 2008; Aremu, 2012; and Olukanni, 2013).

METHODS

The study employed cross-sectional survey method in which structured questionnaire instrument was used to elicit water and sanitation information from head teachers of primary schools in Lagos state.

Instrument Design and Data collection

The first section of the data collection instrument was designed to capture respondents' variables, such as: gender; age; position/ rank; highest educational qualification, and tribe.

The next section elicited data on water availability within school premises, an average child's trekking time to water source and back to classroom was used as a proxy for distance; accessibility was measured in terms of availability of water at each of the water usage points

The last segment contained questions designed to gather information on toilet sanitation issues such as: toilet availability; type of toilet; toilet distance was measured using an average child's trekking time to toilet area and back to classroom as a proxy. Data on availability of hand washing water buckets, soap for washing hands around the toilet area and working conditions of the toilets were collected for conditions and functionality investigation.

Sampling Procedure and Sampling Size

The questionnaire was administered to two hundred and sixty one (261) head teachers of primary schools in Lagos state. The teachers were drawn from seven hundred and fifty one (751) primary schools in thirteen (13) local government areas out of the twenty local government areas in the state.

Sample size for the study was determined using the formular, $n = \frac{N}{1 + (N) \times (e^2)}$

Where;

$N = 751$, $e = .05$ (significance level), therefore, $n = 261$.

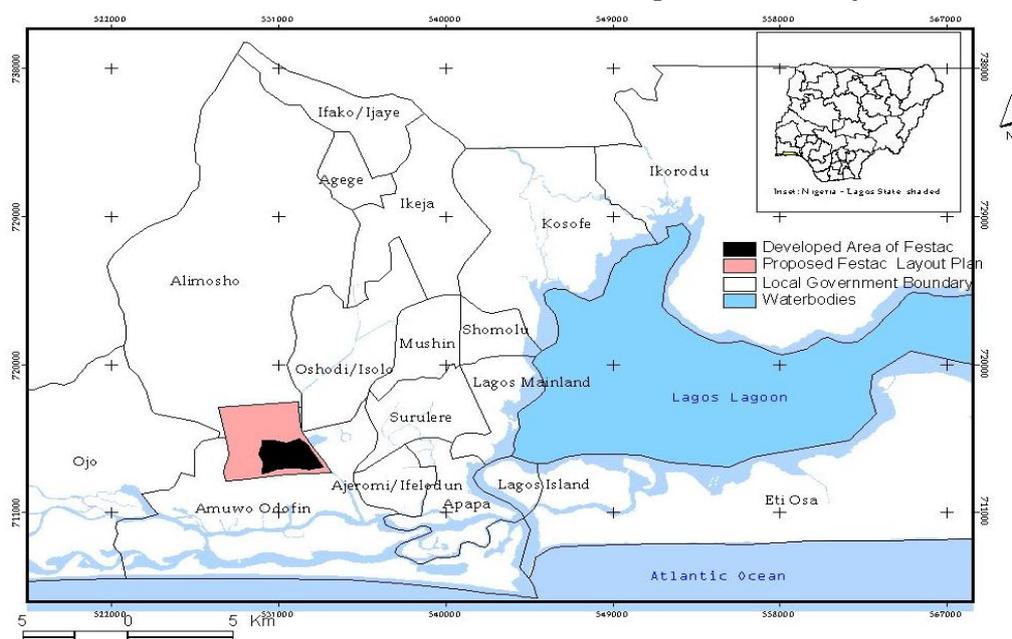
Sampling distribution ratio of 0 .3475 was applied in determining the number of schools to be drawn from each of the thirteen local government areas was calculated from the above equation. Selection of the local governments and schools were based on random sampling technique using blind lucky dip approach.

Detail of the actual number of schools surveyed in each of the local government areas is given in the Sample Size Distribution (**Insert**) **Table 1** below.

Two hundred and sixty one (261) copies of questionnaire set were distributed one to head teacher or the assistant in each of the two hundred and sixty one (261) primary schools pooled in the sample size. Two hundred and fifty seven of them were retrieved out of which two hundred and twenty nine (229) copies representing 87.8% response rate were used for analysis. The remaining twenty eight (28) copies were unusable and rejected for various reasons e.g. incomplete response to mutilation.

The Study Area.

Lagos State is a coastline land mass with southern boundary lying along 180 kilometer distance on Atlantic shorelines in the south western part of Nigeria. It shares northern and eastern boundaries with Ogun State. While Republic of Benin lies on the western side boundary with Lagos state. Lagos became the capital of Nigeria in 1914, it continued to play this administrative function until December 12, 1991 when it lost the position to Abuja Federal Capital Territory.



Source: Adopted from Fasona & Omojola (2004)

Fig.2: Showing Map of Lagos state with Local Government Areas from which Sample schools were drawn.

Lagos State is the second most populous state; with a population figure of 9,013,5341 representing 6.44% of Nigeria's total population and a gender distribution of 51.9% males and 48.1% females. The metropolitan Lagos area (which covers 37% of the Lagos land mass) hosts about 85% of the population, resulting in an average population density of 20,000 persons per sq

km. Population growth is estimated at about 275,000 persons per annum (Roland Igbinoba Real Foundation for Housing and Urban Development, 2009).

RESULTS (Insert Tables 2, 3, 4, & 5)

DISCUSSION

Table 2 above shows that the respondents of this study comprised of 229 head teachers. Each of the respondents attended to the same questionnaire on availability, condition and use of water and toilet infrastructures in the schools respectively. The respondents' characteristics were investigated as means of providing a background to the data used in the study. More females of 189 (82.5%) participated in the study than the other sex. Analysis of the age group showed that a higher percentage (89.9%) of the respondents is in the age bracket of 41 – 60 years. But 122 (52.7%) of the respondents are in the category of assistant head teacher, head teacher, and educational supervisor; while 90 (39.5 %) are in the rank of assistant/deputy/director of schools. Bachelors of education degree is the highest educational possessed by 157 (68.6%) the respondents, other are National Certificate of Education (NCE) 49 (21.4%) and Masters Degree 16 (7.0%) respectively.

On water availability and accessibility within school premises, Table 3 above reveals that 190 (83.0%) respondents have water supply in school. Another group of respondents 35 (15.3%) do not have water in the school. However, water in the schools could come from any of the following sources: shallow well, water tankers, borehole, and public water mains or a combination of them. Borehole is biggest 134 (58.5%), source of water in the schools. It was observed that in most schools water treatment plant for borehole water is either lacking or broken down. As such water from borehole is pumped straight into the storage tanks for circulation to various water use points. Most boreholes in Lagos state are shallow and contained contaminated water. Drinking contaminated water from shallow borehole portends a lot of health risks (Adeyemi, 2011). Nonetheless some pupils still drink the untreated borehole water. Others bring drinking water from home or buy water in sachet called "pure water" in local parlance. Only 21 (9.2%) of the schools depend on public water mains. However, 25 (10.9%) of the schools have more than one source of water supply. Generally, water is within easy reach in schools, in 209 (91.3%) schools trekking time at a child's walking pace to and from water source from the classrooms and offices is between 1 and 4mins. Water is accessible at the water tap stand in 133 (68.1%), and not always accessible for 26 (11.4%), while it was not available at the tap stand in 58 (25.3%) of the schools. Not having water in some of the schools could be complicate control of EVD and other infectious diseases. Larson, and Aiello (2001) revealed that more than 35 new infections have been identified among Asian, African and Latin American children as a result of poor hygiene. In 122 (53.2%) schools water is also accessible for use in washing hand buckets, and in 39 (17.0%) it is not always available, whereas it is not available in 63 (27.5%) of the schools. According to 104 (45.4%) respondents, water is accessible in the drinking water buckets and not always available in 37 (16.2%). Another group of 78 (34.1%) respondents reported that water was not available in drinking water buckets in their schools. Water was also reported in 182 (79.5%) to be accessible in toilets, however, it is not always available in 18 (7.9%) while it is entirely not available in 24 (10.5%) of the schools. According to Moe, and Rheingans (2006) water is necessary for hygiene. The study of the opinion that lack of adequate supply of water renders good hygiene practices difficult in primary schools.

Results on toilet sanitation condition in on Table 5 above shows that majority of the respondents 214 (93.4%) have toilets in their schools, while 12 (5.2%) do not have toilets in their schools. Toilet is an important facility which supports enjoyment of buildings such as

school buildings. UNICEF (2011) strongly proposed availability and adequacy of toilet facilities in schools in terms of numbers and condition. The global standard campaigned by UNICEF is one toilet compartment for every 25 girls, and one toilet compartment for every 50 boys. Among the schools surveyed, 207 (90.4%) respondents confirmed the availability of water cistern type toilet, while pit type of toilet exists in 11 (4.8%) of the schools. According to 213 (93.0%) respondents, toilets are within 4mins of an average child's trekking time to toilet area and back to classroom. In 151 (65.9%) schools, hand washing buckets were available in toilet areas for the pupils' used after defecation, however the same facility was lacking 69 (30.1%). Table 5 clearly shows that soap was not available for hand washing in majority of the schools 120 (52.4%), nonetheless 97 (42.4%) respondents claimed that washing hand soap existing in their schools. National School Health Policy (2006) (NSHP) categorically aims at helping children at school to achieve the maximum health possible to obtain full benefit from their education, but lack of washing hand soap in schools is counterproductive to the laudable objective of NSHP. Handwashing with soap is the single most effective and inexpensive way to prevent diarrheal and other contagious diseases (Global Handwashing Day – Wikipedia). Data on sanitation and functional condition finally shows that 184 (80.3%) are clean and working well, while 13 (5.7%) are not working, locked up although the toilet rooms are clean. Toilets in another 10 (4.4%) schools are dirty and not working.

CONCLUSION AND RECOMMENDATION

On the basis of existing data, the study showed that the state of water and toilet sanitation infrastructures within primary school premises in Lagos state varied considerably in terms of availability, accessibility, type, condition and functionality. The result of the study revealed 15.3% of the schools have no water source of storage tanks. Schools in this category source water from water pushcart vendors, a practice both risky and uneconomical. The affected schools could be connected to city water mains where possible or be provided with borehole, water treatment plant and storage facilities. Among the 58.5% of the schools that use borehole water source, it is important for basic water treatment system to be installed in schools where none exists, while those in state of disrepair should be repaired and put into use.

Drinking, and hand washing water are lacking in 34.1% and 27.5% respectively. In instances, lack of drinking and hand washing water arose due to lack buckets, it is recommended in such instance that schools management authority should arrange a central system of bucket allocation to schools. In addition, the local government education management authorities need to liaise with the state government in the provision of toilets in schools where none presently exists. Also there is the need for both tiers of government to partner in repair and maintenance of toilets in primary school as a means of raising health standards in learning environments in primary schools in the state.

REFERENCES

- Adeyemi, D. (2011). Lagos Water Corporation cautions on proliferation of boreholes. *National Daily Mirror Newspapers*, August, 30.
- Aremu, A.S. (2012). Assessment of sanitation facilities in primary schools within Ilorin, Nigeria. *Journal of Applied Sciences in Environmental Sanitation*, 7 (1): 29 – 33.
- Brown, J.B., Cairaross, S., and Ensink, J.H. (2013). Water, sanitation, hygiene and enteric infections in children. *Arch Dis Child (Online)* June 12: 2013. Doi: 10.1136/archdischild-2011-301528 Available online at <http://adc.bmj.com/content/early/2013/06/11/archdischild-2011-301528.full.html#related-urls>.
- Larson, E. L., and Aiello, A.E. (2001). Hygiene and health: An epidemiologic link? *American Journal of Infection Control (AJIC)*. Vol. 29(4), Pp. 232-238. DOI:10.1067/mic.2001.115679

- Larson, E.L., and Aiello, A.E. (2001). Hygiene and health: an epidemiologic link? *AJIC: American Journal of Infection Control*, 29(4), 232-238. DOI: 10.1067/mic.2001.115679
- Moe, C.L., and Rheingans, R.D. (2006). Global challenges in water, sanitation and health. *Journal of Water and Health* 04 Supplementary. Pp. 41-57. DOI: 10.2166/wh.2005.039.
- Ofofwe, G.E., and Ofili, A.N. (2007). Knowledge, attitude and practice of school health programme among head teachers of primary schools in Egor local government area of Edo state, Nigeria. *Annals of African Medicine*, 6(3), 99 – 103. [Serial online] Available from: <http://www.annalsfrmed.org/text.asp?2007/6/99/5572>
- Olukanni, D.O. (2013). Assessment of wash program in public secondary schools in south – western, Nigeria. *ARPJ Journal of Engineering and Applied Sciences*, 8 (3): 222-228.
- Ukpanukpong, R.U., Lawani, F.O., Utu – Baku, B.A., Fana, N.Y., Uyabeme, R.N., Ajakaye, O.F., Oresegun, O.A., Eze, F.N., and Edoamodu, C.E. (2014). Portable water supply and sanitation practices in selected public primary school pupils in Owerri north local government area, Imo state, Nigeria. *Asian Journal of Plant Science and Research*, 2014, 4(3): 40-45. Available online at www.pelagiaresearchlibrary.com. Accessed on 18/08/2014.
- UNICEF (2007). For every child, health, education, equality, protection: Advance Humanity. Nigeria Country Programme Information Sheet.
- UNICEF. (2011). WASH in schools monitoring package. WHO and UNICEF, 2010. Progress on sanitation and drinking water: 2010 update. Geneva: World Health Organisation and United Nations Children’s Fund.
- UNICEF. (2007). Water, sanitation, and hygiene in Nigeria. Information Sheet
- USAID. (2008). Nigeria water and sanitation profile. U.S. Agency for International Development. Available online at www.usaid.gov. Accessed on 12/03/2014.

Table 1: Sample Size Distribution of the Schools Surveyed in 13 Local Governments in Lagos State.

S/N	Local Government	Number of Schools	Primary	Sample Drawn	Sample Ratio
1.	Kosofe	52		18	34.6%
2.	Surulere	69		24	34.6%
3.	Agege	68		23	34.6%
4.	Oshodi/Isolo	61		21	34.6%
5.	Apapa	26		9	34.6%
6.	Ikeja	35		12	34.6%
7.	Shomolu/Bariga	54		19	34.6%
8.	Ajeromi Ifelodun	76		26	34.6%
9.	Badagry	54		20	34.6%
10.	Ikorodu	71		25	34.6%
11.	Mushin	90		32	34.6%
12.	Mainland	58		20	34.6%
13.	Lagos Island	37		13	34.6%
Total		751		261	

Source: Authors’ Field Survey, 2014.

Table 2: Distribution of Respondents by gender, age, rank/position, highest educational qualification, and tribe (n=229)

<i>Characteristics</i>	<i>Frequency count</i>	<i>Percentage</i>
<u>Gender</u>		
Female	189	82.5%
Male	36	15.7%
Missing	4	1.7%
Total	225	100%
<u>Age group (years)</u>		
20-30	2	.9%
31-40	15	6.6%
41-50	42	18.3 %
51-60	164	71.6%
61 and above	2	.9%
Total	225	98.3%
Missing System	4	1.7%
Total	229	100%
<u>Rank / status</u>		
Asst. Head Teacher	47	20.5%
Head Teacher	71	31%
Edu. Supervisor	4	1.7%
Asst/Deputy/Director of Edu.	90	39.3%
Total	212	92.6%
Missing system	17	7.4%
Total	229	100%
<u>Educational qualification</u>		
NCE	49	21.4%
B.Ed.	157	68.6%
MA / M.Ed.	16	7.0%
Total	222	96.9%
Missing System	7	3.1%
Total	229	100.0%
<u>Tribe / state of origin</u>		
Yoruba	155	67.7%
Ibo	38	16.6%
Edo / Delta	13	5.7%
Others	3	1.3%
Total	209	91.3%
Missing System	20	8.7%
Total	229	100.0%

Source: Authors' Field Survey, 2014.

Table 3: Distribution of Respondents by availability accessibility, sources, and time of walking to water point from the classroom (n=229)

<i>Variables</i>	<i>Frequency count</i>	<i>Percentage</i>
<u>Water Accessibility</u>		
No	35	15.3%
Yes	190	83.0%
Total	225	98.3%
Missing System	4	1.7%
Total	229	100%
<u>Source/s of water</u>		
Shallow Well	11	4.8%
Water Tankers	9	3.9%
Borehole	134	58.5%
Public water mains	21	9.2%
A combination of sources	25	10.9%
Total	200	87.3%
Missing System	29	12.7%
Total	229	100.0%
<u>Trekking time to water point</u>		
0 - 2min trekking.	169	73.8%
3-4mins trekking	40	17.5%
Above 4mins trekking	9	3.9%
Total	218	95.2%
Missing System	11	4.8%
Total	229	100.0%

Source: Authors' Field Survey, 2014.

Table 4: Distribution of Respondents by availability of water for use at: water tap stands, washing hand buckets, drinking water buckets, and toilets (n=229)

<i>Variables</i>	<i>Frequency count</i>	<i>Percentage</i>
<u>Water tap stands</u>		
Not Available	58	25.3%
Not Always Available	26	11.4%
Available	95	41.5%
Always Available	38	16.6%
Total	217	94.8%
System	12	5.2%
Total	229	100.0%
<u>Washing hand buckets</u>		
Not Available	63	27.5%
Not Always Available	39	17.0%
Available	83	36.2%
Always Available	39	17.0%
Total	224	97.8%
System	5	2.2%
Total	229	100.0%
<u>Drinking water buckets</u>		
Not Available	78	34.1%
Not Always Available	37	16.2%
Available	71	31.0%
Always Available	33	14.4%
Total	219	95.6%
System	10	4.4%
Total	229	100.0%
<u>Water in toilets</u>		
Not Available	24	10.5
Not Always Available	18	7.9
Available	111	48.5
Always Available	71	31.0
Total	224	97.8
System	5	2.2
Total	229	100.0

Source: Authors' Field Survey, 2014.

Table 5: Distribution of Respondents by availability of toilets, type, trekking time to toilets, availability of hand washing buckets/basin around the toilet, availability of soap for hand washing after use of toilets, and toilet condition (n=229).

Variables	Frequency count	Percentage
<i>Availability of toilets</i>		
No	12	5.2%
Yes	214	93.4%
Total	226	98.7%
System	3	1.3%
Total	229	100.0%
<i>Type of toilets</i>		
	<i>Frequency count</i>	<i>Percentage</i>
Pit	11	4.8%
Water Cistern	207	90.4%
Total	218	95.2%
System	11	4.8%
Total	229	100.0%
<i>Trekking time to toilets</i>		
	<i>Frequency count</i>	<i>Percentage</i>
0-2mins trekking	195	85.1%
3-4mins trekking	18	7.9%
above 4mins trekking	3	1.3%
Total	216	94.3%
Missing System	13	5.7%
Total	229	100.0%
<i>Availability of Hand washing buckets near toilets</i>		
	<i>Frequency count</i>	<i>Percentage</i>
No	69	30.1%
Yes	151	65.9%
Total	220	96.1%
Missing System	9	3.9%
Total	229	100.0%
<i>Availability of soap for hand washing after use of toilets</i>		
	<i>Frequency count</i>	<i>Percentage</i>
No	120	52.4%
Yes	97	42.4%
Total	217	94.8%
System	12	5.2%
Total	229	100.0%
<i>Sanitation and functional condition of the toilets</i>		
	<i>Frequency count</i>	<i>Percentage</i>
Dirty and Not Working	10	4.4%
Dirty but Working	9	3.9%
Clean, not Working and Locked up	13	5.7%
Clean and Working	184	80.3%
Total	216	94.3%
System	13	5.7%
Total	229	100.0%

Source: Authors' Field Survey, 2014.

BIOCHEMICAL CUES FOR SURVIVAL IN ACUTELY TOXIC CONDITIONS

N.H. Amaeze, A. Onadeko, & A. Braimoh

Ecotoxicology and Conservation Unit, Ecotoxicology Laboratory,
Zoology Department, University of Lagos, Akoka-Yaba, Lagos, Nigeria.
amaezenh@gmail.com

ABSTRACT

When living organisms are exposed to acute concentrations of toxicants, survival may be a function of a combination of genetic, behavioural, biochemical, physiological and sometimes structural adjustments. Relative susceptibility to toxicants is therefore dependent on an organism's survival strategy either innate or acquired. We conducted an assessment of the biochemical responses induced in aquatic animals; *Poecilia reticulata*, *Palaemonetes africanus* and *Clarias gariepinus* exposed to acute concentrations of a petrol additive in a 96 hrs bioassay. *C. gariepinus* was found to be most susceptible to the additive, having the lowest 96 hrs LC₅₀ and surviving individuals of this species equally had the highest levels of lipid peroxidation damage. Although no definite interspecies trend could be inferred from the activities of the anti oxidative stress enzymes, there was evidence of inhibition of catalase, superoxide dismutase and glutathione-s-transferase relative to the control individuals in all three species. Some responses showed significant dose dependent relationships. Overall, the biochemical responses observed in surviving animals showed evidence of relationships with concentrations of exposure, their use for comparing interspecies responses however, must be we caution.

Keywords: Acute toxicity, Tolerance, Oxidative stress, Pollution

INTRODUCTION

Organisms when faced with contaminated environments would naturally modulate their metabolic resources and available energy to enhance their survival (Calow 1991). Biochemical responses of organisms by way of the activities of anti-oxidative stress enzymes and levels of lipid peroxidation damage are currently commonly employed in determining and organisms' stress status and survival mechanisms (Timbrell 2000). Oxidative stress results from the activities of reactive oxygen species (ROS) which includes free radicals and highly reactive forms of oxygen such as hydrogen peroxide, superoxide anion radical, singlet oxygen, hydroxyl radical, nitric oxide and peroxyxynitrate (Collins 2009) which are actual components or breakdown products of diverse toxicants. Although biological systems are naturally equipped with enzymes and other mechanisms to respond to and neutralize the attack of ROS, occasionally such balance are toppled when the onslaught becomes overwhelming for the enzymes to manage (Azqueta et al. 2009). This results in the phenomenon commonly referred to as oxidative stress. Such stress may be linked with the onset of mutations, cancer (Azqueta et al. 2009) or death in acutely toxic systems.

Therefore this study, using aquatic animals (*Poecilia reticulata*, *Palaemonetes africanus* and *Clarias gariepinus*) exposed to acute concentrations of a petrol additive, was designed to investigate the biochemical responses elicited in animals which survive in acutely toxic systems as a way of justifying their relative tolerance and therefore survival.

METHODS

Test animals (Source and Collection): Catfishes (*Clarias gariepinus*) (1.2 ± 0.2cm) were obtained from a local fish farm. Guppies (*Poecilia reticulata*) (2.2 ± 0.5 cm) were collected using scooping nets from ponds in the University of Lagos campus while the brackish water shrimps

(*Palaemonetes africanus*) (1.41 ± 0.38 cm) were collected using sweep nets from the University of Lagos bank of the Lagos lagoon, a relatively unpolluted section. The animals were collected into 10 L plastic cans with perforated lids, three-quarters filled with their habitat water and transported to the laboratory within 1 hour of collection under airy conditions to minimize stress. Laboratory animal cultures, acclimatization and selection of test animals for bioassays: The animals were kept in holding tanks (46cm x 30cm x 40cm) containing their respective habitat water for 5-6 days to allow them acclimatize to laboratory conditions ($28 \pm 20^\circ\text{C}$, R.H $70 \pm 2\%$) before using them in bioassays. They were fed with finely ground Coppens[®] feed during acclimatization. Only animal batches with less than 5% mortality were selected for bioassay.

Petroleum additive used was one which was undergoing pre-approval testing by the Department of Petroleum Resources (DPR), Nigeria. These are routine tests conducted on newly imported products for use in automobiles or the oil industry in Nigeria.

Acute toxicity assay: After a preliminary range finding experiment, bioassay concentrations were selected as follows:

Clarias gariepinus: 0.07, 0.085, 0.1, 0.15, 0.30 ml/L

Poecilia reticulata: 0.6, 0.62, 0.64, 0.68 and 0.70 ml/L

Palaemonetes africanus: 1.0, 1.25, 1.5, 1.75 and 1.85 ml/L

Test concentrations were used to make up their habitat water into 1 L per bioassay tank (17 x 16 x 14 cm). A total of 20 animals per concentration, kept in duplicates of 10 each in clean glass tanks were used for the bioassay. Mortality assessments were carried out after 24, 48, 72 and 96 hrs of exposure. An animal was taken to be dead if it failed to move gently upon prodding with a stainless steel rod within 1-2 min.

Toxicological dose-response data involving quantal response (mortality) were analysed using probit analysis (Finney 1971). The indices of toxicity used were as follows:

LC₅ lethal concentration that will bring 5% mortality of the exposed population

LC₅₀ median lethal concentration that will bring about 50% mortality of the exposed population

LC₉₅ lethal concentration that will bring about 95% mortality of the exposed population

T.F Toxicity factor for relative potency measurements i.e. ratio of 96 hr LC₅₀ of a compound to that of the least toxic compound with the lowest 96 hr LC₅₀ value.

Determination of biochemical responses in test animals: Surviving animals in the highest and lowest concentrations of exposure were randomly selected for biochemical tests. Whole animal homogenates were used for the tests. The samples were assessed for the lipid peroxidation product, malondialdehyde (MDA) using the thiobarbituric acid reaction (TBARS) assay as described by Yagi (1998). Also anti-oxidative stress enzyme activities were assessed using established techniques as follows; superoxide dismutase (SOD) (Sun and Zigma 1978); catalase (CAT) (Aksenes and Naja 1981) glutathione-s-transferase (GST) based on their relatively high activity with 1-Chloro-2,4- dinitrobenzene as a second substrate (Habig and jakoby 1981).

RESULTS AND DISCUSSION

On the bases of 96hr LC₅₀, the petrol additive was found to be 6.10 times and 10.43 times less toxic to *P. reticulata* and *P. africanus* compared to *C. gariepinus*. This implies that the catfish, *C. gariepinus* was least tolerant and most susceptible to the acute toxic action of the additive (Table 1).

Table 1. Relative Acute Toxicity of Petroleum additive (ml/L) acting against *P. reticulata*, *P. africanus* and *C. gariepinus* after 96hrs exposure.

Test Animals	LC ₅	LC ₅₀	LC ₉₅	Probit Equation	Line	S.E	d.f	T.F
<i>Clarias gariepinus</i>	0.005	0.104	2.298	Y= 1.203+ 1.223X		0.874	2	1
<i>Poecilia reticulata</i>	0.494	0.634	0.815	Y= 2.991+15.121X		5.495	3	6.10
<i>Palaemonetes africanus</i>	0.296	1.085	3.970	Y= 0.103+2.919X		2.059	2	10.43

LC are determined at 95% Confidence Limit; S.E- Standard Error; d.f - Degree of freedom; T.F - Toxicity Factor

The results from the biochemical assessments of surviving animals indicates some level of oxidative damage to the cell membranes because the levels of MDA was significantly higher in the surviving animals than in the controls and *C. gariepinus* (*Clarias*), which was least tolerant to the additive had the highest levels as well (Fig. 1). It was also significantly higher in individuals exposed to higher concentrations of the additive, implying some dose dependency. MDA is one of the by products of lipid peroxidation whose level is often used as a measure of oxidative stress (Zielinski and Portner 2000). The relative inhibition of the SOD enzyme activities was least in *C. gariepinus* for both the highest and lowest additive concentrations compared the guppy (*P. reticulata*) and Shrimp (*P. africanus*) (Fig. 2). Expectedly, there was also inhibition in the catalase activities which was however highest in *P. reticulata* and least in *P. africanus* (Fig. 3). Inhibition of CAT is usually linked with that of SOD inhibition because, reduced SOD activities implies lower levels of H₂O₂, the substrate on which CAT acts (Fatima and Ahmad 2005). However, unlike SOD activity, CAT was inhibited more for individuals exposed to higher concentrations of the additive, but there was no significant concentration dependence for both enzymes in *C. gariepinus* based on the concentrations used in this study. The GST activities were also reduced among the three test species for both concentrations of the additive compared to the control individuals (Fig. 4). Otitolaju and Olagoke (2011) also reported inhibition in GST activities in *C. gariepinus* exposed to polycyclic aromatic hydrocarbons. The mechanism for this inhibition is usually explained as resulting from the utilization of microsomal enzyme, GST in catalyzing the conjugation of reduced glutathione with oxidative products (Leaver and George 1998) or the direct inhibition of GST by conjugation products (Srivastava et al. 1999).

The toxicity of the petrol additive examined in this study may be linked with its high concentrations of Cu and Mn among other constituents as indicated in Table 2.

Clearly, the results from the biochemical assay are indicative of some form of oxidative stress in the animals examined given the significantly higher levels of MDA in the exposed animals. The activities of the anti-oxidative stress enzymes examined also showed some active effort at managing the oxidative stress precursors. Their survival therefore may be explained by among other reasons their relative ability to mobilize the respective enzymes to manage the stress pressure from ROS within the additive and/or their break down products.

Apart from MDA levels which were highest in the least tolerant animal, *C. gariepinus*, the findings from the anti-oxidative stress assays could not clearly indicate why the three species examined did not show similar tolerance to the toxicant. This may imply that it is wiser to compare tolerance to toxicants within species than between species as in Otitolaju and Are

(2003) in order to make sound toxicological conclusion. The erratic nature of subtle responses like enzyme activities may also be a factor to consider.

There abounds however from the foregoing, a good opportunity for investigations focused on inter-species tolerance to toxicants.

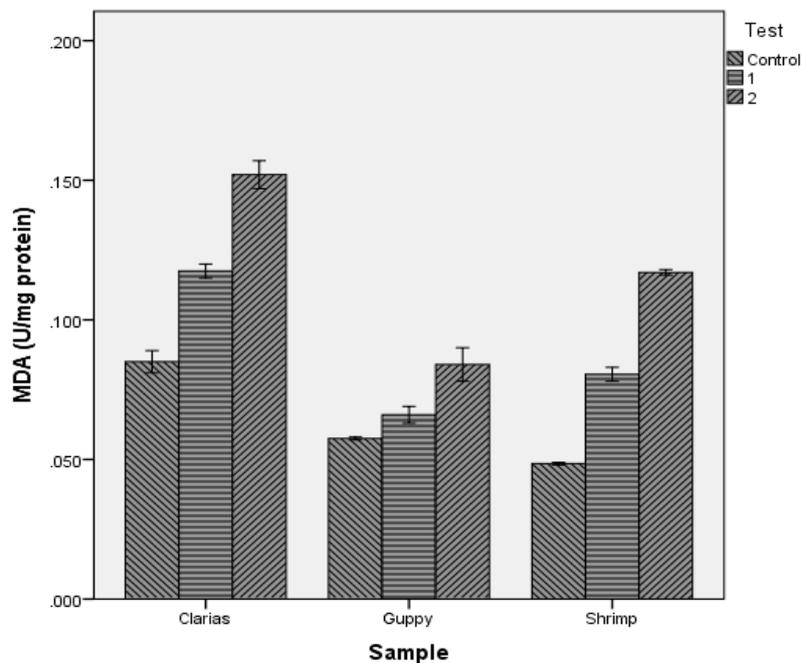


Fig. 1. The levels of MDA in *C. gariepinus* (Clarias), *P. reticulata* (Guppy) and *P. africanus* (Shrimp) after 96hrs exposure to petroleum additive. (Concentrations; **Clarias**: 1=0.3ml/L, 2=0.7ml/L, **Guppy**: 1=0.6ml/L, 2=0.7ml/L, **Shrimp**: 1=1.0ml/L, 2=1.75ml/L)

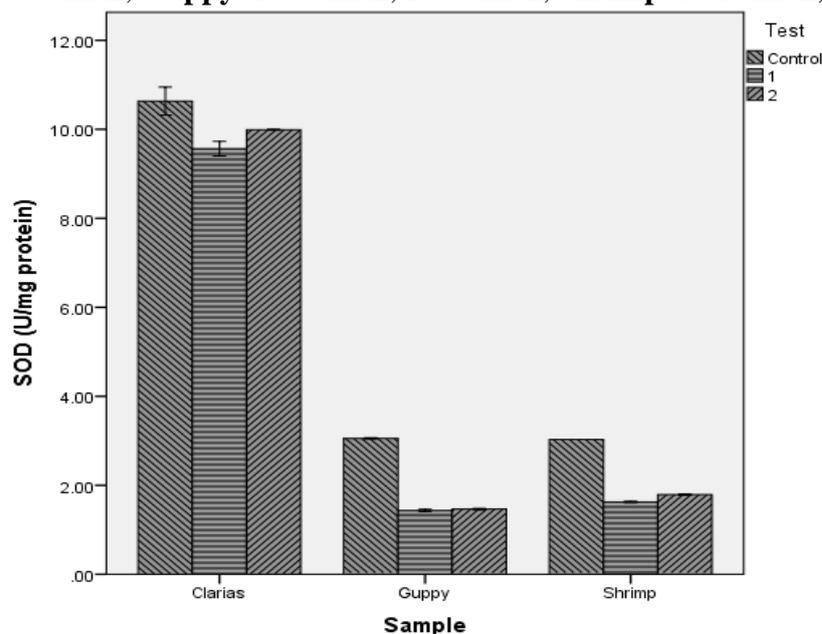


Fig. 2. Inhibition of SOD activity in *Clarias. gariepinus* (Clarias), *Poecilia. reticulata* (Guppy) and *Palaemonete africanus* (shrimp) after 96hrs exposure to petroleum additive (Concentrations; **Clarias**: 1=0.3ml/L, 2=0.7ml/L, **Guppy**: 1=0.6ml/L, 2=0.7ml/L, **Shrimp**: 1=1.0ml/L, 2=1.75ml/L).

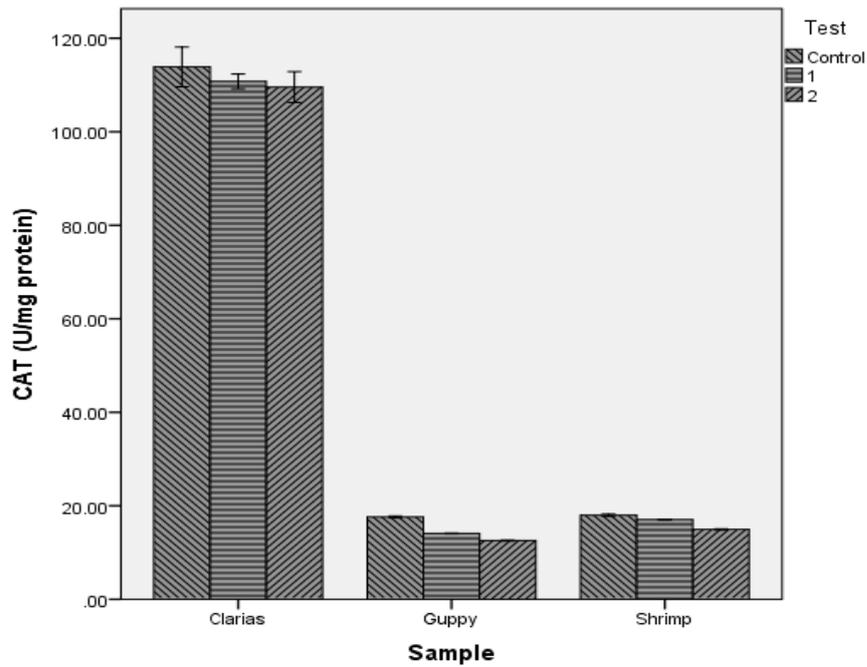


Fig. 3. CAT activity of *C. gariepinus* (Clarias), *P. reticulata* (Guppy) and *P. africanus* (shrimp) after 96hrs exposure to petroleum additive. (Concentrations; **Clarias**: 1=0.3ml/L, 2=0.7ml/L, **Guppy**: 1=0.6ml/L, 2=0.7ml/L, **Shrimp**: 1=1.0ml/L, 2=1.75ml/L)

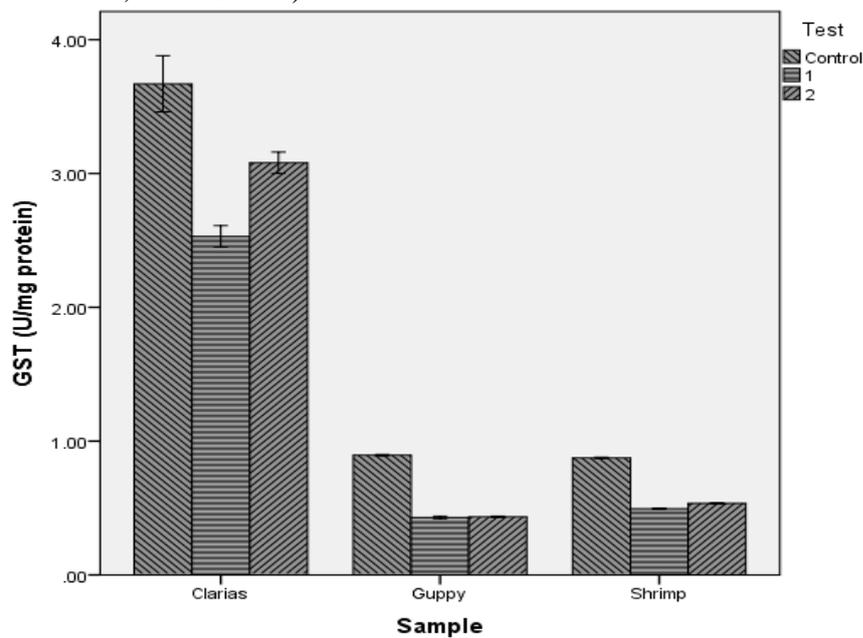


Fig. 4. Activity of GST in *C. gariepinus* (Clarias), *P. reticulata* (Guppy) and *P. africanus* (Shrimps) after 96hrs exposure to petroleum additive (Concentrations; **Clarias**: 1=0.3ml/L, 2=0.7ml/L, **Guppy**: 1=0.6ml/L, 2=0.7ml/L, **Shrimp**: 1=1.0ml/L, 2=1.75ml/L)

Table 2. Physicochemical Characteristics of the Petroleum Additive

Physicochemical Characteristics	Level/Concentration
PH	13.39
Redox Potential (mV)	120.0
Salinity (%)	6.7
Conductivity ($\mu\text{S}/\text{cm}$)	39900
Density (g/dm^3)	1.03
Solubility	Soluble
Total dissolved solids (mg/L)	2000
(Nitrate) NO_3 (mg/L)	0.8
(Cyanide) CN^- (mg/L)	0.08
(SSO_4^{2-}) (mg/L)	ND
Oil and Grease (mg/L)	ND
Phenol (mg/l)	ND
Cd (mg/L)	0.12
Cu (mg/L)	2431.0
Fe (mg/L)	5.26
Mn (mg/L)	33.85
Ni (mg/L)	1.41
Pb (mg/L)	ND
Zn (mg/L)	ND

ND Not detected

REFERENCES

- Aksenses A, Najaa L (1981) Determination of catalase activity in fish. *Comp Biochem Physiol* 69: 893 - 896
- Azqueta A, Shaposhnikov S, Collins AR (2009) DNA oxidation: Investigating its key role in environmental mutagenesis with the comet assay. *Mutation Res* 674: 101 - 108. doi: 10.1016/j.mrgentox.2008.10.013
- Calow P (1991) Physiological costs of combating chemical toxicants: Ecological implications. *Comp Biochem Physiol C* 100: 3 - 6
- Collins AR (2009) Investigating Oxidative DNA damage and its repair using the Comet Assay. *Mutation Res* 681: 24 - 32. doi: 10.1016/j.mrrev.2007.10.002
- Fatima RA, Ahmad M (2005) Certain antioxidant enzymes of *Alium cepa* as biomarkers for detecting the toxic heavy metals in wastewater. *Sci Total Environ* 346: 256 - 273
- Habig WH, Jakoby WB (1981) Biossays for differentiation of glutathione-S-transferases. *Methods Enzymol* 77: 398-405
- Leaver MJ, George SG (1998) A piscine glutathione-S-trnsferase which conjugates the end products of lipid peroxidation. *Mar Environ Res* 46: 71-74
- Otitolaju AA, Olagoke O (2011) Lipid peroxidation and antioxidant defense enzymes in *Clarias gariepinus* as useful biomarkers for monitoring exposure to polycyclic aromatic hydrocarbons. *Environ Monit Assess* 30: 340-346
- Srivastava SK, Hu X, Xia H, Awasthi S, Amin S, Singh SV (1999) Metabolic fate of glutathione conjugate to benzo (a) pyrene- (7R, 8S)-diol (9S, 10R) - epoxide in human liver. *Arch Biochem Biophys* 371: 340-344
- Sun M, Zigma S (1978) An improved spectrophotometric assay of dismutase based on epinephrine antioxidation. *Anal Biochem* 90:81 - 89
- Timbrell J (2000) Toxic Responses to foreign compounds In: Principles of Biochemical Toxicology, 3rd edn. Taylor and Francis, pp. 175-258

- Yagi K (1998) Simple procedure for specific enzyme lipid hydroperoxidases in serum or plasma. *Methods Mol Biol* 108: 107-110
- Zelinski S, Portner H, O (2000) Oxidative stress and antioxidant defense in cephalopods: a function of metabolic rate or age? *Comp Biochem Physiol B* 125: 147-16

MODELLING OF MATERNAL HEALTH CARE USING MULTINOMIAL LOGISTIC REGRESSION

Adewara, Johnson Ademola¹, Ogunniran, Ademola John² & Onyeka-Ubaka, J.N²

¹Distance Learning Institute, University of Lagos

²Mathematics Department University of Lagos

jadewara@unilag.edu.ng

ABSTRACT

Several methods have been adopted to analyze multi-category data but all these methods give unsatisfactory results because of strict assumptions regarding normality, linearity, or homoscedasticity. Multinomial logistic regression is considered as an alternative because it does not assume normality, linearity, or homoscedasticity. Maximum likelihood estimation, probability and fitting of the model were employed in this paper. The result shows that wealth index has a significant impact on the use of public and private health delivery facilities. Educational level, antenatal care, assistance during delivery and place of residence are also an important factor in Maternal Health Care Services. Finally, the educated women, who are wealthy, living in urban areas and who received antenatal care and assistance during delivery are more likely to utilize Maternal Health Care Services (MHCS)

Keywords: Multinomial, Homoscedasticity, Maternal Health, Binomial logit, Maternal morbidity

INTRODUCTION

Maternal healthcare services include the availability of preconception, prenatal, and postnatal care to reduce maternal morbidity and mortality of pregnant women. This involves monitoring and maintaining the progress during and after pregnancy, labour and delivery exercise of a pregnant women. The World Health Organization (WHO) estimated that 587,000 maternal deaths (WHO, 2010) deaths occur in Sub-Saharan Africa, with Nigeria accounting for about 10% of all maternal deaths globally (WHO, 2004; Adam et al., 2005). Modeling of maternal health care data involves much risk which includes creating an awareness, identification, monitoring and reporting, planning and mitigation etc. The maternal healthcare data are categorical dependent variables which include one or more independent variables, which are usually (but not necessarily) continuous, by using probability scores as the predicted values of the dependent variable. The data, either categorical or continuous, can be modeled using multinomial logistic regression. Several methods were used to analyze multi-category data include multinomial probit regression and multiple-group discriminant function analysis all these methods give unsatisfactory results as a result of strict assumptions such as normality, linearity, or homoscedasticity that are difficult to meet. The Multinomial logistic regression is considered to be an alternative analysis because; it does not assume normality, linearity, or homoscedasticity listed above with the exception of multicollinearity (Hosmer & Lemeshow, 2000).

Multinomial logistic regression is a simple extension of binary logistic regression that allows for more than two categories of the dependent or outcome variable. Like binary logistic regression, multinomial logistic regression uses maximum likelihood estimation to evaluate the probability of categorical membership. Multinomial logistic regression does necessitate careful consideration of the sample size and examination for outlying cases. Like other data analysis procedures, initial data analysis should be thorough and include careful univariate, bivariate, and multivariate assessment.

The basic principle of multinomial logistic regression is similar to that of binomial logistic regression, in that it is based on the probability of membership of each category of the dependent variable. The multinomial logistic regression compares the probability of each of $j-1$ categories to a baseline or reference category. In a way we can say that we are fitting $j-1$ separate binary logistic models, where we compare category one to the baseline category, category two to the baseline and so on. In practice software, algorithms allow us to model the comparisons to the baseline simultaneously using maximum likelihood estimation, which is better as doing it sequentially could lead to misestimating the standard errors. This paper seeks to model Maternal Health Care Services (MHCS) data using maximum likelihood estimates, predicted probability and assess the fit and significance of the predictors of the MLR based on a set of explanatory variables. The remainder of the paper is organized as follows: Section 2 Multinomial Logistics Regression Section 3, deals with Methods, *Section 4.0 The results* while section 5.0 the *conclusion*.

LITERATURE REVIEW

Mathematically, a multinomial logit model is a combination of binomial logit models, all compared against a reference alternative. The basic concept of multinomial logistic regression was generalized from binary logistic regression, in that it is based on the probability of membership of each group of the response variable.

The logistic regression model assumes that the categorical response variable has only two values, they are: 1 for success and 0 for failure. The logistic regression model can be extended to situations where the response variable has more than two values, and there is no natural ordering of the categories. Natural ordering can be treated as nominal scale; such data can be analyzed by slightly modified methods used in dichotomous outcomes. This method is called the multinomial logistic regression. Let π_j denote the multinomial probability of an observation falling in the j^{th} category, to find the relationship between this probability and the p explanatory variables, X_1, X_2, \dots, X_p . The multiple logistic regression models is

$$\log \left[\frac{\pi_j(x_i)}{\pi_c(x_i)} \right] = \alpha_{0i} + \beta_{1j}x_{1i} + \beta_{2j}x_{2i} + \dots + \beta_{pj}x_{pi} \quad (1)$$

Where $j = 1, 2, \dots, (c-1)$, $i = 1, 2, \dots, n$. Since all the π^s add to unity, this reduces to

$$[\pi_j(x_i)] = \frac{\exp(\alpha_{0i} + \beta_{1j}x_{1i} + \dots + \beta_{pj}x_{pi})}{c-1 + \sum_{j=1} \exp(\alpha_{0i} + \beta_{1j}x_{1i} + \dots + \beta_{pj}x_{pi})} \quad (2)$$

$j = 1, 2, \dots, (c-1)$, the model parameters are estimated by the ML method.

Multinomial logistic regression (MLR) was applied as an extension of binary logistic regression to model utilization of maternal health care services, where, each response variable level (public health facility and private health facility) is compared to a reference level (home) providing two binary logistic regression models. The general MLR model proposed by Moutinho and Hutcheson (2011) is expressed as:

$$\log \left[\frac{\Pr(Y=j)}{\Pr(Y=j)} \right] = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_kx_k \quad (3)$$

The model of utilizing maternal health care services between the three places of deliveries can therefore be represented using two (i.e., $j-1$) logit models.

$$\log \left[\frac{\Pr(Y=\text{Public health facility})}{\Pr(Y=\text{Home})} \right] = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_kx_k \quad (4)$$

$$\log \left[\frac{\Pr(Y=\text{Private health facility})}{\Pr(Y=\text{Home})} \right] = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_kx_k \quad (5)$$

The intercept β_0 is the value of the response category when all the explanatory variables are equal to zero. $\beta_1, \beta_2, \dots, \beta_k$ are the regression coefficients of x_1, x_2, \dots, x_k . Each of the regression coefficients explains the size of the contribution of risk factor x_i relative to a baseline category. A negative regression coefficient means that the independent variable decreases the probability of the outcome, while a positive regression coefficient means that the variable increases the probability of that outcome (Bhadra 2005, Washington et al. 2011 and Moutinho et al, 2011); a large regression coefficient means that the risk factor strongly favors the probability of that outcome, while a near-zero regression coefficient means that that risk factor has little influence on the probability of that outcome (Petrucci 2009 and Moutinho et al,2011).

We denote the probability that a woman delivered at home (baseline category) by π_0 and this is estimated by $\frac{\Lambda}{\pi_0}$. The probability that a woman delivered at a private health facility is denoted by π_1 and the estimate by $\frac{\Lambda}{\pi_1}$. The probability that a woman delivered at a private health facility is denoted by π_2 and is estimated by $\frac{\Lambda}{\pi_2}$, the response probabilities satisfying $\sum_{j=0}^2 \pi_j=1$, our baseline category is (home=0). From the parameter estimates (Table 4.9), we can calculate these probabilities by two steps:

First, we can calculate $\text{Iog} \left[\frac{\frac{\Lambda}{\pi_1}}{\frac{\Lambda}{\pi_0}} \right]$ and $\text{Iog} \left[\frac{\frac{\Lambda}{\pi_2}}{\frac{\Lambda}{\pi_0}} \right]$ as the response variable has

three categories, which means that there are 2 equations as follows:

$$\text{Let } Y_1 = \text{Iog} \left[\frac{\frac{\Lambda}{\pi_1}}{\frac{\Lambda}{\pi_0}} \right] \text{ and } Y_2 = \text{Iog} \left[\frac{\frac{\Lambda}{\pi_2}}{\frac{\Lambda}{\pi_0}} \right]$$

We now calculate $\frac{\Lambda}{\pi_1}$, $\frac{\Lambda}{\pi_2}$ and $\frac{\Lambda}{\pi_0}$ as follows, where exponential (e) = 2.71828 is the base of the system of natural logarithms:

$$\frac{\Lambda}{\pi_1} = \frac{\exp(y_1)}{1 + \exp(y_1) + \exp(y_2)} \quad (6)$$

$$\frac{\Lambda}{\pi_2} = \frac{\exp(y_2)}{1 + \exp(y_1) + \exp(y_2)} \quad (7)$$

$$\frac{\Lambda}{\pi_0} = \frac{1}{1 + \exp(y_1) + \exp(y_2)} \quad (8)$$

Where the (1) term in each denominator and in the numerator of $\frac{\Lambda}{\pi_0}$ represents $\exp(\hat{\alpha}_0 + \hat{\beta}_0 x)$, for $\hat{\alpha}_0 = \hat{\beta}_0 = 0$, Agresti (2007). $\frac{\Lambda}{\pi_1}$, $\frac{\Lambda}{\pi_2}$ and $\frac{\Lambda}{\pi_0}$ give the various probabilities of any case falling in group. The interpretation of β can be done using the odds ratios concept. Exponenting the regression coefficient β_j for predictor X_j yields the odds ratio (e^{β_j}). Odds ratio is the change in the odds of Y given a unit change in X_j when all other explanatory variables are held constant.

METHODS

The data for this work was extracted from the Nigeria Demographic Health Survey (NDHS) 2008. It is a nationally representative survey of 33,385 women of age 15-49 years. The unit of

analysis for this study is Every Married Woman (EMW) who had at least one live birth in the last five years preceding the survey. The sample size for this study consists of 18028 Every Married Woman (EMW). The SPSS (version 20) software was used to compute the maximum likelihood estimation of the model parameters through the Newton- Raphson's iterative procedure. The variables considered are: X_{10} =Age Group(15-19yrs), X_{11} =Age Group(20-29yrs), X_{12} =Age Group(30-39yrs), X_{20} = Urban Resident, X_{21} =Rural resident X_{30} =No Education, X_{31} =Primary Education, X_{32} =Secondary Education, X_{33} = Higher Education, X_{42} =Traditionalist, X_{50} = Wealth Index (poorest), X_{51} = Wealth Index (poorer), X_{52} = Wealth Index (middle), X_{53} =Wealth Index (richer), X_{60} = Antenatal Care, X_{70} =Assistance During Delivery.

RESULTS

Table 4.1 shows the result of AIC and BIC of the model fitted to judge the closeness. The result shows that our model AIC, BIC and -2log likelihood are very close, therefore, the smaller the value, the better the fit. The Chi-square value was also computed. The result shows that Chi-square statistic is significant: $\chi^2(32) = 10212.429$, $p < .000$, which indicates that the full model is significantly better, or more accurate, than the null model. Also, the deviance test is conducted the result shows that the model was well-fitted and has non-significant deviance.

Table 4.1: Model Fitting Information

Model	Model Fitting Criteria			Likelihood Ratio Tests		
	AIC	BIC	-2Log Likelihood	Chi-Square	Df	Sig.
Intercept Only	13231.966	13247.536	13227.966			
Final	3083.537	3348.232	3015.537	10212.429	32	.000

Table4. 2: Goodness-of-Fit

	Chi-Square	Df	Sig.
Pearson	2343.892	1702	.000
Deviance	1338.045	1702	1.000

Table 4.3 is the Nagelkerke's measure of the strength of relationship between the dependent variable and the explanatory variables. The result shows a moderately (52.9%) strong relationship between the predictors and the prediction

Table 4.3:Pseudo R-Square Square

Cox and Snell	.437
Nagelkerke	.529
McFadden	.328

Table 4.4 is the likelihood ratio test of the model which shows that the variables age, religion, wealth index, antenatal care, assistance during delivery, type of place of residence and highest level of educational. The result shows that all the variables mentioned above are all significant contributors to explaining differences in place of delivery. The values of the -2log likelihood of reduced model obtained for the variables are such as: antenatal care (4155.519), assistance during delivery (3763.809), wealth index (3665.984), educational level (3417.204), religion (3257.855), place of residence (3055.744) and age (3044.265). The chi-square statistic obtained showed that the model is significance.

The Parameters of the model that were estimated are shown in Table 5.0

The models for the parameter estimated are:

$$\text{Iog} \left[\frac{\text{Pr}(\text{Public health facility})}{\text{Pr}(\text{Home})} \right] = -3.077 - 0.097X_{12} + 0.188X_{20} - 1.822X_{30} - 1.383X_{31} - 0.866X_{32} - 1.666X_{42} - 1.909X_{50} - 1.494X_{51} - 1.095X_{52} - 0.539X_{53} + 2.113X_{60} + 3.869X_{70} \quad (9)$$

This implies that a woman of the age group (15-19yrs) has a decrease probability of delivering at a public health facility rather than women between the ages (40-49yrs). A woman who is an urban resident has an increase probability of delivering at a public health facility than women in the rural area. A woman with no educational background primary/secondary but uses public health facility has a low probability health maternal care, compared to a woman with higher education. A woman within the wealth index (poorest/poorer/) has a decrease probability of delivering at a public health facility than a woman with the wealth index (richest). A woman who receives antenatal care has an increases probability of delivering at a public health facility than those who do not receive.

$$\text{Iog} \left[\frac{\text{Pr}(\text{Private health facility})}{\text{Pr}(\text{Home})} \right] = -1.774 - 0.398X_{10} - 0.258X_{11} - 0.425X_{20} - 1.984X_{30} - 1.017X_{31} - 0.590X_{32} - 1.622X_{41} - 2.283X_{50} - 2.012X_{51} - 1.613X_{52} - 1.00X_{53} + 1.955X_{60} + 2.487X_{70} \quad (10)$$

The result of the model above states that woman within the age group of (15-19yrs) has a decrease probability of delivering at a private health facility rather than a woman between (40-49yrs). A woman who is an urban resident has an increase probability of delivering at a private health facility than a woman in the rural area. The probability of a woman who delivered at a private health facility with no education/primary/secondary is lower compared to a woman with a higher education. A woman with poorest/poorer wealth index has a decreased probability of

Table 4.4: Likelihood Ratio Tests

Effect	Model Fitting Criteria			Likelihood Ratio Tests		
	AIC of Reduced Model	BIC of Reduced Model	-2 Log Likelihood of Reduced Model	Chi-Square	Df	Sig.
Intercept	3083.537	3348.232	3015.537 ^a	.000	0	.
Age	3100.265	3318.249	3044.265	28.728	6	.000
Religion	3313.855	3531.839	3257.855	242.318	6	.000
Wealth index	3717.984	3920.398	3665.984	650.447	8	.000
Antenatal care	4219.519	4468.644	4155.519	1139.983	2	.000
Assistance	3827.809	4076.933	3763.809	748.272	2	.000
Residence	3119.744	3368.869	3055.744	40.207	2	.000
Educational level	3473.204	3691.189	3417.204	401.668	6	.000

delivering at a private health facility than a woman with rich wealth index. Also, a woman with good antenatal care has an increase probability of delivering at a private health facility than a woman who does not. Finally, a woman with assistance during delivery has increase probability of delivering at a private health facility than those who do not.

Predictions from the MLR Model

Predicted probability of utilizing MHCS through delivery at a public health facility and private health is calculated using variables that were consistent. The result showed that there is a strong association in the MLR model. The following variables are used: antenatal care, place of residence, wealth-index, educational level and assistance during delivery. The data was modeled using predicted model of equation 11 and 12.

$$\text{Iog} \left[\frac{\text{Pr}(\text{Public health facility})}{\text{Pr}(\text{Home})} \right] = -3.979 + 0.155X_{20} - 1.931X_{30} - 1.416X_{31} - 0.900X_{32} - 1.904X_{50} - 1.495X_{51} - 1.088X_{52} - 0.545X_{53} + 2.136X_{60} + 3.881X_{70} \quad (11)$$

$$\text{Iog} \left[\frac{\text{Pr}(\text{Private health facility})}{\text{Pr}(\text{Home})} \right] = -2.980 + 0.301X_{20} - 2.581X_{30} - 1.209X_{31} - 0.682X_{32} - 2.184X_{50} - 1.931X_{51} - 1.532X_{52} - 0.996X_{53} + 2.022X_{60} + 2.715X_{70} \quad (12)$$

Table 4.5: Predicted probabilities for Some Selected Cases

					Probabilities of Utilizing MHCS		
Place of Residence	Educational Level	Wealth Index	Antenatal Care	Assistance During Delivery	Public Health Facility	Private Health Facility	Home
Rural	No Education	Poorest	Yes	Yes	0.14	0.04	0.82
Rural	No Education	Poorest	No	No	0.00	0.00	1.00
Urban	Primary	Richest	Yes	Yes	0.39	0.42	0.18
Urban	Higher	Richer	Yes	Yes	0.57	0.32	0.11

A lot of information can be gained from the predicted probabilities presented in Table 4.5. For example, Women who are Rural Residents are more likely to deliver at home with probabilities (1.00, 0.82) compared to Urban Residents. The probabilities show that women who are educated are more likely to deliver at both public and private health facilities with probabilities 0.57, 0.39, 0.42 and 0.32 respectively compared to the uneducated ones. The effect of wealth index is particularly noticeable when comparing delivery at public and private health facilities.

CONCLUSION

The model was able to reveal that wealth index has a significant impact particularly for the comparison between delivery at public and private health facilities. Educational level, antenatal care, assistance during delivery and place of residence are also an important factor in Maternal Health Care Services. This assists in distinguishing between places of delivery and the wealth index of a woman. Finally, the educated women, who are wealthy, living in urban areas and who received antenatal care and assistance during delivery are more likely to utilize MHCS

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REFERENCES

Adam T, Lim S, Melita S, Bhutta ZA, Fostad D (2005). Cost effectiveness analysis of strategies for maternal and neonatal health in developing countries Br. Med. J. 331:1107.

- Agresti, A. (2007). *An Introduction to Categorical Data Analysis*. Second Edition. John Wiley & Sons, Inc. New York.
- Hosmer, D.W. and Lemeshow, S. (2000) **Applied logistic regression**. US, Wiley-Interscience,
- Menard, S.W. (2002). *Applied Logistic Regression Analysis*. Second Edition. Sage Publications, Inc. USA.
- Moutinho, L. A. and Hutcheson, G. D. (2011). *Dictionary of Quantitative Methods in Management*. Sage Publications, Inc. USA.
- Peng, C. J. and Nichols, R. N. (2003). Using Multinomial Logistic Models to Predict Adolescent Behavioural Risk. *Journal of Modern Applied Statistical Methods*, Vol. 2, Iss. 1, Article 16.
- Bhadra, D. (2005). Choice of Aircraft Fleets in the U.S Domestic Scheduled Air Transportation System: Findings from a Multinomial Logit Analysis. *Journal of the Transportation Research Forum* 44(3), 143-162.
- Petrucci, C. J. (2009). A Primer for Social Worker Researchers on How to Conduct a Multinomial Logistic Regression. *Journal of Social Service Research*, 35(2), 193-205.
- Washington, S.P., Karlaftis, M. G. and Mannering, F.L. (2011). *Logistic Regression, Discrete Outcome Models and Ordered Probability Models: Statistical and Econometric Methods for Transportation Data Analysis*. Chapman and Hall/CRC, 303-359.
- World Health Organization (WHO) (2004). Making pregnancy safer: The critical role of the skilled attendant. A joint statement by WHO, KM and FIGO
<http://wholibdoc.who.int/publication/2004/9241591692>
- World Health Organization (WHO) (2010), *maternal health* [Online] Available from:
http://www.who.int/topics/maternal_health/en/ Accessed: (May 10, 2010).

GENOTOXIC AND TOXICOLOGICAL EFFECTS OF DICHLORVOS (DDVP) ON MICE: *Mus musculus*

Ajagbe E.F¹, Aneyo I.A.¹ & Odeigah P.G.C.²

¹Department of Zoology, Faculty of Science, University Of Lagos, Akoka, Lagos, Nigeria.

²Department of Cell Biology and Genetics, Faculty of Science, University Of Lagos, Akoka, Lagos. sadeajagbe@yahoo.com

ABSTRACT

Dichlorvos as a pesticide is found in the environment through release by humans in concentration known to be toxic to aquatic life and mammalian organisms. Mice, *Mus musculus*, were exposed to various concentrations of dichlorvos 90,100,110 and 120µg/L per body weight. The pesticide was introduced into the mice feed for 28days. The need to consider a greater range of factors contributing to potential health effects of combined exposures makes the risk assessment process more complex compared to the assessment of single chemicals. There were higher sperm head abnormalities in all the experimental groups as compared with the untreated control. Statistical analysis of sperm head abnormality score showed that there was a significant ($p < 0.05$) difference in occurrence of sperm head abnormalities in test animals. The abnormalities observed were: knobbed hook, pin-head and banana shaped sperm head. The occurrence of the sperm head abnormalities was also found to be dose dependent. The implication of the observed increase occurrence of sperm head abnormalities on the reproductive health of humans is of great concerns to the environmentalist and toxicologists.

Keywords: Chemical Toxicity, Inhalation Toxicity, Sperm deformity, Organophosphate pesticides

INTRODUCTION

Humans are subjected to a range of chemical exposures from the environment. Chemicals in air, water, soil and food, occupational exposures and lifestyle factors, all contribute to a complex exposure situation in our daily life. It has long been known that toxicity can be modified by simultaneous or sequential exposure to multiple agents in the environment. For some combined or mixed exposures the health effects may increase more than what would be expected from simply adding the effects of the individual components, therefore there is a concern that several less studied complex exposures may have a large impact on our health as a result of combined or mixed effects. Thorpe *et al.*, (1972).

Evaluation of genetic toxicity is an important component of the safety assessment of chemicals, including pharmaceuticals, agricultural chemicals, food additives and industrial chemicals. Up to the present time, genotoxicity has been regulated mainly on the basis of qualitative outcomes of hazard identification assays, i.e. decisions are often based on classification as positive or negative for genotoxic potential. (Thybaud *et al.*, 2007)

Dichlorvos is a synthetic organic chemical used as an insecticide. Dichlorvos does not occur naturally in the environment, but is manufactured by industry. Dichlorvos is sold under many trade names including Vapona[®], Atgard[®], Nuvan[®], and Task[®]. Dichlorvos may also be called DDVP, which is an abbreviation for its full chemical name. As a pesticide, dichlorvos is commonly referred to as DDVP, which is an abbreviation for 2,2-dichlorovinyl dimethyl phosphate (Farm Chemical Handbook 1984).

Like other insecticides in this class, dichlorvos is not only extremely toxic to insects, but also can be toxic to humans if high enough doses are received. After acute exposure to high concentrations of dichlorvos by any route, signs such as: nausea, vomiting, diarrhea, bronchial

secretion, dyspnea, increased salivation, and urinary frequency and incontinence can result from over stimulation of the parasympathetic autonomic nervous system. (Hays *et al.*, 2007).

Dichlorvos is mutagenic in a number of in vivo test systems. There is also evidence in studies on rats and mice that dichlorvos is carcinogenic in these species. Based on this evidence, the EPA has classified dichlorvos as a probable human carcinogen (EPA 2003).

Exposure to dichlorvos occurs by the inhalation of sprays or vapors from impregnated resins, by skin contact, or orally as a residue in food (WHO/FAO, 1993).

The most likely routes of exposure for people living near hazardous waste sites would be by breathing dichlorvos-contaminated air, drinking dichlorvos-contaminated water, or skin contact with dichlorvos-contaminated soil. Monitoring of the air, drinking water, and soil levels of dichlorvos at these sites is necessary to predict the possibility of adverse health effects. Savolainen (2001).

Dichlorvos is rapidly absorbed and degraded in all mammalian species (FAO/WHO, 1993). Dichlorvos metabolism after different routes of administration in man, rat, mouse, swine and hamsters has been reported to be rapid, with similar metabolites in all species (WHO/FAO, 1993). Hutson *et al.*, 1972a; Page *et al.*, 1972).

Air samples from commercial insecticide storage facilities and vehicles used by applicators were analyzed for dichlorvos residues. Storage facilities had much higher level of dichlorvos in air (0.53ppb) compared to office rooms (0.04 ppb). Vehicles that were used to store compressed air spraying equipment and the insecticide had a mean air levels of 0.94 ppb dichlorvos (Wright and Leidy, 1980).

All these studies indicate that occupational exposure to dichlorvos was frequent and detectable among pesticide applicators. As mentioned earlier, dichlorvos ranked among the three most frequently applied pesticides by pest control operators in 1974 (ATSDR, 1997).

Studies have linked pesticide exposure with decreased sperm quality, a higher sperm density with lower pesticide exposure (Swan and Kruse, 2003). Hormone disruption is considered a possible contributor to low sperm count and dozen of pesticides are known or suspected hormone disrupters (Wyrobek and Bruce 1975).

As there was a few literature available on the toxicological and genotoxicity testing of Dichlorvos, the present study was considered.

METHODS

Test Animals/Animal Husbandry

Male and female adult mice, *Mus musculus*, which served as the bioassay organisms were obtained from the Department of Zoology (Botanical Garden), University Of Lagos The mice were fed with 40 g commercially available sterilized feed per day and water ad libitum. Only healthy mice 8–10wks old weighing around 18-26 g were selected for experimentation. The mice were housed in suspended mesh-bottom edge cages with tins attached underneath that contained holes and which were covered with gauze and net in order to prevent the mice from escaping, for at least 14 days to acclimatize to laboratory conditions ($29 \pm 2^\circ\text{C}$ and Relative Humidity- $70 \pm 2\%$) before commencement of bioassay.

Ethics

The experiment was carried out by utilization of whole and live mice. However, aiming for the protection and welfare of animals, studies were conducted in accordance with the Nigerian and University of Lagos Ethics Committee guidelines for experiment with whole animals. The mice belonging to either of groups were sacrificed in compliance with the ethical regulations formulated by the Ethical Committee of the University.

Exposure cages (L×B×H 530 cm by 350 cm by 230 cm) with well covered roofs, with tins attached underneath that contained holes and which were covered with gauze and net in order to prevent the mice from escaping while being utilized for the assay. The exposure cages were kept in the laboratory at room temperature, with a specific concentration per body weight per cage for treatment at specified time.

The mean lethal dose LD₅₀ of Dichlorvos (DDVP), that is; oral LD₅₀ value for DDVP per body weight was determined before carrying out this study. DDVP was administered into the mice feed according to body weight of different group of mice utilized for the study. The various concentrations considered per body weight are; 90,100,110 and 120µg/L.

Inhalation Exposure

This study was conducted in exposure chambers into which air containing dichlorvos was introduced. In this case tins attached underneath that contained holes and which were covered with gauze and net in order to prevent the mice from escaping served as the exposure chamber. In this study therefore, food and water were in the chambers during the exposure. An air concentration of dichlorvos was expressed in units of either µg/L. Since inhalation exposure to dichlorvos is more likely to be in vapor phase, air concentrations are also presented as the equivalent parts per million (ppm) (Hayes 1982).

Assessment of Sperm Morphology

Sperm head abnormality assay

Albino male mice sperm abnormality was tested according to the method of Wyrobek *et al.*, (1983). The treated and untreated control male mice were sacrificed on day 7, day 14 and day 28, by cervical dislocation and surgically removed sperm was stripped from the vasa deferentia with a pair of iridectomy scissors, a drop of dense spermatozoa was then picked up quickly with the tips of the tweezers and put into 0.5 ml normal saline after anesthetization. The epididymis were excised and minced with fine scissors in physiological saline in a petri dish. A fraction of each suspension was mixed with 1% Eosin Y solution (10:1) (v/v) for 30 minutes. Air dried smears were prepared after the sperm has dispersed. Smears were made on clean, grease- free slides after staining the cells with a mixture of normal saline (9:1) (v/v) for 45 minutes. The slides were air-dried and coded for subsequent examination under microscope and different abnormalities were recorded. All scoring of morphological types of sperm were done from coded slides without prior knowledge of a particular genotype.

Cytological evaluation for sperm-head abnormalities was carried out using a binocular microscope at 1000x under oil immersion. Differences between the control and experimental groups were analyzed by a One Way Analysis of Variance (ANOVA).

RESULTS

Body Weight Effects

The body weight of mice exposed to atmospheres containing 5 mg dichlorvos/m³ (0.6 ppm) and the untreated control mice were also determined. The body weight of the animals decreased as the exposure days was increasing, which could be attributed to symptoms of lethal doses which include; growth retardation, weight loss, lack of appetite and visual impairment (ranging from red spots in the eyes to conjunctivas and complete blindness).

Analysis of sperm head abnormalities were made after 28 days of exposure to Dichlorvos.

The results of sperm head abnormality counts showed that there was a high level of abnormality in the sperm head of mice exposed to Dichlorvos.

Statistical analysis; Analysis of variance (ANOVA) of the mean values of occurrence of sperm head abnormality showed that there was a significant ($p < 0.05$) difference in occurrence of sperm head abnormality in test animals based on the various concentrations used for the assay. The abnormalities observed were sperm head with knobbed hook (D), pin-head (I) and banana-shaped head (J) according to (Fig. 1) which was used as the key for identification of various abnormalities.

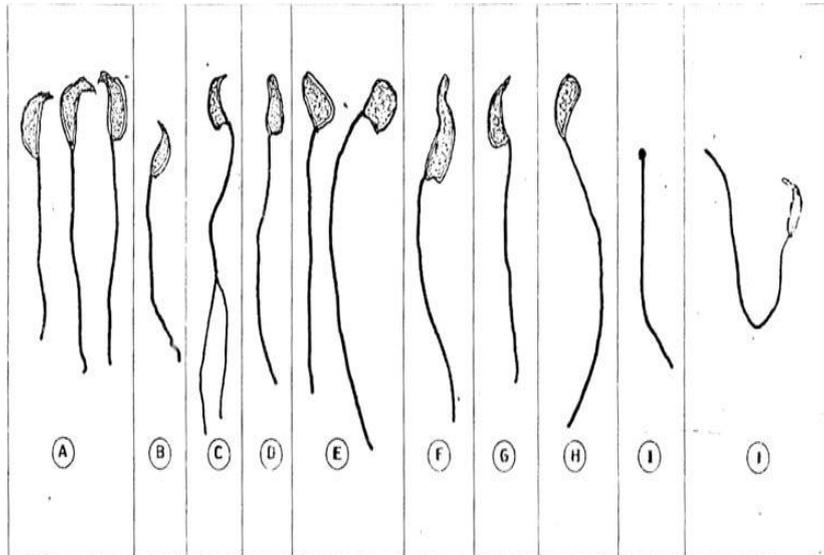


Fig. 1: Observed shapes of normal and abnormal heads. (a) normal sperm (b) sperm with no hook (c) two tails (d) knobbed hook (e) amorphous head (f) mean bent hook (g) hook at wrong angle (i) pin-head (j) banana-shaped head after Otubanjo and Mosuro (2001)

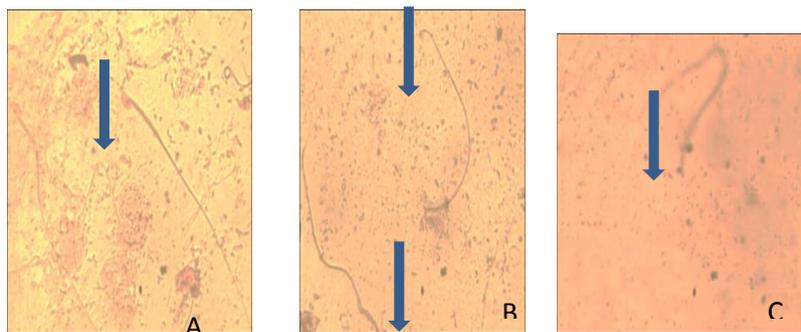
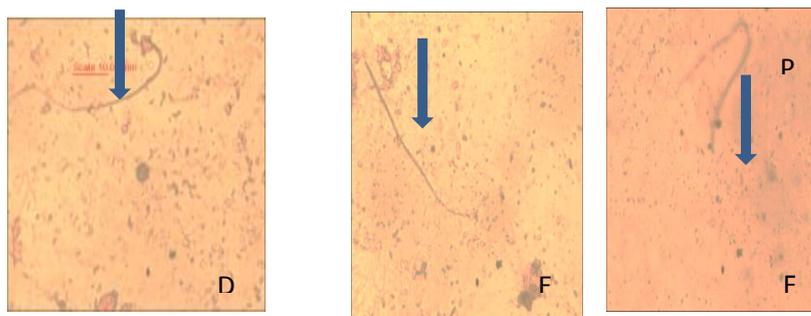


Fig. 1: (A-C) showing various abnormal sperm-heads



F

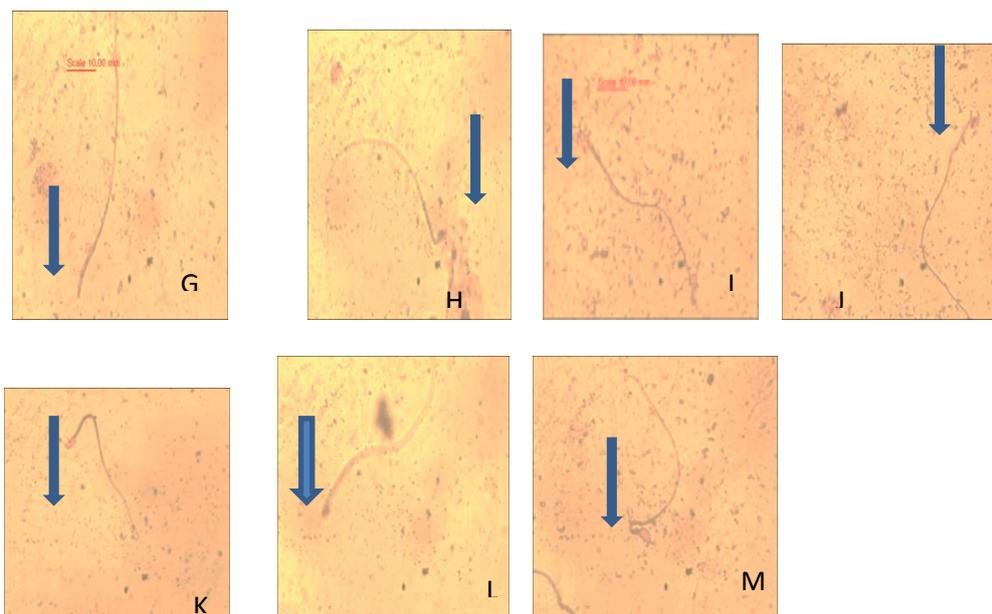


Fig. 2: (D-M) showing various abnormal sperm-heads

Table 1: Percentage Mean Sperm Morphology of Mice Exposed to Different Concentration of Dichlorvos

	Concentration				
Parameter	90 µg/L	100 µg/L	110 µg/L	120 µg/L	Control
Day 7	101.1±3.71abc	84.00±2.82abc	94.00±22.64ab	94.00±5.65abc	372.0±7.07
Day 14	88.50±7.77abc	81.50±12.02ab	98.50±0.70abc	96.00±12.73ab	394.0±7.07
Day 28	199.0±5.65abc	88.50±6.36abc	87.00±4.24ab	252.0±28.35abc	348.0±7.07

Parameters on each row with different suffixes are significantly different at $P < 0.05$.

Body Movement

Animal behavior was determined through body movement during days 7, 14 and 28 of the bioassay. All body movement which include- raising of head; mouth, limbs and tail were noted and counted. Two animals including replicates were taken per concentration for body movement against the untreated control.

Table 2: Mean Body Movement of Mice Exposed to Different Concentration of Dichlorvos

	Concentration				
Parameter	90 µg/L	100 µg/L	110 µg/L	120 µg/L	Control
Day 7	31.50±7.78ab	31.50±7.77ab	24.00±1.44ab	31.00±8.48ab	61.50±3.53
Day 14	29.50±0.70abc	27.50±3.53ab	28.50±2.12ab	28.50±2.12ab	61.50±3.53
Day 28	25.00±2.82ab	23.00±1.41ab	25.00±1.44ab	27.00±2.82a	61.50±3.53

Parameters on each row with different suffixes are significantly different at $P < 0.05$.

DISCUSSION

The toxicological and genotoxic effects of DDVP were studied on albino mice. At first LD_{50} values for DDVP in mice were calculated. For this purpose, different concentrations of DDVP were used, that is; 183,161,130, and µg/g BW. The result was 100% mortality at high concentration and it decreased with low doses. The LD_{50} value came to be 106.00µg/g BW.

Some observations like: restlessness, secretions in eyes and weakness were found in the mice. These are typical signs of intoxication of the insecticide.

This study is in agreement with the reports of USDHHS1993; USEPA 1999; that acute inhalation in humans and other animals such as tightness of chest, pupil constriction, blurred vision, and headaches. Acute oral exposure results in nausea, vomiting, cramps, and diarrhea.

This study supports the findings of Noble 2002, on exposure of Kibbutz residents' to organophosphate pesticides, during spray drift and found different symptoms of nausea, abdominal pain, headache, cough, throat irritation, eye irritation, diarrhea, unusual tiredness, dizziness and skin haemorrhages

Studies by Ryhanen *et al.*, 1984; and Kozłowska *et al.*, 1988 show that due to high vapour pressure, DDVP is a great danger to the occupationally exposed workers indulged in DDVP formulation.

Several reasons have been put forward to explain the increase in the frequency of occurrence of sperm head abnormalities in organisms exposed to some chemicals. Damage to the sperm cell is said to occur either by physiological, cytotoxic or genetic mechanism. Odeigah (1997) reported that exposure to the chemicals could produce pituitary hypothalamic or sex hormonal effects which in turn could affect spermatogenesis or exposure could cause abnormalities in seminal fluid resulting in functional or structural impairment of sperm.

The development of abnormal sperm head morphology and variations in DNA content of spermatozoa are often genetically controlled. The occurrence of sperm head abnormalities have also been attributed to the chromosomal aberrations that occur during the packaging of genetic material in the sperm head or occurrence of point mutation in testicular DNA (Bruce and Heddle 1979). It may also arise as a consequence of naturally occurring level of mistakes in the spermatozoon differentiating process during spermatogenesis (Bakare *et al.*, 2005).

In the present study, a significantly increased frequency of sperm head abnormalities was observed in the spermatozoa of treated mice which is in accordance with the study conducted by Wyrobek and Bruce 1978.

According to Savolainen (2001), Bruce and Heddle (1979) there are two mechanisms by which chemicals might indirectly affect sperm cell function and morphology: firstly, exposure to chemicals could produce pituitary-hypothalamic or sex hormonal effects which in turn could affect spermatogenesis and secondly exposure could cause abnormalities in seminal fluid, resulting in functional or structural impairment of sperm.

The scoring of sperm head abnormalities in the mice is technically easy but the interpretation of results can be confounded by a number of factors such as variable periods of treatment prior to sample collection, frequency of sampling and method of collection or preparation of the sperm smear. Multiple samples from the sample individual may show wide range in sperm abnormalities even in the control mice. In spite of this variability there are many clear examples of chemically induced increases in sperm abnormalities, which is in agreement with the study of Odeigah (1997).

Populations in the vicinity of hazardous waste sites may be exposed to dichlorvos for brief periods. Exposure would most likely occur by the inhalation route, but dermal exposure by contact with contaminated soil is also possible. Cases of accidental and intentional poisonings in humans (Hayes 1982) indicate that the central and peripheral nervous systems are the major target organs for dichlorvos toxicity by the oral and dermal routes. It can be inferred from animal

studies that this is true for inhalation exposure as well (Durham *et al.*, 1957). This study however, is in support with this view.

The finding from this study is in agreement with the studies of Gallo and Lawryk, 1991; Swan and Kruse, 2003, that linked pesticides exposure with decreased sperm quality, a higher sperm density with lower pesticide exposure. Hormone disruption is considered a possible contributor to low sperm count and dozen of pesticides are known or suspected hormone disrupters. This study also agrees with the findings of Pages *et al.*, 2002, that treatment with 1-40 mg of lindane/kg of body weight disrupts testicular morphology, decreases spermatogenesis, inhibits testicular steroid genesis, reduces plasma androgen concentrations and may adversely affect reproductive performance in males.

CONCLUSION

In the light of present observations, it is suggested that;

- Indiscriminate use of DDVP should be avoided.
- Matured male individuals should avoid places where DDVP is being used.
- Clear instructions on method of application and precautions should be printed on the containers of DDVP to avoid mishaps.

REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR), 1990. Toxicological profile for chlorobenzene. A. Hanta, Department of Health and Human Service, Atlanta, GA. assays. *Canada J. Genetic Cytol.* **21**: 319–33.
- Bakare, A.A, Mosuro, A.A. and Osibanjo, O. (2005). An in vivo evaluation of mice. *Mutat Res.* **497**:131–138.
- Bruce, W.R. and Heddle, J.A. (1979). The mutagenic activity of 61 agents as determined by the micronucleus, Salmonella and sperm abnormality assays. *Can. J. Genetic. Cytol*, **21**: 319-334.
- Durham, W. F., Gaines, T. B., McCauley, R. H., Sedlak, V. A., Mattson, A. M. and Hayes, W. J., jr (1957) A. M. A. *Arch. industr. Hlth*, **15**: 340
- Farm Chemical Handbook (1994). Farm Chemical handbook: pesticide dictionary. Meister Publishing Company, Willoughby, OH. C70-C71.
- Gallo M.A. and Lawryk N.J. Organophosphorus Pesticides. (1991) *In Handbook of Pesticide* A.G. Gonall, C.J, Bardawill, M.M .David, 1949, Determination of total protein. *J. Biol. Chem.* **177**:751-760.
- Hayes W.J. and Laws E.R. (1982) Eds. *Academic Press*, New York, NY, 3-5 pp.
- Hays S.M., Becker R.A., and Leung H.W., Aylward L.L., and Pyatt D.W. (2007) .Biomonitoring equivalents: a screening approach for interpreting biomonitoring results from a public health risk perspective. *Reg Toxicol Pharmacol*, **47**: 96–109.
- Hutson, D.H. and Hoadley E.C. 1972a. The comparative metabolism of (14-C- vinyl) dichlorvos in animals and man. *Arch. Toxikol.* **30**(1): 9-18.
- Noble D. (2002). Modelling the heart: insights, failures and progress. *Bioassays* **24**: 1155–1163.
- Odeigah, P.G.C. (1997). Sperm head abnormalities and dominant lethal effects of formaldehyde in albino rats. *Mutation Research* **389**: 141-148.
- Otubanjo, O.A. and Mosuro, A.A. (2001). An in vivo evaluation of induction of abnormal sperm morphology by some anthelmintic drugs in mice. *Mutat Res.* **497**: 131–138.
- Pages, N., Sauvet, M.P., Bouvet, S. and Goudey-Perriere, F. (2002). Reproductive toxicity of Lindane, *J. Soc. Biol* **196**(4): 325-338. Organophosphate poisoning in rabbits. *Int. J. Biochem.* **16**: 687-690.

- Savolainen K. (2001). Understanding the toxic actions of organophosphates. In: Krieger R.I. (Ed.). Handbook of Pesticide Toxicology, Vol. 2 Academic Press, San Diego, 1013–1041 pp.
- Swan, S.H. and Kruse, R.L. (2003). Semen quality in relation to biomarkers of pesticide exposure.
- Thybaud, V., Aardema, M. and Clements, J. (2007). Strategy for genotoxicity testing: hazard identification and risk assessment in relation to in vitro testing. *Mutat. Res.* **627**: 41-58.
- Thorpe, E., A.B. Wilson, K.M. Dix and D. Blair. 1972. Teratological studies with dichlorvos vapour in rabbits and rats. *Arch. Toxikol.* **30**(1): 29-38.
- USDHHS. (1993): Preliminary Estimates from the 1993 National Household Survey on Drug Abuse. U.S. Department of Health and Human Services, Substance Abuse and Mental Health Services Administration, Washington, DC.
- U.S. EPA. (1999). Guidelines for Carcinogen Risk Assessment. Review draft. NCEA-F-0644, Jul 1999.
- U.S. Environmental Protection Agency (2003). Chlorobenzene. Integrated.
- World Health Organization/Food and Agriculture Organization (1993) of the United Nations and Geneva. (WHO/FAO, 1993).
- WHO (World Health Organization, 1991) IARC Monograph on Evaluation of Carcinogenic Risks to Humans, **53**: 267-299.
- Wright H.M.(2003).The Physical and Theoretical Chemistry Laboratory. Oxford University, USA.
- Wyrobek, A.J.and Bruce, W.R. (1978).The induction of sperm- induction of abnormal sperm morphology in mice by landfill leachates. *Mutat Res.* **582**: 28–34.

IMPACTS OF DECEMBER 2006 SOLAR FLARES ON AFRICAN EQUATORIAL GPS-TEC

A. O. Akala¹, E. O. Somoye², E. O. Oyeyemi¹ & A. O. Adewale¹

¹Department of Physics, University of Lagos, Akoka, Yaba, Lagos, Nigeria

²Department of Physics, Lagos State University, Ojo, Lagos, Nigeria
aakala@unilag.edu.ng

ABSTRACT

Strong solar activities were observed on the 6 and 13th December, 2006; a minimum phase of solar cycle 23. These flares, in the magnitude of X6.5 and X3.4 on December 6 and 13, 2006 respectively, were absolutely unexpected, being a year of low solar activity. This study presents the impacts of the solar flares on African equatorial TEC measurements. TEC data from three African equatorial GPS stations, namely; Libreville (0.36°N, 9.67°E, 8.04°S mag. lat), Gabon; Mbarara (0.60°S, 30.74°E, 9.00°S mag. lat), Uganda; and Malindi (3.00°S, 40.20°E, 10.98°S mag. lat), Kenya were used for the study. The data were obtained from the International GNSS Service (IGS) network (<ftp://cddis.gsfc.nasa.gov/gps/data/daily>). Satellites' biases were removed from the raw data to obtain true slant TEC, which we converted to vertical TEC (VTEC), using a mapping function. The periods of flares occurrences were matched with the VTEC data to observe the effects of the flares on GPS-TEC. Both flares caused noticeable enhancements in TEC measurements at the three stations. These results further revealed the need for the space science community to also pay attention to the impacts of space weather on space and ground based systems during the minimum phases of solar cycles.

Keywords: *Flares; Equatorial GPS-TEC; Africa; Magnetic reconnection; Radio technology*

INTRODUCTION

In December 2006, the active sunspot region 10930 on the sun unleashed four X-class solar flares on the earth's atmosphere. Solar flares are eruptive events that emanate from the sun's surface, leading to a release of huge amounts of energy through the magnetosphere to the earth's atmosphere (Holman, 2012).

Solar flares are usually associated with accelerated charged particles, which are caused by magnetic reconnection. When two oppositely directed magnetic field components interact, the field lines topology changes as the lines break and reconnect, causing the charged particles to orbit round the field lines. The inflowing magnetic fields induce the formation of a thin current sheet which allows reconnection to occur (Ratcliffe, 1972). Most of the original magnetic energy is converted to kinetic energy, much of which is thermal. On the sun, magnetic reconnection happens on solar arcades (a series of closely occurring loops of magnetic lines of force). The sudden release of energy in this reconnection is the origin of the particle acceleration. The unconnected magnetic helical field and the material that it contains may violently expand outwards forming a coronal mass ejection (CME). This also explains why solar flares typically erupt from what are known as the active regions on the sun, where magnetic fields are much stronger on the average. X-ray and gamma-ray emissions are produced in the interaction of the accelerated particles with ions in the ambient thermal plasma.

Solar energetic particles (SEPs) and their associated radiation from solar flares present health hazard to passengers on high altitude polar flights, and also to men on astronautic missions. Furthermore, solar eruptive events can wreck havoc on man-made systems, such as, communication and navigation systems (Cerruti et al., 2006; 2008; Kintner et al., 2009; Carrano

et al., 2009), electrical power grids, and satellite systems in space. These havocs could further lead to severe socio-economic consequences.

The occurrence of solar flares causes the ionosphere to ionize and expand more, thereby enhancing its total electron content (TEC). TEC is one important parameter that has over-bearing influences on radio signals that propagate through the ionosphere (Klobuchar, 1996). Consequently, understanding TEC variations is very cardinal in designing robust systems that rely on trans-ionospheric radio technology. The aim of this study is to investigate the responses of African equatorial GPS-TEC to these solar flares, with a view to seeing how precise positioning service providers in Africa could continue to account for solar radio bursts in their operational plans at all phases of solar cycles.

METHODS

This study used the solar flare data of December, 2006 (www.spaceweather.com). The responses of GPS-TEC measurements from three African equatorial GPS stations: namely; Libreville (0.36°N, 9.67°E, 8.04°S mag. lat), Gabon; Mbarara (0.60°S, 30.74°E, 9.00°S mag. lat), Uganda; and Malindi (3.00°S, 40.20°E, 10.98°S mag. lat), Kenya to the flares were also investigated. Figure 1 shows the geographical locations of the GPS stations. The GPS-TEC data were obtained from the International GNSS Service (IGS) network (<ftp://cddis.gsfc.nasa.gov/gps/data/daily>). The data were archived in RINEX format. Satellites' biases were obtained from the Data Centre of the Bern University, Switzerland, and they were removed from the raw slant TEC data to produce the corresponding true slant TEC, and thereafter converted to vertical TEC (VTEC) by assuming that the ionosphere is a thin shell at an altitude of 350 km, via a mapping function given by Mannucci et al. (1993) and Ma and Maruyama (2003). In order to quantify the extent of the response of GPS TEC observations at each station to each solar flare, we compare the mean GPS TEC observations for the quiet days ($Kp \leq 2$) over the month with those of the actual days of the flare. Thereafter, following Akala et al. (2013), we evaluated the percentage variation of the GPS TEC measurements during the days of flares from those of the quiet days.

$$\%Variation = \left(\frac{TEC_F - TEC_Q}{TEC_Q} \right) \times 100 \quad (1)$$

where TEC_F is the maximum VTEC for a storm day, and TEC_Q the maximum VTEC for a quiet day.

RESULTS AND DISCUSSION

Table 1 shows the solar flare parameters for 5, 6, 13, and 14th December, 2006. The solar flares of 5 and 6th December, 2006 recorded the highest magnitudes, densities in terms of proton per cubic centimeter, and sunspot numbers, but the slowest of all the flares. It is important to mention that it was only the solar flare of 5th December that occurred during the day-time hours. In fact, the flare occurred around the time of the day when the sun is overhead (high solar irradiance angle) at all the stations. The solar flare of 14th December recorded the least magnitude, but the fastest of all the four flares.

Figure 2 shows the VTEC measurements for the 5–7th December, 2006, and the corresponding average measurements over the quiet days of the month for Libreville, Mbarara, and Malindi respectively. The highest TEC values were recorded at Libreville; 39.0 and 41.6 TECU on the 5th and 6th respectively. The values were recorded as 31.7 and 32.0 TECU for the same days at Mbarara, and as 33.2 and 33.4 TECU at Malindi. The peak of the average TEC measurements over the quiet days of the month were recorded as 32.0, 25.0, and 26.0 TECU at Libreville, Mbarara, and Malindi respectively. Figure 3 is the same as Figure 2, but for the 12–14th December, 2006. Here, the highest TEC value was recorded at Libreville; 32.0 TECU on the

13th. There was a data gap at Libreville on the 14th. The values were recorded as 24.6 and 31.0 TECU at Mbarara on the 13th and 14th respectively, and as 25.7 and 28.8 TECU at Malindi on the same days. In terms of % variations in TEC measurements as a result of flare-induced enhancements, the 5th December solar flare recorded 21.9% at Libreville, 26.8% at Mbarara, and 28.5% at Malindi. On the 6th December, the values were recorded as 30.0%, 28.0%, and 27.8% respectively at the three stations. The 13th December solar flare did not cause any noticeable enhancement in TEC measurements at the three stations. On the 14th December, the % variations in TEC measurements are 24.0% at Mbarara, 10.8% at Malindi.

Figure 4 shows the VTEC measurements for different satellites during the time of occurrence of the solar flare on the 5th December, 2006 at Libreville, Mbarara, and Malindi. The transparent bar represents the periods of sudden increase in TEC due to the enhanced radiation caused by the solar flare. All the other flares, except the 5th December flare occurred during the night-time hours at all the stations, hence, this analysis concentrated on only the 5th December flare. Within the time of the day at which the flare attained its peak value, a sudden increase in TEC, in the rate of about 0.5 TECU/min was observed (Figure 4). These sudden enhancements in TEC might have been caused by the more ionization and expansions in the ionosphere due to the occurrence of the solar flare. The sudden increments in TEC within the period of occurrences were not so noticeable for the other flares, reason being that they occurred during the night, when there was no solar radiation. However, the impacts of their occurrences were felt later during the day-time when the sun becomes active as the TEC values were observed to increase during the days of the flare as compared to the average values of TEC over the quiet days ($K_p < 2$) of the month (December, 2006), although, the event of the 13th December did not record any noticeable impact on TEC observations. Generally, the highest TEC values were recorded on the 6th December at all the stations, follow by the 5th December flare. Magnetic reconnection usually occurs on a densely looped magnetic field lines (arcades) on the surface of the sun (active region). The sudden release of energy in this reconnection gives rise to particles acceleration. In other words, the unconnected magnetic helical fields' ends and their constituents violently expand outwards to form massive eruptions that spew outwards from the surface of the sun towards the earth's atmosphere.

Of all the four flares, the 6th December flare recorded the greatest proton density, and the 13th December flare recorded the least (Table 1). Perhaps, the loop of the magnetic fields on the surface of the sun on the 6th of December was denser than the other magnetic loop densities during the days of other flares. This could also account for the highest proton density that was recorded by the solar flare plasma of 6th December. The huge proton density of the solar flare plasma on the other hand could have enhanced the collisions of accelerated particles with ambient electrons and ions, to further thermalize the plasma to record the highest daily sunspot number, in comparison to other days of the investigation. This might also be the reason for the high strength of the flare, in terms of X-ray emissions. The density of the magnetic fields on the surface of the sun, which caused the 13th December flare, might be very low, given the low proton density recorded during the flare (Table 1). This might be responsible for the low geoeffectiveness of the 13th December solar flare.

On a station-by-station basis, TEC recorded highest values at Libreville, and the impacts of the flares were more noticeable at the station. The reason for the observed increase in TEC in the Atlantic side as compared to the eastern side of the continent is not yet well understood. Paznukhov et al. (2012) had earlier reported the dominance of equatorial plasma bubbles in the Atlantic side of Africa, compared to the eastern side. They ruled out the possibility of spread-F seeding as the cause of the observed differences, given the small scale of the region involved, but

suspected that the differences in the ionospheric electrodynamics over the regions as a likely candidate for the observed differences. To establish these inferences on a firmer footing, further studies on ionospheric electrodynamics at different longitudes within the equatorial anomaly region of Africa would be required.

CONCLUSION

The 6th December solar flares impacted most on African equatorial GPS-TEC, causing an increment of about 10 TECU in TEC. The next most impacted event was the event of 5th December, while the 13th December flares did not show any noticeable impact on African equatorial GPS-TEC. Solar flares could cause sudden increase in TEC at the rate in the order of 0.5 TECU/min or more in the sun-lit side of the earth, depending on the strength of the flare. Proton density is an important parameter that dictates the geoeffectiveness of a solar flare. Generally, the impacts of the flares were more at Libreville than the other stations investigated, and TEC also recorded highest values at Libreville. Surprisingly, these solar flares occurred during a solar minimum phase. This suggests that the impacts of solar flares on systems that rely on tran-ionospheric technology should be given scientific and technical attentions at all phases of solar activity.

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REFERENCES

- Akala A. O., A. B. Rabiou, E. O., Somoye, E. O. Oyeyemi, and A. B. Adeloje (2013), The Response of African equatorial GPS-TEC to intense geomagnetic storms during the ascending phase of solar cycle 24, *J. Atmos. Solar-Terrest. Phys.*, 98, 50 – 62, doi:10.1016/j.jastp.2013.02.006.
- Carrano, C. S., C. T. Bridgwood, and K. M. Groves (2009), Impacts of the December 2006 solar radio bursts on the performance of GPS, *Radio Sci.*, 44, RS0A25, doi:10.1029/2008RS004071.
- Cerruti, A. P., P. M. Kintner, D. E. Gary, L. J. Lanzerotti, E. R. de Paula, and H. B. Vo (2006), Observed solar radio burst effects on GPS/Wide Area Augmentation System carrier-to-noise ratio, *Space Weather*, 4, S10006, doi:10.1029/2006SW000254.
- Cerruti, A. P., P. M. Kintner Jr., D. E. Gary, A. J. Mannucci, R. F. Meyer, P. Doherty, and A. J. Coster (2008), Effect of intense December 2006 solar radio bursts on GPS receivers, *Space Weather*, 6, S10D07, doi:10.1029/2007SW000375.
- Holman, G. D. (2012), Solar Eruptive Events, *Physics Today*, April 2012, 56–61.
- Kintner, P. M. Jr., O'Hanlon, B., Gary, D. E., Kintner, P. M. S. (2009), Global Positioning System and Solar Radio Burst Forensics, *Radio Science*, 44, RS0A08.
- Klobuchar, J. A. (1996), Ionospheric effects on GPS. In: Parkinson, B.W., Spilker, J.J. (Eds.), *Global Positioning System: Theory and Applications*, vol. 2. Progress in Astronautics and Aeronautics, American Institute of Aeronautics and Astronautics, Washington DC, 164, 485–515.
- Ma, G., T. Maruyama (2003), Derivation of TEC and estimation of instrumental biases from GEONET in Japan. *Annales Geophysicae* 21, 2083–2093.
- Mannucci, A. J., B. D. Wilson, C. D. Edwards (1993), A new method for monitoring the earth's ionosphere total electron content using the GPS global network. In: *Proceedings of ION GPS-93*, Institute of Navigation, 1323–1332.

- Mannucci, A. J., B. T. Tsurutani, B. A. Iijima, A. Komjathy, A. Saito, W. D. Gonzalez, F. L. Guarnieri, J. U. Kozyra, R. Skoug (2005), Dayside global ionospheric response to the major interplanetary events of October 29–30, 2003 “Halloween Storms”. *Geophysical Research Letters* 32, <http://dx.doi.org/10.1029/2004GL021467>, L12S02.
- Paznukhov, V. V., C. S. Carrano, P. H. Doherty, K. M. Groves, R. G. Caton, C. E. Valladares, G. K. Seemala, C. T. Bridgwood, J. Adeniyi, L. L. N. Amaeshi, B. Damtie, F. D’Ujanga Mutonyi, J. O. H. Ndeda, P. Baki, O. K. Obrou, B. Okere, and G. M. Tsidu (2012), Equatorial plasma bubbles and L-band scintillations in Africa during solar minimum, *Annales Geophysae*, 30, 675–682.
- Ratcliffe, J. A. (1972), *An Introduction to the Ionosphere and Magnetosphere*, Cambridge University Press, London NW1 2DB, Great Britain.

FIGURE CAPTIONS

Figure 1: A map of Africa, showing the GPS stations

Figure 2: VTEC measurements, 5–7th December, 2006 (continuous line), average measurements over the quiet days of the month (dotted lines) for (A) Libreville [Ngkl], Garbon; (B) Mbarara [Mbar], Uganda; and (C) Malindi [Mali], Kenya.

Figure 3: VTEC measurements for 12–14th December, 2006 (continuous line) and the average measurements over the quiet days of the month (dotted lines) at (A) Libreville [Ngkl], Garbon; (B) Mbarara [Mbar], Uganda; and (C) Malindi [Mali], Kenya.

Figure 4: VTEC measurements for different satellites during the time of occurrence of the solar flare on the 5th December, 2006 at (A) Libreville [Ngkl], Garbon; (B) Mbarara [Mbar], Uganda; and (C) Malindi [Mali], Kenya. The dot-line bar represents the periods of sudden increase in TEC due to the enhanced radiation caused by the solar flare.

Table 1: Solar Flares Parameters for December, 2006 (Source: www.spaceweather.com)

Date	X-Class	Time (UT)	Speed (Km/s)	Density (Protons/cm ³)	Sunspot No.
05/12/06	X9.0	10:35	402.7	4.7	43
06/12/06	X6.5	18:45	600.1	4.9	59
13/12/06	X3.4	02:40	645.0	0.6	27
14/12/06	X1.5	22:15	845.0	2.4	21

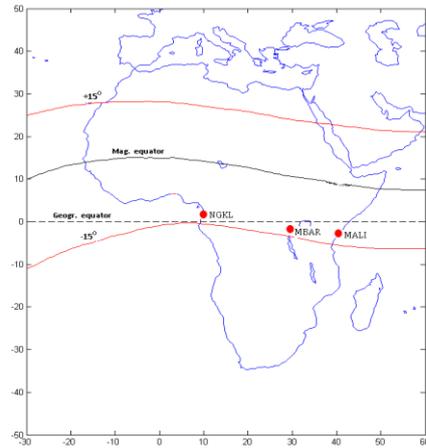


Figure 1: A map of Africa, showing the GPS stations

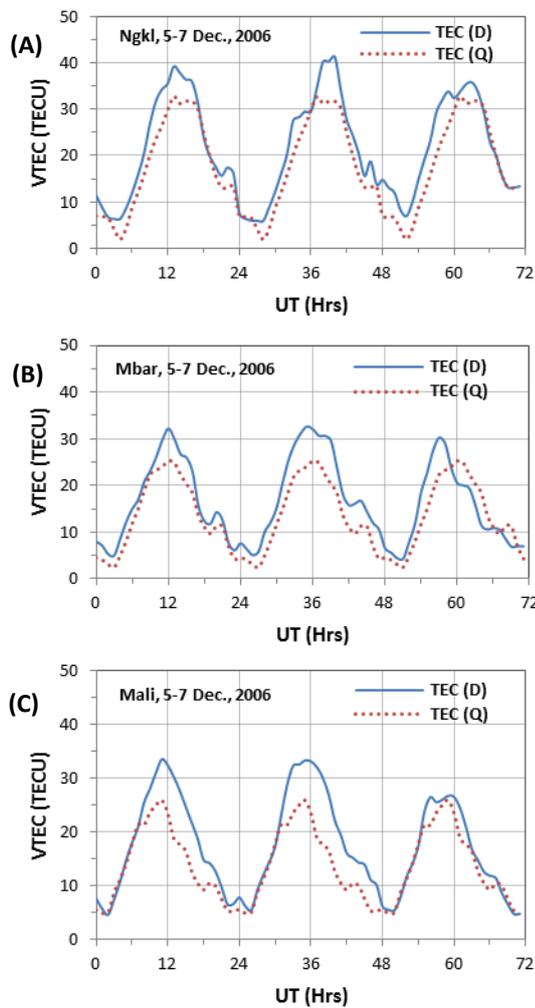


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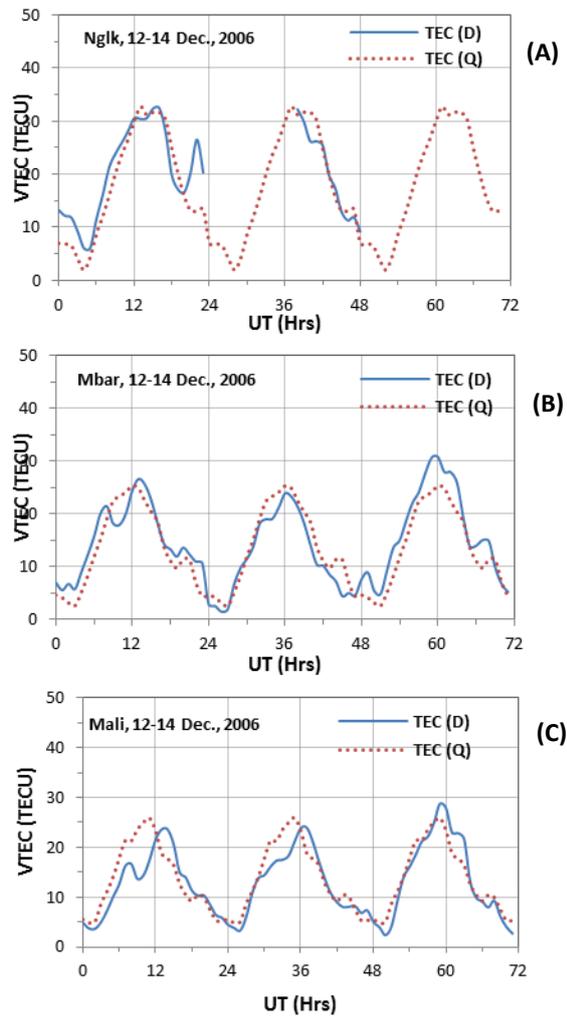


Figure 3: VTEC measurements for 12–14th December, 2006 (continuous line) and the average measurements over the quiet days of the month (dotted lines) at (A) Libreville [Ngkl], Garbon; (B) Mbarara [Mbar], Uganda; and (C) Malindi [Mali], Kenya.

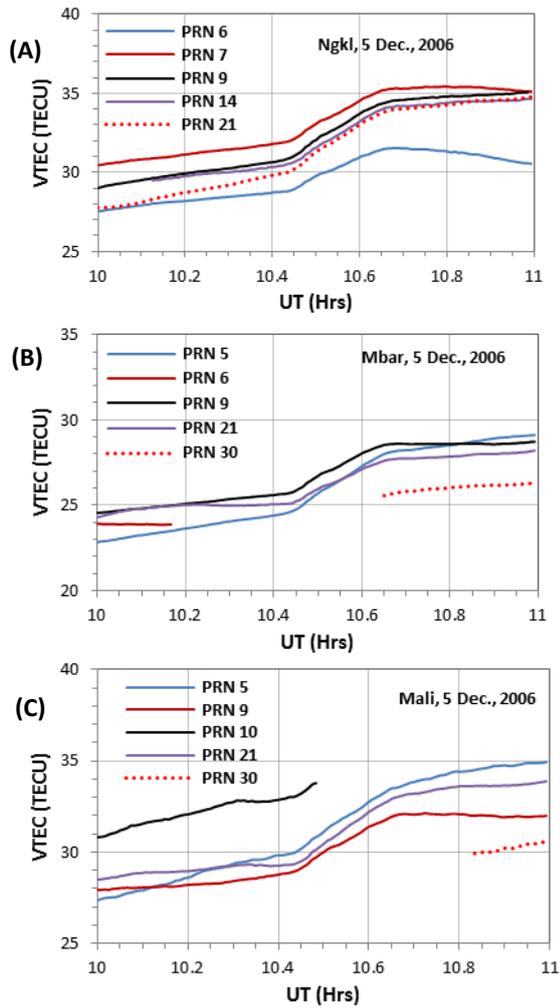


Figure 4: VTEC measurements for different satellites during the time of occurrence of the solar flare on the 5th December, 2006 at (A) Libreville [Ngkl], Garbon; (B) Mbarara [Mbar], Uganda; and (C) Malindi [Mali], Kenya. The transparent bar represents the periods of sudden increase in TEC due to the enhanced radiation caused by the solar flare.

L-STABLE ALGORITHM FOR PARABOLIC EQUATIONS WITH INTEGRAL BOUNDARY CONDITIONS

B. I. Akinnukawe, O. A. Akinfenwa & S. A. Okunuga

Department of Mathematics, University of Lagos, Lagos, Nigeria
 akinnukaweb@yahoo.com, oakinfenwa@unilag.edu.ng, sokunuga@unilag.edu.ng

ABSTRACT

The paper describes the derivation of a method based on Collocation and Interpolation technique known as Second Derivative Block Backward Differentiation Formula (SDBBDF) for the numerical solution of parabolic equations. The one-dimensional parabolic equation subject to integral boundary conditions is first discretized into a system of ordinary differential equations (ODEs) with initial conditions using Method of Lines. Then the derived block method (SDBBDF) is used to solve the resulting ODEs. The stability properties of the block method are investigated using the boundary locus plot and the method was found to be L-stable. The derived method is implemented on standard problems of parabolic equations and the results obtained shows that the method is reliable and efficient for the class of problem considered.

Keywords: *Parabolic equation, Method of lines, L-stability, Second Derivative Block Backward Differentiation Formula, Collocation and Interpolation technique*

INTRODUCTION

Consider the second-order Parabolic Differential Equation

$$\frac{\partial u(x, t)}{\partial t} = \frac{\partial^2 u(x, t)}{\partial x^2} + Q(x, t), \quad 0 < x < X, \quad 0 < t \leq T \quad (1)$$

subject to initial conditions

$$u(x, 0) = f(x), \quad 0 \leq x \leq X \quad (2)$$

$$u(0, t) = \int_0^X r_1(x, t)u(x, t)dx + s_1(t), \quad 0 < t \leq T \quad (3)$$

$$u(X, t) = \int_0^X r_2(x, t)u(x, t)dx + s_2(t), \quad 0 < t \leq T \quad (4)$$

where $Q(x, t), f(x), r_1(x, t), r_2(x, t), s_1(t), s_2(t)$ are given continuous functions which satisfies the existence and uniqueness conditions. In recent years, the investigation of problems for partial differential equations with integral conditions has become very important due to their practical interpretations. Cannon [5] is one of the first researchers to investigate this class of problems where integral conditions are used for the one-dimensional heat conduction equation. Other authors that proffer numerical methods for the solution of such problems are Li et al. [13], Dehghan [6-7] and Friedman [1]. Also, various problems arising from heat conduction [3], thermo-elasticity [10], plasma physics [2] and chemical engineering [14] can be reduced to integral problems. In this work, the approximate solution to the parabolic problem (1)-(4) will be given based on L-stable SDBBDF. The method of lines is used to reduce (1) with its initial conditions (2) and its integral boundary conditions (3) and (4) to a system of N first-ordinary differential equations with initial conditions of the form

$$\frac{dU_i}{dt} = AU_i(t) + v_i(t), \quad t > 0 \quad (5)$$

with initial conditions

$$U_i(x, 0) = f_i(x), \quad i = 1, 2, \dots, N - 1 \quad (6)$$

where

$$A = \frac{1}{(\Delta x)^2} \begin{bmatrix} -2 & 1 & 0 & 0 & \dots & 0 \\ 1 & -2 & 1 & 0 & \dots & 0 \\ 0 & 1 & -2 & 1 & \vdots & \vdots \\ 0 & 0 & \ddots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & \dots & 1 & -2 \end{bmatrix}$$

In equation (5), the vector $v(t)$ arises from the use of integral boundary conditions $u(0, t)$ and $u(X, t)$ in (3) and (4). Solving (5) subject to (6) using L-stable Second Derivative Block Backward Differentiation Formula (SDBBDF) of order 5 will lead to the numerical solution of the given parabolic equation (1). Block methods were first introduced by Milne [9] and since then various block methods have been developed (see [4], [8], [9]). Block methods perverse the Runge-Kutta traditional advantage of being self starting and also have the novel property of simultaneously producing approximate solutions of the IVPs at more than one point.

The rest of this paper is presented as follows: the numerical method is derived in section 2 and analysis of the derived block method is presented in section 3. The numerical results produced by this method are given in section 4 and the last section ends this paper with a brief conclusion.

METHODS

In this section, we develop the main method SDBDF with its additional method derived from its second derivative combined to form the 2-step Second Derivative Block Method on the interval t_n to $t_{n+2} = t_n + 2h$ where h is the chosen step length. The main method SDBDF is of the form

$$u_{n+2} = \sum_{j=0}^1 \alpha_j u_{n+j} + \sum_{j=0}^2 \beta_j f_{n+j} + h^2 \gamma_2 g_{n+2} \quad (7)$$

where $u_{n+j} = u(t_n + jh)$, $f_{n+j} \equiv f(t_n + jh, u(t_n + jh)) = u'(t_n + jh)$ and

$$g_{n+2} \equiv \frac{df(t_n+2h, u(t_n+2h))}{dt} = u''(t_n + 2h),$$

t_n is a node point and $\alpha_j, \beta_j, j = 0, 1, 2, \gamma_2$ are parameters to be obtained from the multistep collocation and interpolation techniques. The exact solution $U(t)$ is assumed to exist and unique in $[t_0, t_2]$, we approximate the exact solution $U(t)$ by seeking the continuous solution $u(t)$ of the form

$$u(t) = \sum_{j=0}^{p+q-1} b_j \varphi_j(t), \quad t \in [t_0, t_2] \quad (8)$$

where b_j are unknown coefficients and $\varphi_j(t) = t^j, j = 0(1)5$ are the polynomial basis functions of degree 5. The number of interpolation points p and the number of the distinct collocation points q are chosen to satisfy $p = 2$ and $q = 4$. The proposed method is constructed by imposing the following conditions:

$$u_{n+i} = \sum_{j=0}^5 b_j t_{n+i}^j, \quad i = 0, 1 \quad (9)$$

$$f_{n+i} = \sum_{j=0}^5 j b_j t_{n+i}^{j-1}, \quad i = 0(1)2 \quad (10)$$

$$g_{n+i} = \sum_{j=0}^5 j(j-1) b_j t_{n+i}^{j-2}, \quad i = 2 \quad (11)$$

Equations (9), (10) and (11) lead to a system of $p + q$ equations which is solved to obtain the coefficients $b_j, j = 0(1)5$. The values of b_j are substituted into (8) to yield the continuous form

$$u(t) = \sum_{j=0}^1 \alpha_j(t) u_{n+j} + h \sum_{j=0}^2 \beta_j(t) f_{n+j} + h^2 \gamma_2(t) g_{n+2} \quad (12)$$

Where $\alpha_j(t), j = 0, 1, \beta_j(t), j = 0, 1, 2, \gamma_2$ are continuous coefficients given as

$$\alpha_0(t) = 1 - \frac{120}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{160}{23} \left(\frac{t-t_n}{h}\right)^3 - \frac{75}{23} \left(\frac{t-t_n}{h}\right)^4 + \frac{12}{23} \left(\frac{t-t_n}{h}\right)^5$$

$$\alpha_1(t) = \frac{120}{23} \left(\frac{t-t_n}{h}\right)^2 - \frac{160}{23} \left(\frac{t-t_n}{h}\right)^3 + \frac{75}{23} \left(\frac{t-t_n}{h}\right)^4 - \frac{12}{23} \left(\frac{t-t_n}{h}\right)^5$$

$$\beta_0(t) = \left(\frac{t-t_n}{h}\right) - \frac{131}{46} \left(\frac{t-t_n}{h}\right)^2 + \frac{265}{92} \left(\frac{t-t_n}{h}\right)^3 - \frac{28}{23} \left(\frac{t-t_n}{h}\right)^4 + \frac{17}{92} \left(\frac{t-t_n}{h}\right)^5$$

$$\beta_1(t) = -\frac{64}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{116}{23} \left(\frac{t-t_n}{h}\right)^3 - \frac{63}{23} \left(\frac{t-t_n}{h}\right)^4 + \frac{11}{23} \left(\frac{t-t_n}{h}\right)^5$$

$$\beta_2(t) = \frac{19}{46} \left(\frac{t-t_n}{h}\right)^2 - \frac{89}{92} \left(\frac{t-t_n}{h}\right)^3 + \frac{16}{23} \left(\frac{t-t_n}{h}\right)^4 - \frac{13}{92} \left(\frac{t-t_n}{h}\right)^5$$

$$\gamma_2(t) = -\frac{7}{46} \left(\frac{t-t_n}{h}\right)^2 + \frac{17}{46} \left(\frac{t-t_n}{h}\right)^3 - \frac{13}{46} \left(\frac{t-t_n}{h}\right)^4 + \frac{3}{46} \left(\frac{t-t_n}{h}\right)^5$$

The main discrete method (SDBDF) is generated by evaluating (12) at the point $t = t_{n+2}$ to obtain

$$u_{n+2} = \frac{7}{23} u_n + \frac{16}{23} u_{n+1} + \frac{h}{23} (2f_n + 16f_{n+1} + 12f_{n+2}) - \frac{2}{23} h^2 g_{n+2} \quad (13)$$

Differentiating (12) twice with respect to t , we have

$$u''(t) = \frac{1}{h^2} \left[\sum_{j=0}^1 \overline{\overline{\alpha_j(t)}} u_{n+j} + h \sum_{j=0}^2 \overline{\overline{\beta_j(t)}} f_{n+j} + h^2 \overline{\overline{\gamma_2(t)}} g_{n+2} \right] \quad (14)$$

Where

$$\overline{\overline{\alpha_0(t)}} = -\frac{240}{23} + \frac{960}{23} \left(\frac{t-t_n}{h}\right) - \frac{900}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{240}{23} \left(\frac{t-t_n}{h}\right)^3$$

$$\overline{\overline{\alpha_1(t)}} = \frac{240}{23} - \frac{960}{23} \left(\frac{t-t_n}{h}\right) + \frac{900}{23} \left(\frac{t-t_n}{h}\right)^2 - \frac{240}{23} \left(\frac{t-t_n}{h}\right)^3$$

$$\overline{\overline{\beta_0(t)}} = -\frac{131}{23} + \frac{795}{46} \left(\frac{t-t_n}{h}\right) - \frac{336}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{85}{23} \left(\frac{t-t_n}{h}\right)^3$$

$$\overline{\overline{\beta_1(t)}} = -\frac{128}{23} + \frac{696}{23} \left(\frac{t-t_n}{h}\right) - \frac{756}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{220}{23} \left(\frac{t-t_n}{h}\right)^3$$

$$\overline{\overline{\beta_2(t)}} = \frac{19}{23} - \frac{267}{46} \left(\frac{t-t_n}{h}\right) + \frac{192}{23} \left(\frac{t-t_n}{h}\right)^2 - \frac{65}{23} \left(\frac{t-t_n}{h}\right)^3$$

$$\overline{\overline{\gamma_2(t)}} = -\frac{7}{23} + \frac{51}{23} \left(\frac{t-t_n}{h}\right) - \frac{78}{23} \left(\frac{t-t_n}{h}\right)^2 + \frac{30}{23} \left(\frac{t-t_n}{h}\right)^3$$

The additional method is generated by evaluating (14) at the point $t = t_{n+1}$ to obtain

$$h^2 g_{n+1} = \frac{120}{46} u_n - \frac{120}{46} u_{n+1} + \frac{h}{46} (31f_n + 64f_{n+1} + 25f_{n+2}) - \frac{8}{46} h^2 g_{n+2} \quad (15)$$

The methods (13) and (15) are combined to obtain 2-step SDBBDF of order 5 as

$$\left. \begin{aligned} h^2 g_{n+1} &= \frac{120}{46} u_n - \frac{120}{46} u_{n+1} + \frac{h}{46} (31f_n + 64f_{n+1} + 25f_{n+2}) - \frac{8}{46} h^2 g_{n+2} \\ u_{n+2} &= \frac{7}{23} u_n + \frac{16}{23} u_{n+1} + \frac{h}{23} (2f_n + 16f_{n+1} + 12f_{n+2}) - \frac{2}{23} h^2 g_{n+2} \end{aligned} \right\} \quad (16)$$

Analysis of SDBBDF

The stability properties, consistency, convergence, local truncation error and order of SDBBDF method are discussed in this section. The method can be represented by a matrix finite difference equation in block form as

$$A_1 U_\omega = A_0 U_{\omega-1} + h(B_1 F_\omega + B_0 F_{\omega-1}) + h^2 D_1 G_\omega \quad (17)$$

where

$$\begin{aligned} U_\omega &= (u_{n+1}, u_{n+2}, u_{n+3}, \dots, u_{n+k-1}, u_{n+k})^T \\ U_{\omega-1} &= (u_{n-k+1}, u_{n-k+2}, u_{n-k+3}, \dots, u_{n-1}, u_n)^T \\ F_\omega &= (f_{n+1}, f_{n+2}, f_{n+3}, \dots, f_{n+k-1}, f_{n+k})^T \\ F_{\omega-1} &= (f_{n-k+1}, f_{n-k+2}, f_{n-k+3}, \dots, f_{n-1}, f_n)^T \\ G_\omega &= (g_{n+1}, g_{n+2}, g_{n+3}, \dots, g_{n+k-1}, g_{n+k})^T \end{aligned}$$

and the matrices A_1 , A_0 , B_1 , B_0 and D_1 are 2 by 2 matrices whose entries are given by the coefficients of equation (16) as

$$A_1 = \begin{pmatrix} \frac{120}{46} & 0 \\ \frac{16}{23} & 1 \end{pmatrix}, A_0 = \begin{pmatrix} 0 & \frac{120}{46} \\ 0 & \frac{7}{23} \end{pmatrix}, B_1 = \begin{pmatrix} \frac{64}{46} & \frac{25}{46} \\ \frac{16}{23} & \frac{12}{23} \end{pmatrix}, B_0 = \begin{pmatrix} 0 & \frac{31}{46} \\ 0 & \frac{2}{23} \end{pmatrix},$$

$$D_1 = \begin{pmatrix} -1 & -\frac{8}{46} \\ 0 & -\frac{2}{23} \end{pmatrix}$$

Local Truncation Error and Order of SDBBDF

The local truncation error associated with 2-step SDBBDF methods can be defined to be the linear difference operator

$$L[u(t_n); h] = \sum_{j=0}^2 [\alpha_j u(t_n + jh) - h\beta_j u'(t_n + jh)] - h^2 \gamma_2 u''(t_n + 2h), \quad (18)$$

Assume that $u(t_n)$ is differentiable as often as needed, then by using Taylor series expansion to expand $u(t_n + jh)$, $u'(t_n + jh)$ and $u''(t_n + 2h)$ in (4.20) about t_n , we have

$$u(t_n + jh) = \sum_{m=0}^{\infty} \frac{(jh)^m}{m!} u^{(m)}(t_n), \quad u'(t_n + jh) = \sum_{m=0}^{\infty} \frac{(jh)^m}{m!} u^{(m+1)}(t_n)$$

$$u''(t_n + 2h) = \sum_{m=0}^{\infty} \frac{(2h)^m}{m!} u^{(m+2)}(t_n)$$

Substitute $u(t_n + jh)$, $u'(t_n + jh)$ and $u''(t_n + 2h)$ into (18) to obtain

$$L[u(t_n); h] = C_0 u(t_n) + C_1 h u'(t_n) + C_2 h^2 u''(t_n) + \dots + C_m h^m u^{(m)}(t_n) + \dots \quad (19)$$

where C_m , $m = 0, 1, 2, \dots$ are constants given in terms of α_j and β_j

$$\left. \begin{aligned} C_0 &= \sum_{j=0}^2 \alpha_j \\ C_1 &= \sum_{j=0}^2 (j\alpha_j - \beta_j) \\ C_2 &= \frac{1}{2!} \sum_{j=0}^2 j^2 \alpha_j - \sum_{j=0}^2 j\beta_j - \sum_{j=1}^2 \gamma_j \\ &\vdots \\ C_m &= \frac{1}{m!} \left[\sum_{j=0}^2 j^m \alpha_j - m \sum_{j=0}^2 j^{m-1} \beta_j - m(m-1) \sum_{j=1}^2 j^{m-2} \gamma_j \right] \end{aligned} \right\} \quad (20)$$

The block method (16) is said to have a maximal order of accuracy m if

$$C_0 = C_1 = C_2 = \dots = C_m = 0, C_{m+1} \neq 0$$

and if

$$L[u(t_n); h] = C_{m+1} h^{m+1} u^{(m+1)}(t_n)$$

C_{m+1} is the error constant and $C_{m+1}h^{m+1}u^{m+1}(t_n)$ is the principal local truncation error at the point t_n . Therefore, the values of the error constant calculated for SDBBDF (16) is given as $\left(\frac{13}{2760}, \frac{1}{1035}\right)^T$ with order $(5,5)^T$ where T is the transpose.

Zero-Stability

The zero stability of the method in (17) is determined as the limit $h \rightarrow 0$ and the difference system (17) tends to

$$A_1 U_\omega = A_0 U_{\omega-1}$$

whose first characteristics polynomial $\rho(V)$ is given by

$$\rho(V) = \det[VA_1 - A_0] = \frac{60}{23}V(V - 1)$$

Following the definition, the block method (17) is zero stable for $\rho(V) = 0$ and satisfies $|V_j| \leq 1, j = 1, 2$. Thus 2-step Second Derivative Block Backward Differentiation Formulas (SDBBDF) of order 5 is zero stable.

Consistency and Convergence

The block method (17) is consistent since it has order $m = 5 > 1$. Since the block method is consistent and zero-stable, and then the method (17) converges.

Region of Absolute Stability

The stability properties of the SDBBDF (17) is determined by applying the derived block formulae to the test equation

$$u' = \lambda u \quad (21)$$

Applying (17) to (21) and let $z = \lambda h$, we have

$$A_1 U_\omega = A_0 U_{\omega-1} + zB_1 U_\omega + zB_0 U_{\omega-1} + z^2 D_1 U_\omega$$

which can also be written as

$$U_\omega = R(z)U_{\omega-1}$$

where

$$R(z) = \frac{A_0 + zB_0}{A_1 - zB_1 - z^2 D_1}$$

$R(z)$ is an amplification matrix that has eigenvalues of the form $\mu_1, \mu_2 = 0, \mu_2$ where the dominant eigenvalue μ_2 is a rational function dependent on z given by

$$\mu_2(z) = \frac{2.6087 + 2.08696z + 0.652174z^2 + 0.0869565z^3}{2.6087 - 3.13043z + 1.69565z^2 - 0.521739z^3 + 0.0869565z^4}$$

$\mu_2(z)$ is the Stability Function of SDBBDF (17). The Region of Absolute Stability (RAS) of the 2-step SDBBDF is plotted using the boundary locus techniques. RAS plots the real values (x-axis) against the imaginary values (y-axis) of the block method.

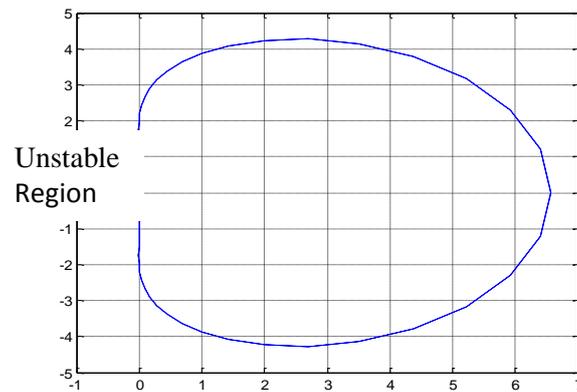


Fig.1 RAS of 2-step SDBBDF

In Fig.1, the unstable region is the interior of the curve while outside the curve is the stable region which corresponds to the 2-step SDBBDF (17). Clearly, it is obvious that the method is L-stable since the stability region contains the entire left half complex plane and in addition $\lim_{z \rightarrow \infty} \mu_2(z) = 0$.

RESULTS

This section deals with some numerical examples executed in MAPLE 17 software to show the efficiency of the derived block method on parabolic equations.

Example 1: From [see Dehghan [6]], we consider the PDE (1) subject to the initial condition (2) and integral boundary conditions (3)-(4) with the following

$$f(x) = x^2,$$

$$Q(x, t) = \frac{-2(x^2 + t + 1)}{(t + 1)^3},$$

$$s_1(t) = -\frac{1}{4(t + 1)^2},$$

$$s_2(t) = \frac{3}{4(t + 1)^2},$$

$$r_1(x, t) = x,$$

$$r_2(x, t) = x,$$

The exact solution is $U(x, t) = \frac{x^2}{(t+1)^2}$. Some methods in [6] were compared with the derived block method (SDBBDF) for the solution of example 1 and it is shown that SDBBDF performed better than the existing methods in [6]. The relative errors of the numerical value of $u(0.6,1.0)$ by SDBBDF and some methods in [6] and Li and Wu [13] are compared in Table 1. Table 2 shows the numerical error of example 1 at $t = 1$.

Table 1: Relative errors of numerical values of $u(0.6,1.0)$ for Example 1

Δt	BTCS [6]	Crandall [6]	FTCS [6]	Dufort-Frankel [6]	Li and Wu [13]	SDBBDF
0.05	7.3E-02	3.8E-03	7.5E-02	7.8E-02	1.6E-03	5.4E-05

BTCS-Backward Time Centered Space, FTCS-Forward Time Centered Space

Table 2: Numerical Results for Example 1 at $t = 1$

x	Exact ($U(x, t)$)	SDBBDF($u(x, t)$)	Error($U(x, t) - u(x, t)$)
0.1	0.0025	0.0024755	2.444E-05
0.2	0.01	0.0099652	3.473E-05
0.3	0.0225	0.0224587	4.123E-05
0.4	0.04	0.0399542	4.575E-05
0.5	0.0625	0.0624506	4.938E-05
0.6	0.09	0.0899456	5.434E-05
0.7	0.1225	0.12245160	4.839E-05
0.8	0.16	0.16006866	6.867E-05
0.9	0.2025	0.20313845	6.385E-04

Example 2: we consider the PDE (1) subject to the initial condition (2) and integral boundary conditions (3)-(4) with the following

$$f(x) = 1 + \cos(x),$$

$$Q(x, t) = 0,$$

$$s_1(t) = \frac{1}{2} + e^{-t} - t - e^{-t}(-1 + \cos(1) + \sin(1) + t \sin(1)),$$

$$s_2(t) = 1 + e^{-t} \cos(1) - \frac{t}{2e} (2(-1 + e) + e^{-t}(e - \cos(1) + \sin(1))),$$

$$r_1(x, t) = x + t,$$

$$r_2(x, t) = te^{-x},$$

which has an exact solution $U(x, t) = 1 + e^{-t} \cos(x)$. Table 3 shows the numerical results of example 2 at $t = 1$ using $\Delta t = 10^{-2}$ and 10^{-3} solved with SDBBDF.

Table 3: Numerical Results for Example 1 at $t = 1$ using SDBBDF

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
10^{-2}	8.82E-04	1.87E-05	3.15E-05	3.09E-05	3.86E-05	3.41E-05	3.12E-05	1.07E-05	5.45E-04
10^{-3}	4.41E-06	1.06E-06	4.12E-07	5.54E-07	5.37E-07	5E-07	3.75E-07	4.67E-07	2.43E-06

CONCLUSION

An L -stable Second Derivative Block Backward Differentiation Formula (SDBBDF) has been employed successfully for the numerical solution of parabolic problems with integral conditions. Applying the classical method of lines, the parabolic problem with integral conditions is converted into a system of Ordinary Differential Equation (ODE). Then the resulting ODE is solved using SDBBDF. The numerical results show that SDBBDF is accurate and reliable for the class of problems considered.

REFERENCES

1. A. Friedman, Monotonic decay of solutions of parabolic equations with nonlocal boundary conditions, Quart. Appl. Math. 44, 401-407 (1986).
2. A.A Samarski, Some problems in the modern theory of differential equation. Differ. Uraven. 16, 1221-1228 (1980).

3. B. Cahlon, D.M. Kulkarni & P. Shi, Stepwise stability for the heat equation with a nonlocal constraint. *SIAM J. Numer. Anal.* 32,571-593 (1995).
4. D. Sarafyan, Multistep methods for the numerical solution of ODEs made self-starting, Tech. report No. 495, Mathematics research center, Madison (1965).
5. J.R. Cannon, The solution of the heat equation subject to the specification of energy. *Quart. Appl. Math.* 21, 155-160(1963).
6. M. Dehghan, Efficient techniques for the second-order parabolic equation subject to nonlocal specifications. *Appl. Numer. Math.* 52, 39-62 (2005).
7. M. Dehghan, A computational study of the one-dimensional parabolic equation subject to nonclassical boundary specifications. *Numer. Methods Partial Differential Eq.* 22, 220-257(2006).
8. O.A. Akinfenwa, S.N. Jator & N.M. Yao, A Continuous Hybrid Method for solving Parabolic PDEs, *Assoc. for the advancement of Modelling and Simulation techniques in Enterp.*, Vol.48 No 1 pp 17-27 (2011).
9. P. Onumanyi, D.O. Awoyemi, U.W. Sirisena & S.N. Jator, New linear multistep methods with continuous coefficients for first order initial value problems, *J. Nig. Math. Soc.* 13, pp 37-51 (1994).
10. P. Shi, Weak solution of evolution problem with a nonlocal constraint. *SIAM J. Math. Anal.* 24, 46-58 (1993).
11. W.E. Milne, *Numerical Solution of differential equations*, John Wiley and Sons, New York (1953).
12. W.E. Schiesser, *Numerical Method of Lines*. Academic Press, San Diego (1991).
13. X.Y. Li & B.Y. Wu, New algorithm for nonclassical parabolic problems based on the reproducing kernel method. *Math. Sciences* (2013) 7:4.
14. Y.S. Choi & K.Y. Chan, A parabolic equation with nonlocal boundary conditions arising from electrochemistry. *Nonlinear Anal.* 18, 317-331 (1992).

AXIAL DEFORMATION OF COMPOSITE BARS WITH VARYING CROSS SECTIONS

¹Akinola, A. P & ²Borokinni, A. S.

Department of Mathematics Obafemi Awolowo University, Ile-Ife, Nigeria.

Distance Learning Institute, University of Lagos, Akoka, Nigeria

aborokini@unilag.edu.ng, aakinola@oauife.edu.ng

ABSTRACT

This work considered the deformation of bars of uniform and varying cross sections subjected to axial loading using finite element method. The governing equation for the deformation of elastostatic bodies provided the needed information in obtaining displacement of particles in the case of one-dimensional composite bodies in equilibrium such as bars. The finite element solution for axial deformation of homogenous bar, gave the exact solution when quadratic element was used. It was also obtained that the finite element solution for an axial deformation of homogeneous bar of varying cross section, gave an approximate solutions to a good degree of accuracy for the case in which the bar was discretized into two elements where quadratic element method had been adopted. Using this method, the finite element solutions for the axial deformation of composite bars of varying cross sections were presented. Results obtained were compared to cases in which the composite bars were homogenized with a view to showing the accuracy of the finite element method for cases in which the exact solutions were difficult to obtain through existing analytical tools. Reliability of the homogenization method was confirmed by comparing results from homogenized bars to cases of homogeneous bars where their exact solutions are known. The results also showed that locations of materials in bars depending on purpose of exploitation affect deformations in bars, and these should be considered by structural engineers if they were to reduce disasters and cost resulting from modern day infrastructures and constructions.

Keywords: Homogenous bars, Composite bars, Material properties, Finite element method, Homogenization.

INTRODUCTION

In engineering, the most common classification of structures is based upon a combination of the geometric configuration and the loading characteristics of the structure. From geometric and loading point of view, the simplest structure is a bar (Theodre, 1974). Practical examples of problems involving deformation of bars are provided by deformation of slender bodies under their own weights and concrete piers supporting bridges (Reddy, 2006). A bar is a crucial element to complex structures such as skyscrapers, bridges, machines, cranes among others.

Structural and design engineers are interested in reducing cost and disasters. Increased rate of collapse of structures are thought by many to be the results of corrupt practices. However, insufficient analyses of deformation of structural members also contribute to the problem. The so called 'substandard materials' may be used for the same purpose provided information on deformation on structural member is well understood (Akinola et. al., 2011). For this reason, composite materials such as steel-concrete and aluminium- bases composites had been studied (Ramesh and Senthivelan 2010; Ying et. al., 2010).

Thus a good object of study is composite bars of varying cross sections which requires the application of a method which gives high degree of accuracy to the solution of axial deformation of composite bars especially in cases where the exact is difficult to be obtained using available analytical tools. Finite element method is a useful tool in this regard, and has been used in

solving many initial- boundary valued problems in structural and solid mechanics which includes problems arising from deformation of reinforced composite columns (Sezen and Moehle, 2004). Finite element method is derived from discretizing weak formulation of a boundary value problem. It requires reformulating a boundary value problem into an equivalent variational problem, domain of the problem being partition into subdomains and then a function is defined and approximated on each subdomain (Han and Reddy 1999).

Since the exact solution may be difficult to obtained, the finite element solutions are often verified through experimental results, but experimental results are also expected to have some errors when compared to the exact solutions. Homogenization method can be used as a tool to verify the accuracy of the finite element solutions (Akinola et. al., 2011).

Formulations and Statement of the Problem

Consider the boundary value problem

$$\frac{d}{dx} \left(EA \frac{du}{dx} \right) + \rho g A = 0; \quad 0 < x < L \quad (1)$$

$$u(L) = 0; \quad \left(EA \frac{du}{dx} \right)_{x=0} = -P. \quad (2)$$

Equations (1) and (2) are respectively the governing equation for the axial deformation of a bar of length L metre, and the boundary conditions (Reddy 2006). u m is the axial displacement, A m is the cross sectional area, E N/m² is the material characteristics of the bar, ρg N is the body force due to gravity. If $\rho = 1$, A and E are constants the exact solution is given by (Borokinni 2012);

$$u(x) = \frac{g(L^2 - x^2)}{2E} + \frac{P(L - x)}{EA}. \quad (3)$$

This work will consider finite element solutions of deformation of homogeneous and composite bars of varying cross sections.

Most of the approximation methods for solving differential equations seek solution of the form

$$U(x) = \sum_{j=1}^N C_j \varphi_j. \quad (4)$$

$U(x)$ represents the approximate solution, and $\varphi_j (j=1, \dots, N)$ are approximate functions. Finite element solution also take the form (4) but uses the concept of variational method (Oden 1973), while variational method uses tools from calculus of variation, which is the technique for determining an extremum or stationary function which minimizes or maximizes a functional (Reddy 2006). This technique is very useful in constructing finite element model for this research work.

Formulation of Material Characteristics and Cross Sectional Areas of Bars

We shall consider homogeneous, composite and homogenized bars. Material characteristics E will be taken as constant in each subdomain of the whole domain after discretization so that E becomes piecewise continuous function in the domain of the problem (1) and (2). If $E=E(x)$, then for a bar of unit length, we shall assume that;

$$E(x) = \begin{cases} E_1, & 0 \leq x \leq \frac{1}{2} \\ E_2, & \frac{1}{2} \leq x \leq 1, \end{cases} \quad (5)$$

Where E_1 , and E_2 are constants. Clearly $E=E(x)$ is piecewise continuous in the interval $[0, 1]$. In the sequel, we shall consider the effect of this on bars of constant and varying cross sections.

Uniform and Varying Cross Sections

In the case of a bar of uniform cross section, the solution of the boundary value problem (1) is given by (3). Clearly, the deformation is invariant of the type of cross section whether circular, elliptical or rectangular for the same value of cross sectional area. For any planar figure, the cross sectional area at a point x in $[0, L]$ is given by (Borokinni 2012)

$$A(x) = (ax + b)(cx + d); \quad 0 \leq x \leq L, \quad (6)$$

Where a , b , c and d are constants.

Finite Element Model

Consider the governing equation for the axial deformation of a bar given by equation (1), the variational form which reduces the condition for differentiability for u is given by (Reddy 2006; Han and Reddy 1999);

$$0 = - \int_0^1 \left(EA \frac{dw}{dx} \frac{du}{dx} \right) dx + \int_0^1 Agw dx + \left(wEA \frac{du}{dx} \right) \Big|_0^1, \quad (7)$$

where w is the weight function, and $\rho = 1$.

Finite element method seeks solution of the form

$$U_n^e = \sum_{j=1}^n u_j^e \psi_j^e, \quad (8)$$

where u_j^e are the nodal values of u at the nodes and ψ_j^e are called the interpolation functions. e indicates the element's number after the domain has been discretized.

For the problem at hand, we will discretized the domain into two elements of equal length so that the nodes are $x_1=0$, $x_2=1/4$, $x_3=1/2$, $x_4=3/4$ and $x_5=1$.

For an arbitrary element e , the weak form is

$$0 = - \int_{x_e}^{x_{e+1}} \left(EA \frac{dw}{dx} \frac{du}{dx} \right) dx + \int_{x_e}^{x_{e+1}} Agw dx + \left(wEA \frac{du}{dx} \right) \Big|_{x_e}^{x_{e+1}}. \quad (9)$$

By substituting (8) in (9) and taking $w = \psi_j^e$ we have finite element model given by;

$$\sum_{j=1}^n K_{ij}^e u_j^e = f_i^e + Q_i^e; \quad (i = 1, \dots, n), \quad (10)$$

where Q_i^e are expression due to the boundary of the interfaces of the bar, and

$$K_{ij}^e = \int_{x_e}^{x_{e+1}} \left(EA \frac{d\psi_i^e}{dx} \frac{d\psi_j^e}{dx} \right) dx, \quad f_i^e = \int_{x_e}^{x_{e+1}} Ag\psi_i^e(x) dx. \quad (11)$$

We will use quadratic element method by choosing U_h^e as a quadratic function of the form

$$U_h^e(x) = c_1^e + c_2^e x + c_3^e x^2. \quad (12)$$

We will determine the interpolation functions ψ_i^e by expressing c_i^e in terms of the nodal values u_i^e . This implies that we will solve the system of equations

$$u_h^e(x_i^e) = \sum_{j=1}^3 c_j^e (x_i^e)^{j-1}, \quad (i = 1, 2, 3). \quad (13)$$

The interpolations are;

$$\psi_1^1(x) = 1 - 6x + 8x^2, \quad \psi_2^1(x) = 8x - 16x^2, \quad \psi_3^1(x) = 8x^2 - 2x \quad (14)$$

and

$$\psi_1^2(x) = 6 - 14x + 8x^2, \quad \psi_2^2(x) = -8x + 24x - 16x^2, \quad \psi_3^2(x) = 3 - 10x + 8x^2. \quad (15)$$

We will use the local indices to assemble the elements, where u_i^e is the nodal value at index i in element e . The assembly equation then becomes;

$$\begin{pmatrix} K_{11}^1 & K_{12}^1 & K_{13}^1 & 0 & 0 \\ K_{21}^1 & K_{22}^1 & K_{23}^1 & 0 & 0 \\ K_{31}^1 & K_{32}^1 & K_{33}^1 + K_{11}^2 & K_{12}^2 & K_{13}^2 \\ 0 & 0 & K_{21}^2 & K_{22}^2 & K_{23}^2 \\ 0 & 0 & K_{31}^2 & K_{32}^2 & K_{33}^2 \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \\ U_5 \end{pmatrix} = \begin{pmatrix} f_1^1 \\ f_2^1 \\ f_3^1 + f_1^2 \\ f_2^2 \\ f_3^2 \end{pmatrix} + \begin{pmatrix} Q_1^1 \\ Q_2^1 \\ Q_3^1 + Q_1^2 \\ Q_2^2 \\ Q_3^2 \end{pmatrix}, \quad (16)$$

where

$$u_1^1 = U_1, u_2^1 = U_2, u_3^1 = u_1^2 = U_3, u_2^2 = U_4, u_3^2 = U_5.$$

We will solve the matrix equation (16) for U_i , ($i=1, 2, \dots, 5$). From the boundary condition (2), $U_5 = 0$, $Q_2^1 = 0$, $Q_2^2 = 0$, $Q_3^1 + Q_1^2 = 0$ and $Q_1^1 = P$.

On homogenization of the boundary value problem (1) and (2), and assuming $\rho = 1$ we have (Akinola 1992)

$$\frac{d}{dx} \left(\left\langle \frac{1}{E} \right\rangle^{-1} A \frac{d \langle u \rangle}{dx} \right) + gA = 0; \quad 0 < x < L \quad (17)$$

$$\langle u \rangle(L) = 0; \quad \left(\left\langle \frac{1}{E} \right\rangle^{-1} A \frac{du}{dx} \right)_{x=0} = -P, \quad (18)$$

Where $\left\langle \frac{1}{E} \right\rangle = \int_0^1 \frac{1}{E(x)} dx$, and $\langle u \rangle$ is called effective or average solution. Let

$\langle u \rangle(x) = v(x)$ and $L = 1$, then for uniform cross sectional area we have;

$$v(x) = \frac{g(L^2 - x^2)}{2h} + \frac{P(L - x)}{hA}, \quad (19)$$

where $h = \langle \frac{1}{E} \rangle^{-1}$. For n - different materials arranged in the bar, we have;

$$h = \langle \frac{1}{E} \rangle^{-1} = n \left(\sum_{i=1}^n \frac{1}{E_i} \right)^{-1}, \quad (20)$$

where E_i ($i=1, \dots, n$) are constants.

RESULTS AND DISCUSSION

For a bar of unit length and uniform cross section, the finite element solution to the boundary value problem (1) and (2) following Akinola et. al., (2011) is given by;

$$\begin{aligned} U_h(x) &= U_h^1(x) \\ &= \frac{1}{E} \left[\left(\frac{g}{2} + \frac{P}{A} \right) (1 - 6x + 8x^2) + \left(\frac{15g}{32} + \frac{3P}{4A} \right) (8x - 16x^2) \right. \\ &\quad \left. + \left(\frac{3g}{8} + \frac{P}{2A} \right) (8x^2 - 2x) \right]; \end{aligned}$$

$$0 \leq x \leq \frac{1}{2}. \quad (21)$$

$$\begin{aligned} U_h(x) &= U_h^2(x) \\ &= \frac{1}{E} \left[\left(\frac{3g}{8} + \frac{P}{2A} \right) (6 - 14x + 18x^2) \right. \\ &\quad \left. + \left(\frac{7g}{32} + \frac{P}{4A} \right) (-8 + 24x - 16x^2) \right]; \quad \frac{1}{2} \leq x \leq 1. \quad (22) \end{aligned}$$

On simplifying (18) and (19), we have

$$U_h(x) = \frac{1}{E} \left(\frac{g(1 - x^2)}{2} + \frac{P(1 - x)}{A} \right); \quad 0 \leq x \leq 1. \quad (23)$$

Clearly, the finite element method with two quadratic element gives the exact solution for the axial deformation of a homogeneous bar of uniform cross section.

Suppose the homogeneous bar is of varying cross section. Recall that we assume that the cross section varies in the form $A(x) = (ax + b)(cx + d)$ which can be transformed to a bar of varying circular cross section of the form

$$A(x) = q(x + k)^2, \quad (24)$$

where q and k are constants.

Suppose $q=1$ and $k=1$, then we have

$$A(x) = (x + 1)^2. \quad (25)$$

Thus from the boundary value problem (1) and (2), the exact solution for homogeneous bar of varying cross section is given by

$$u(x) = \frac{1-x}{2E(x+1)} \left[\frac{g}{3} (x^2 + 4x + 2) + P \right]. \quad (26)$$

Let us now determine the finite element solution for the axial deformation of a homogeneous bar of varying cross section. We will determine f_i^e and K_{ij}^e , where

$$f_i^e = g \int_{x_e}^{x_{e+1}} (x+1)^2 \psi_i^e(x) dx; \quad K_{ij}^e = E \int_{x_e}^{x_{e+1}} (x+1)^2 \frac{d\psi_i^e}{dx} \frac{d\psi_j^e}{dx} dx.$$

The assembly equation becomes;

$$E \begin{pmatrix} \frac{173}{30} & -\frac{103}{15} & \frac{11}{10} & 0 & 0 \\ -\frac{103}{15} & \frac{256}{15} & -\frac{51}{5} & -\frac{71}{5} & \frac{21}{10} \\ \frac{11}{10} & -\frac{51}{5} & \frac{106}{5} & \frac{496}{15} & -\frac{283}{15} \\ 0 & 0 & -\frac{71}{5} & \frac{289}{15} & \frac{583}{30} \\ 0 & 0 & \frac{21}{10} & -\frac{15}{15} & \frac{30}{30} \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \\ U_5 \end{pmatrix} = \begin{pmatrix} \frac{13g + 160P}{160} \\ \frac{160}{21g} \\ \frac{40}{89g} \\ \frac{240}{41g} \\ \frac{40}{53g + 160Q_3^2} \\ \frac{160}{160} \end{pmatrix}. \quad (27)$$

The solution of equation (27) (where $P = 1, g = 10$ and $E = 1$) is given by;

$$U_1 = 3.8345, \quad U_2 = 3.3612, \quad U_3 = 2.5279, \quad U_4 = 1.3956.$$

The finite element solution for the axial deformation of homogeneous bar of varying cross section is given by

$$U_h(x) = U_h^1(x) = 3.8345 - 1.1732x - 2.88x^2; \quad 0 \leq x \leq \frac{1}{2} \quad (28)$$

$$U_h(x) = U_h^2(x) = 4.0026 - 1.8962x - 2.1064x^2. \quad \frac{1}{2} \leq x \leq 1 \quad (29)$$

The table below compares the exact and finite element solution of a homogeneous bar of varying cross section $A = (x + 1)^2$, with $P = 1, g = 10, E = 1$ and $L = 1$.

Table 1. Axial Deformation of a Homogeneous Bar of Varying Cross Section

I	x_i	Finite Element solution	Exact solution
1	0.0000	3.8345	3.8333
2	0.1000	3.6883	3.6954
3	0.2000	3.4847	3.4889
4	0.3000	3.2233	3.2218
5	0.4000	2.9044	2.9000
6	0.5000	2.5279	2.5278
7	0.6000	2.1066	2.1083
8	0.7000	1.6431	1.6441
9	0.8000	1.1375	1.1370
10	0.9000	0.5898	0.5886
11	1.0000	0.0000	0.0000

Finite Element Solution for the Axial Deformation of Composite Bar of Uniform and Varying Cross Section Made of Two Materials

Following the earlier assumption made from (5) for a bar composed of different materials, and substituting this in (11) we have

$$K_{ij}^e = \int_{x_e}^{x_{e+1}} \left(E_e A \frac{d\psi_i^e}{dx} \frac{d\psi_j^e}{dx} \right) dx, \quad f_i^e = \int_{x_e}^{x_{e+1}} A g \psi_i^e(x) dx. \quad (30)$$

For a bar of uniform cross section, the assembly equation becomes;

$$A \begin{bmatrix} \frac{14}{3}E_1 & -\frac{16}{3}E_1 & \frac{2}{3}E_1 & 0 \\ -\frac{16}{3}E_1 & \frac{32}{3}E_1 & -\frac{16}{3}E_1 & 0 \\ \frac{2}{3}E_1 & -\frac{16}{3}E_1 & \frac{14}{3}(E_1 + E_2) & -\frac{16}{3}E_2 \\ 0 & 0 & -\frac{16}{3}E_2 & \frac{32}{3}E_2 \end{bmatrix} \begin{pmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \end{pmatrix} = \frac{1}{12} \begin{pmatrix} g + \frac{12P}{A} \\ 4g \\ 2g \\ 4g \end{pmatrix}. \quad (31)$$

where $U_5=0$. From the assembly equation (31), the nodal values are

$$U_1 = \frac{g(E_2 + 3E_1)}{8E_1E_2} + \frac{(E_1 + E_2)P}{2E_1E_2A}, \quad U_2 = \frac{3g(4E_2 + 3E_1)}{32E_1E_2} + \frac{(2E_1 + E_2)P}{4E_1E_2A},$$

$$U_3 = \frac{1}{E_2} \left(\frac{3g}{8} + \frac{P}{2A} \right), \quad U_4 = \frac{1}{E_2} \left(\frac{7g}{32} + \frac{P}{4A} \right). \quad (32)$$

Table 2 shows the finite element solution for the axial deformation of a composite bar of constant cross section made of two materials, where $E_1 = 1, E_2 = 2, g = 10, P = 1$ and $A = 1$.

Table 2: Axial Deformation of Composite bar of Uniform Cross Section

i	x_i	$U_1(E_1 = 1)$	$U_2(E_2 = 2)$	$v(x)$	U_{c_1}	U_{c_2}
1	0.0000	6.0000	3.0000	4.5000	5.1250	3.8750
2	0.1000	5.8500	2.9250	4.3875	4.3250	3.7250
3	0.2000	5.6000	2.8000	4.2000	3.6250	3.4750
4	0.3000	5.2500	2.6250	3.9375	3.0250	3.1500
5	0.4000	4.8000	2.4000	3.6050	2.5250	2.6750
6	0.5000	4.2500	2.1250	3.1875	2.1250	2.1250
7	0.6000	3.6000	1.8000	2.7000	1.8000	1.8000
8	0.7000	2.8500	1.4250	2.1375	1.4250	1.4250
9	0.8000	2.0000	1.0000	1.5000	1.0000	1.0000
10	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

From table 2, U_i ($i = 1, 2$) is the axial deformation of the homogeneous bar when the material characteristics is E_i , and U_{c_1} is the finite element solution for the axial deformation of a composite bar made of two materials with $E_1 = 1$ and $E_2 = 2$, and U_{c_2} is the finite element solution for the axial deformation of a composite bar with $E_1 = 2$ and $E_2 = 1$. $v(x)$ is the axial deformation of the homogenized bar of uniform cross section, and it is the solution of homogenized boundary value problem (17) and (18). Notice that $v(x) = \frac{U_1 + U_2}{2} = \frac{U_{c_1} + U_{c_2}}{2}$, which shows that homogenization could serve as way to verify the accuracy of the solution to the boundary value problem.

For axial deformation of composite bar of varying cross section we have assumed $A(x) = (x + 1)^2$. The assembly equation for this case becomes

$$\begin{bmatrix} \frac{173}{30}E_1 & -\frac{103}{15}E_1 & \frac{11}{10}E_1 & 0 \\ -\frac{103}{15}E_1 & \frac{256}{15}E_1 & -\frac{51}{5}E_1 & 0 \\ \frac{11}{10}E_1 & -\frac{51}{5}E_1 & \frac{(91E_1 + 121E_2)}{10} & -\frac{75}{5}E_2 \\ 0 & 0 & -\frac{71}{5}E_2 & \frac{496}{15}E_2 \end{bmatrix} \begin{pmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \end{pmatrix} = \begin{pmatrix} \frac{13g + 160P}{160} \\ \frac{160}{21g} \\ \frac{40}{89g} \\ \frac{240}{41g} \\ \frac{40}{53g + 160Q_3^2} \\ \frac{160}{160} \end{pmatrix}. \quad (33)$$

From the assembly equation, the nodal values are

$U_1 = 2.5705$, $U_2 = 2.0973$, $U_3 = 1.2640$, $U_4 = 0.6978$. The finite element solution is given by

$$U_h(x) = U_h^1(x) = 2.5705 - 1.1726x - 2.8808x^2, \quad 0 \leq x \leq \frac{1}{2} \quad (34)$$

$$U_h(x) = U_h^2(x) = 2.0016 - 0.9488x - 1.0528x^2, \quad \frac{1}{2} \leq x \leq 1. \quad (35)$$

Table 3 shows the finite element solutions of axial deformation of composite bar with varying cross section. The table shows results of the homogeneous bars (U_1 at $E = 1$ and U_2 at $E = 2$). Table 3 also shows result when the bar is homogenized, where the effective solution is given by

$$v(x) = \frac{1-x}{2h(x+1)} \left[\frac{g}{3} (x^2 + 4x + 2) + P \right], \quad (36)$$

Where $h = \langle \frac{1}{E} \rangle^{-1} = \frac{2E_1E_2}{E_1+E_2}$. From table 3, U_{C_1} is the finite element solution for the axial deformation of a composite bar made of two materials with $E_1 = 1$ and $E_2 = 2$, and U_{C_2} is the finite element solution for the axial deformation of a composite bar with $E_1 = 2$ and $E_2 = 1$, and $V(x)$ represents the average of U_{C_1} and U_{C_2} .

Table 3: Axial Deformation of Composite Bar of Varying Cross Section

i	x_i	U_1	U_2	$v(x)$	U_{C_1}	U_{C_2}	$V(x)$
1	0.0000	3.8345	1.9172	2.8750	2.5705	3.1812	2.8759
2	0.1000	3.6883	1.8442	2.7716	2.4244	3.1065	2.7655
3	0.2000	3.4847	1.7423	2.6167	2.2207	3.0034	2.6121
4	0.3000	3.2233	1.6117	2.4163	1.9594	2.8728	2.4161
5	0.4000	2.9044	1.4522	2.1750	1.6405	2.7143	2.1774
6	0.5000	2.5279	1.2640	1.8958	1.2640	2.5279	1.8960
7	0.6000	2.1066	1.0533	1.5813	1.0533	2.1066	1.5800
8	0.7000	1.6431	0.8216	1.2331	0.8216	1.6431	1.2324
9	0.8000	1.1375	0.5688	0.8528	0.5688	1.1375	0.8532
10	0.9000	0.5898	0.2949	0.4414	0.2949	0.5898	0.4424
11	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

It is obvious that arrangement of material in a bar affect the deformation of the bar. From table 3, when $E_1 = 1$ and $E_2 = 2$, the deformation at $x = 0$ is reduced when compared to the cases where $E_1 = 2$ and $E_2 = 1$. Also the homogenization serves the purpose of verifying the accuracy of the finite element method which can be observed from table 2 and table 3. From table 2 and table 3, it is clear that $V(x) = \frac{U_1+U_2}{2} = \frac{U_{C_1}+U_{C_2}}{2}$.

CONCLUSION

It has been shown that material locations in bars affect the axial deformation of bars. This work suggests to Engineers that appropriate composite bars can have equivalent or better effect when homogeneous bars are used. However, it should be noted that optimum location regime of materials is important. This is because materials that are arranged without prior knowledge of analysis of deformation of composite bars could be disastrous.

In cases where the exact solutions are difficult to obtain, homogenization principle has proved useful in determining the accuracy of the finite element method.

REFERENCES

Akinola, A. P. (1992). On tensor and the mechanical characteristics of a composite. *3rd symposium of reseach council of Zimbabwe*, (pp. 26-38). Zimbabwe.

- Akinola, A. P., Borokinni, A. S., Fadodun, O. O., & Olokuntoye, B. A. (2011). Finite element modeling of deformation in composite bar. *Ife Journal of Science* , 13 (2), 389-396.
- Borokinni, A. S. (2012). *Analysis of deformation of composite bars using finite element method*. Ile-Ife: Postgraduate school, Obafemi Awolowo University.
- Han, W., & Reddy, B. D. (1999). *Plasticity: Mathematical theory and numerical analysis*. Springer Verlag.
- Ramesh, B., & Senthivelan, T. (2010). Formability characteristics of aluminium based composites. *Int. J. Eng & Tech* , 2, 1-6.
- Reddy, J. N. (2006). *An introduction to the finite element method*. New York: McGraw-Hill.
- Sezen, H., & Moehle, J. (2004). Strength and deformation capacity of reinforced concrete columns with limited ductility. *13th WCEE*, (p. no. 279). Vancouver.
- Theodore, R. T. (1974). *Energy principles in structural mechanics* (international edition ed.). Kogakusha: McGraw-Hill.
- Ying, W., Yuan, X., & Pengfei, W. (2010). Non-linear finite element analysis of steel-concrete composite-filled tubular column joints. *Int. J. Nonlinear Science* , 9 (3), 341-348.

PHYTOCHEMISTRY, PROXIMATE AND MINERAL INVESTIGATIONS OF WHOLE PLANT OF *EMILLIA COCCINEA* FROM SOUTH-EASTERN NIGERIA

Asekun, O.T., Asekunowo, A.K. & Familoni, O.B

Department of Chemistry, University of Lagos, Akoka, Yaba, Nigeria
oasekun@unilag.edu.ng

ABSTRACT

Secondary metabolites, proximate analysis and mineral content of the methanol extracts of *Emillia coccinea*, an under-exploited plant used for skin infections in South-Eastern Nigeria was investigated using standard methods. The secondary metabolites in *Emilia coccinea* were flavonoids, phenols, alkaloid, cardiac glycosides, tannins, saponins, anthraquinones and sterols. The total protein, fats, carbohydrate, ash, and moisture content were carried out using the Association of Official Analytical Chemists methods. The proximate contents are as follows moisture, ash, fiber, protein, fats and carbohydrate in decreasing order. Elemental nutrients: Ca, Mg, Cu, K, Zn, Na, Fe Cr and Cd were analyzed using atomic absorption spectrometry; this revealed the presence of most of the nutrients in significant concentrations in the whole plant. The presence of these essential nutrients and minerals found in *E. coccinea* may suggest its utilization for medicinal applications in healthcare management systems, and in particular in management of skin infections.

Keywords: *Emilia coccinea*, medicinal values. Secondary metabolites, Proximate analysis, Nutrients.

INTRODUCTION

The increased rate of skin diseases among children and young adults in the world especially in Africa is alarming. Knowledge of the chemical constituents of plants will aid in discovery of new drugs and their therapeutic strength, hence, justify their use in folk medicine. *Emilia coccinea* (Asteraceae family) is an annual plant growing to 0.6 by 0.3m high in both tropical and temperate regions. It is known as ‘Odundun do’, ‘Odundun-owo’, or ‘Odundun-okun’ in Yoruba, and ‘Ogwu afo’ in Igbo. The leaves are eaten raw or stewed. In herbal medicine, the leaves and roots are used in the management of craw-craw, abscesses of the breast, yaws, lice, fever, ringworm, syphilis, hernia, gonorrhoea, measles, cough, jaundice and snakebite (Odugbemi, 2006). It is also used to treat ear infection (Tabuti *et al.*, 2003). Some bioactivities have been confirmed in the laboratory. These include anti-diarrhoeal, antimicrobial and fungicidal activities (Ogbebor and Adekunle, 2005; Ndip *et al.*, 2007).

Phytochemical screening has revealed the presence of alkaloids, tannin, saponin, steroids, terpenoids flavonoids and cardiac glycosides (Edeoga *et al.*, 2003; Mroczek *et al.*, 2004).

Mineral contents of the plant have not been reported.

METHODS

Collection and Preparation of Plant Materials

The whole plants of *Emilia coccinea* were collected from Imo State, Eastern part of Nigeria in March 2012. The plant was authenticated by Mr Odeho, University of Lagos Herbarium, washed, air-dried, pulverized and kept in airtight container until ready for use.

Extraction of Plant Material

100g pulverized whole plant of *E. coccinea* were defatted with n-hexane and extracted with methanol for 72hours and filtered. The filtrates were concentrated to dryness using *vacuo* at 40°C to obtain a crude dark brown extract.

Phytochemical Analysis

The tests were done to find the presence of the active phytochemical constituents (such as alkaloids, Phenols, tannin, cardiac glycosides, quinone, flavonoids, terpenoids, cardenolide, steroids, anthraquinones and saponin). The metabolites were determined by dissolving 2 g each of the methanol extract in different solvents and reagents. These were analyzed using methods described by Harbone (1984), Sofowora (1982) and Trease (1989).

Proximate Analysis

Analysis for proximate contents of the dried powder of *Emilia coccinea* was done by methods described by Association of Official for Analytical Chemistry-AOAC (1999). The sample was analyzed for moisture contents, carbohydrates, crude fibre, crude protein, total ash, crude fats (lipids). The nitrogen value which is the precursor for protein of a substance was determined by micro – kjeldahl method. The nitrogen value was converted to protein by multiplying to a factor of 6.25. All the proximate values were reported in percentage (AOCS 2000; Okwu and Morah, 2004).

Mineral Analysis

The mineral content of the whole *E. coccinea* plant was investigated for its elemental composition by using atomic absorption spectrophotometer (AAS). The solution for the determination of mineral element was prepared by wet digestion using the aqua-regia method. 5g of the pulverized plant sample was accurately weighed into a crucible and transferred into a preheated muffle furnace at 550°C for 5 hours. To the ash sample, 10ml aqua regia (nitric acid and hydrochloric acid, 1:3) was added and made up to mark with de-ionized water in a 50ml beaker. The resulting solution was stirred and filtered through a whatman no 540 filter paper and the filtrate taken for analysis.

The elements magnesium, calcium, iron, copper, chromium, cadmium, potassium, sodium and zinc were determined from the above solution using the atomic absorption spectrophotometer Analyst 200 model.

Statistical Analysis

Results were presented in simple concentrations based on percentages and all data were expressed as Mean \pm S.D of three independent values for each variable.

RESULTS

The methanol extraction gave a sticky brown extract with a yield of 3.2%.

The results of phytochemical composition of the methanolic extract of whole plant of *Emilia coccinea* revealed the presence of alkaloids, flavonoids, saponins, tannins, anthraquinones, phenol, steroids and cardiac glycosides. Terpenoids, cardenolides and quinones were absent as shown in the plant (Table 1).

The proximate analysis of *E. coccinea* revealed that the whole plant contained: 9.98% protein, 30.96% crude fat, 0.37% moisture, 4.77% ash, 5.41% crude fiber and 56.90% carbohydrates (Table 2). The result showed that the plant has appreciable amount of carbohydrate and fat, 30.96% and 56.90% respectively.

The mineral composition analysis of *E. coccinea* revealed the presence of varying amounts of minerals in the order: Cu > Ca > Mg > Zn > Fe > Na > K as shown (Table 3). The mineral content which was reported for the first time, to the best of my knowledge, implies that the whole plant of *E. coccinea* contain appreciable amounts of minerals which could be valuable in the disease prevention related to malnutrition.

DISCUSSION

The result from proximate analysis of *E. coccinea* (Table 2) showed higher content of carbohydrate (56.90%) compared to leaves of *Amaranthus hybridus* (52.18%) (Akubugwo *et al.*, 2007). The high carbohydrate in this study agrees with that of Novak and Haslberger, (2000), which confirm the high nutritional values of *E. coccinea*. Carbohydrates are considered to contribute to the bioactivity of plants. Carbohydrates or high fibre fraction of diets, broadly classified as polysaccharides or indigestible carbohydrates are known to inhibit colonization of pathogenic microbial flora in the intestines (Guarner and Malagelada 2003), hence, contribute significantly to anti-fungal activity of the plant. The protein content suggests its importance in cellular function and tissue regeneration (Whitney and Rolfes 2005). High fats content (30.96%) shows the health benefits of this plant for malnourishment management. The moderate fibre (5.41%), very low moisture (0.37%) and (4.77%) total ash contents implies its digestibility and high absorption rate to provide energy requirements for cellular and gastrointestinal functions. Preliminary phytochemical screening of whole plant of *E. coccinea* reveals the presence of medicinally active phytochemicals which could be responsible for the bioactive properties of the plant. This result is in accordance with the result obtained (Edeoga, *et al.*, 2005), whose aqueous extract also revealed the presence of cardiac glycosides, flavonoids, saponins, alkaloids, steroids, tannins, alkaloid and terpenoid. It is also similar to another report from South-west Nigeria which reported alkaloids, flavonoids, phenols, tannins and saponins present in *E. coccinea*, however, anthraquinones, cardiac glycosides and sterols were not reported.

The presence of alkaloids in the plant may explain its antifungal activities; alkaloids are reported to have antifungal activities (Rios and Recio, 2005). The presence of anthraquinones also supports the use of the plant in treating fungal skin infection like crawl-crawl and ringworm (Lai *et al.*, 2004), hence, add to its medicinal value. The phenol and flavonoids found in this plant are known to be source of plant based antioxidants which protect the organs and tissues in the body from oxidative cell damage. The high poly-phenolic contents correlate with its wide range of physiological and health benefits such as, anti-allergic, antiviral, antibacterial, antifungal anti-inflammatory and anti-parasitic activities (Pietta, 2000; Yue *et al.*, 2004; Gerald *et al.*, 2007). Appreciable concentrations of various elements were revealed from the elemental analysis whole plant of *E.coccinea*. Calcium has 677mg/kg, magnesium 567mg/kg, copper 683mg/kg, zinc 113mg/kg, these elements were found in high concentration while potassium 29mg/kg, sodium 42mg/kg and iron 42mg/kg were found to be in moderate concentration when compared to other elements. The mineral composition was lower than the values reported (Faleye *et al.*, 2012). Magnesium helps maintain muscles, nerves, bones and zinc. The above observed elements have physiological importance and maintenance of cellular enzymatic functions; especially calcium. Oxygen transport and cellular activity are enhanced by elements such as copper and iron. Zinc found in significant amount in the plant is an important requirement in protein synthesis, normal body development and recovery from illnesses and management of diabetes (Muhammad *et al.*, 2011). Chromium which is involved in insulin regulation and sugar metabolism was absent in the plant. Cadmium was also absent. The ratio of sodium to potassium is however greater than one which is above the recommended value (FDN 2002), this might be of great concern due to the probability of increasing high blood pressure .

CONCLUSION

The results of this investigation justify the ethno-botanical use of *Emilia coccinea* plant. Hence, further work need to be done to quantify the secondary metabolites present and also to isolate the bioactive metabolites.

REFERENCES

- Akubugwo, I. E.; Obasi, N. A.; Chinyere, G. C. and Ugbogu A. E. (2007). Nutritional and chemical value of *Amaranthus hybridus* L. leaves from Afikpo, Nigeria, *African Journal of Biotechnology*, **6** (24): 2833-2839.
- AOAC (1999). Official Methods of Analysis of Association of Official Analytical Chemists, 16th edition, Washington DC, 1:600-792.
- AOCS (American oil chemist society) (2000). Official Methods of Analysis 5th edition. Association of official analytical chemists, Washington, DC, USA.
- Edeoga, H.O.; Okwu, D. E.; Mbaebie, B.O. (2005). Phytochemical constituents of some Nigerian medicinal plants, *African Journal of Biotechnology* **4** (7): 685-688
- Faleye, F.J.; Odeyemi, A.T.; Aderogba, A.A. (2012). Evaluation of the chemical composition and antimicrobial activities of three Nigerian medicinal plants. *Elixir Appl. Biology* **45**:7652-7656
- FND (2002). Food and nutrition board, Institute of medicine, National Academy of Sciences, Dietary reference intake for Energy, Carbohydrate, Fibre, Fat, Fatty acid, Cholesterol, Protein and Amino acid (micro-nutrients) www.nap.edu
- Gerald, N. T.; Jules, R. K.; Donatien, G. (2007). Antidiarrhoeal and antimicrobial activities of *Emilia coccinea* (Sims) G. Don extracts. *Journal of Ethnopharmacology*, **112**(2): 278–283.
- Guarner, F. and Malagelada, J. R. (2003). Gut flora in health and disease. *The Lancet*, **361**(9356): 512-519
- Harborne, J.B. (1973). *Phytochemical Methods*, Chapman and Hall limited. London: 11 – 113.
- Lai, C.K; Poon, W.T; Chan, A.Y.W; Chan, K.W, Tse, K.C; Chan, T.M; Lai, K.N. (2004). Aggravation of non-steroidal anti-inflammatory drug-induced hepatitis and acute renal failure for slimming drug containing anthraquinones, *Nephrol Dial Transplant*, **19**(7):1916-1917
- Muhammad, A.; Dangoggo, S. M.; Tsafe, A. I.; Itodo, A. U. and Atiku, F. A. (2011). Proximate, mineral and anti-nutritional factors of Gardenia aqualla (Gauden dutse) fruit pulp. *In Pakistan J Nur*, **10**(6): 577-581
- Mroczeka, K.; Ndjokob, K. G.; Kurt, H. (2004). On-line structure characterization of pyrrolizidine alkaloids in *Onosma stellulatum* and *Emilia coccinea* by liquid chromatography–ion-trap mass spectrometry. *Journal of Chromatography*, **1056**: 91–97
- Ndip, R. N.; Malange, T. A. E; Mbulla, S. M.; Luma, H. N.; Agnes, M.; Ndip, L. M.; Nyongbela, K.; Wirmum, C.; Efange, S. M. N. (2007). In vitro anti- Helicobacter pylori activity of extracts of selected medicinal plants from North West Cameroon, *J. Ethnopham.* **114**: 452-457.
- Novak, W. K., and Haslberger, A. G. (2000). Substantial equivalence of antinutrients and inherent plant toxins in genetically modified novel foods. *Food and Chemical Toxicology*, **38**(6): 473-483.
- Odugbemi, T. (2006). *Outlines and Pictures of Medicinal Plants from Nigeria*. 1st Edn., University of Lagos Press, Nigeria, ISBN: 978-38235-9-0: 283.
- Ogbebor, N. and Adekunle, A. T. (2005). Inhibition of conidial germination and mycelia growth of *Corynespora asiicola* (Berk and Curt) of rubber (*Hevea brasiliensis* muell. Arg.) using extracts of some plants, *African Journal of Biotechnol.*, **4**: 996-1000.
- Okwu, D. E. and Morah, F. N. (2004). Mineral and nutritive value of *Dennettia tripetala* fruits. *Fruits* **59**(6): 437 – 442.
- Pietta, P. G. (2000). Flavonoids as antioxidants. *Journal of natural products*, **63**(7), 1035-1042.
- Rios, J. L., and Recio, M. C. (2005), Medicinal plants and antimicrobial activity. *Journal of ethnopharmacology*, **100**(1): 80-84.
- Sofowora, A. O. (1982). *Medicinal Plants and Traditional Medicine in Africa*, Spectrum Books, Limited Ibadan, Nigeria, 6 & 154

- Tabuti, J.R.S., Lye, K.A. and Dhillion, S.S. (2003). Traditional herbal drugs of Bulamogi, Uganda: plant use and administration. *Journal of Ethnopharmacology* **88**: 19–44.
- Trease, G. E and Evans, M. D. (1989). A text book of Pharmacognosy. 13th Ed. Builler Tindall and Caussel London: 176-180
- Whitney, E. N. and Rolfes, S. R (2005). Understanding Nutrition, 10th Ed. Thomson/Wadsworth Publishing Co., Belmont, CA.
- Yue, M. E., Jiang, T. F., and Shi, Y. P. (2004). Fast determination of flavonoids in *Hippophae rhamnoides* and its medicinal preparation by capillary zone electrophoresis using dimethyl- β -cyclodextrin as modifier. *Talanta*, **62**(4): 695-699.

TABLES

Table 1: Phytochemical Compositions of Whole Plant of *Emilia coccinea*

Phytochemicals Compositions	Methanol extract
Alkaloids	+
Flavonoids	+
Saponins	+
Terpenoids	-
Tannins	+
Cardenolides	-
Anthraquinones	+
Phenols	+
Sterols	+
Quinones	-
Cardiac glycosides	+

Key: - = Absent; + = Present

Table 2: Proximate Composition of *Emilia coccinea*

Nutrients	Moisture content	Crude ash	Crude fibre	Protein	Crude fat	Total carbohydrate
Compositions (%)	0.37 ± 0.123	4.77 ± 0.006	5.41 ± 0.005	9.98 ± 0.040	30.96 ± 0.006	56.90 ± 0.250

Mean values of three determinations, mean ± S.D

Table 3: Mineral composition of *Emilia coccinea*

Elements	Concentration (ppm)
Calcium	0.677 ± 0.003
Magnesium	0.567 ± 0.003
Iron	0.042 ± 0.004
Copper	0.683 ± 0.035
Chromium	-
Potassium	0.029 ± 0.168
Cadmium	-
Zinc	0.113 ± 0.004
Sodium	0.042 ± 0.005

Mean values of three determinations, mean ± S.D

A FLEXIBLE COLUMN-BASED ACCESS CONTROL MODEL FOR CONVENTIONAL MEDICAL RECORD

Nureni A. Azeez, Adefemi F. Olayinka & E.P Fasina
Department of Computer Sciences, University of Lagos, Nigeria
nazeez@unilag.edu.ng

ABSTRACT

Patient Medical Record is undoubtedly known to contain sensitive information and should therefore be guarded against any form of vulnerable attack. The motive behind Conventional Medical Record (CMR) is to electronically gather information that has to do with patients from different departments in any given hospital, medical insurance company or atypical standard clinic. Obviously, CMR has provided in no small measure various benefits for health services through optimum savings in terms of cost, efficiency, reasonable turnaround time, precision and speed. Despite these benefits, CMR poses great security and privacy challenges due to the fact that all patients' medical records are maintained and sustained in a centralised system which as a result may inadvertently, deliberately and carelessly be accessed, modified, manipulated, altered or misused by illegal and unauthorised parties. To circumvent these challenges therefore, the authors propose a Flexible Column-Based Access Control (FCBAC) Model for CMR. This model is proposed since CMR has its sensitive information stored in columns. The objective is to achieve privacy and security of patients' data by enforcing access restrictions and control policies on sensitive and valuable information in columns. The paper describes the design of a novel and efficient architecture which was used to investigate and implement FCBAC. A database of CMR records is used to depict a partial implementation of this scheme and the results obtained showed the efficiency of FCBAC in securing patient information. The prototype was implemented using Java Runtime Environment 1.7.0.7 (32-bit) for the workflows that define the prototype's task. The results show that the prototype is effective, reliable and efficient as aimed at achieving proposed framework for access control, security and privacy.

Keywords: Patient, Medical record, Privacy, Access control, Column-based.

INTRODUCTION

No nation in the globe will take with levity, the security of its patient's information in the hospital be it a private or government owned. The sensitive nature of the medical information regarding any patient has undoubtedly created a serious research forum for many security experts in the area of electronic health care system. Prominent among the approaches being employed to handle this challenge include but not limited to role based access control (RBAC) (Zhao & Chadwick, 2008), mandatory access control (MAC) (McLean, 2008), discretionary access control (DAC) and access control list (ACL). These are regarded as popular security models. Computer systems have been used to run multiple applications and serve multiple users since its invention. This in the long run, has led to heightened awareness of data security issues. System administrators and software developers have therefore focused on different kinds of access control to ensure that only authorized users are given access to certain data, resources or operations.

Availability, integrity and confidentiality are important features in information security. These features are great issues and concern both in the military and commercial sectors. Confidentiality has in no small measure received a great attention; this could be attributed to its main relevance in the military applications. Integrity however is most applicable and useful to both the

commercial and industrial applications. This is to ensure that data are protected and secured from alteration and modification by unauthorised users (McLean, 2008).

Information systems in other fields may also make availability of information its major concern. Thus the need for security models that handles these three concerns in health care systems quite well is needed. This project introduces another kind of security model that takes the three major concerns of information in an information system into consideration. This model is known as the Column Based Access Control Model which is aimed at handling security challenges in CMR.

Related Work

A lot of projects has been carried out and implemented for achieving security and privacy for patient information. South Africa (Health, 2010) and European Union (Epsos, 2010) are well known cases that could be easily referenced in this regard.

DAC as one of the prominent security models could not guarantee the required privacy. This is due to the fact that the database management cannot establish and provide adequate data protection on sensitive information that is contained in a column (Harrison&Ruzzo, 1976).

MAC (Jajodia, 1991) on the other hand can provide access control for databases at column or cell-level. The access control is however not flexible, therefore will not adapt to changes with time.

Some other approaches have been proposed for achieving access control and maintaining adequate security for patient's information (Jin &Ahn, 2009). Some of these approaches adopt RBAC security model which has inadequate feature to secure sensitive health related information (Lunt & Denning, 1990).

The structure of role, policy management and role permission in electronic health system are so complex (Yang &Barringer, 2007). Sensitive and vital information are usually placed and distributed in columns in electronic health database. Column based access control has the required capabilities to provide protection for information stored in a column.

To this end, the authors propose a flexible column-based access control model for conventional medical record. Few of the existing security models that have been adopted in the past for similar projects are explained hereunder.

a. Role Based Access Control

Role based access control was first implemented in 1992 by David Ferraiolo and Rick Kuhn and is presently the predominant model for advanced access control.(Sandhu R. S., Coyne, Feinstein, & Youman, 2014)

In order to ensure strong management and governance in an organization, a robust framework around access control is necessary. This can be attained using the Role Based Access Control (RBAC) framework and an enterprise-wide role definition system.

A role could be regarded as the foundation and basis for access control policy and principle. Roles are usually created by the system administrators depending on the job schedules and functions in a typical establishment. Permissions are granted to those roles and thereafter users are finally assigned the roles base on their job specifications in an organisation (Sandhu R. S., Coyne, Feinstein, & Youman, 1996).

Two main ways by which RBAC assigns permissions to any user are management role assignment policies and management role groups. Either of these methods assigns users with appropriate permissions in order to carry out their jobs. Another advanced method of assigning permissions to users is called the direct user role assignment (Microsoft, 2012). Figure 1 shows a graphical representation of RBAC.

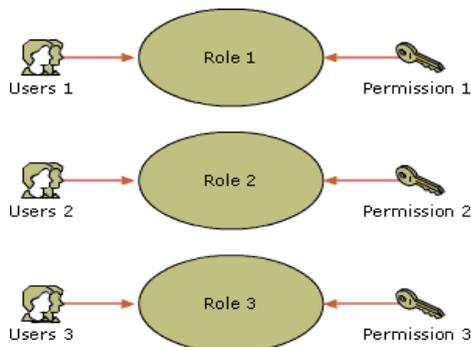


Figure 1 : graphical representation of the rbac model

b. Clark-Wilson Model

The Clark-Wilson model is a security model that was first described in a 1987 paper (A Comparison of Commercial and Military Computer Security Policies) by David D. Clark and David R. Wilson (A computer Scientist and an Accountant) and updated in 1989 (Blake, 2000). The model is primarily concerned with information integrity and this is maintained by preventing corruption of data items in a system as a result of error or malicious intent.

Clark and Wilson partitioned all data in a system into two: constrained data items (CDI) and unconstrained items (UDI). The (CDI) are objects that the integrity model is applied to and they must be protected while (UDI) are objects whose integrity is not assured by the model (Ge, Polack, & Laleau). Two approaches are therefore used for protection on the data items. The integrity verification procedure (IVP) which is the first procedure checks and ensures that data are very valid. The transformation procedure (TP) which is the second approach manipulates the data items from a valid state to another valid state.

If only a transformation procedure is able to change data items, the integrity of the data is maintained. Integrity enforcement systems usually require that all transformation procedures be logged, to provide an audit trail of data item changes.(Blake, 2000). The graphical representation of the Clark Wilson model is depicted in Figure 2.

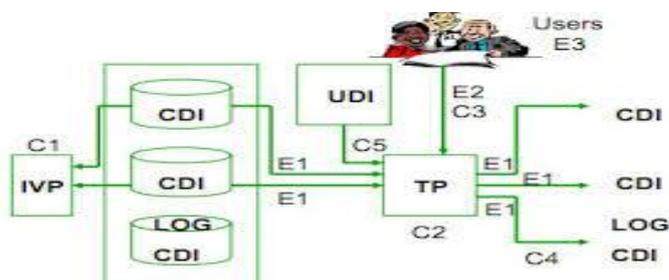


Figure 2: graphical representation of the Clark Wilson model

c. Lattice-Based Access Control (LBAC)

LBAC is a difficult access control security models based on the relationship and interaction between subjects (such as groups or organizations) and objects (such computers, and applications).

These models were developed by Bell and Lapadula and first formally defined by Denning in 1976. Although they were developed for military systems, the theory and concepts are however applicable to any system that involves information flow. These systems are basically concerned with confidentiality but can deal with some aspects of integrity (Sandhu R. S., Lattice-Based Access Control Models, 1993).

In this model, a lattice is adopted to state the security level that a particular object should have and which a subject might gain access to. The subject is permitted to access and retrieve any object if the level of the security of a subject is more than or the same as that of an object. The strength of this model is its attention to confidentiality. It also applies to integrity to some extent. Its weakness however is its tenuousness to availability of information.

d. Access Control List

According to (Ellen & Rouse, 2006), an access control list (ACL)

“is a table that tells a computer operating system which access rights a particular user has to a particular system object, such as a file directory or individual file. Each object to be accessed has a security attribute that identifies its access control list and this list has an entry for each system user with access privileges”

Anytime a subject makes a request for an operation on any object using ACL security model, the OS confirms the ACL for an appropriate and applicable entry to know if the demanded operation is allowed, authorised or permitted. For instance, if a file has an ACL that contains (Brad, edit), this would give Brad permission to edit the file.

It can further be explained and described as a list of Access Control Entries (ACE). Each ACL specifies and classifies a trustee and identifies as well the access permissions and rights denied or allowed for that particular trustee.

The security descriptor (contains the security information associated with a securable object) for a securable object can contain two types of ACLs, a DACL and a SACL (Microsoft, 2014).

ACL security models are used in file systems, networks and very recently, SQL implementations. It is evident therefore, that ACL models deal mainly with confidentiality and does not really involve itself with integrity or availability of information. Herein lays its strength and weakness.

e. Take-Grant Protection Model

This model is a security model mainly used to disprove and establish the protection of a computer system that adheres to certain rules.

The Take-Grant System is “a model that helps in determining the protection in a computer system. This system was introduced by Jones, Lipton, and Snyder to show that it is possible to decide on the safety of a computer system even when the number of subjects and objects are very large, or unbound. This can be accomplished in linear time based on the initial size of the system” (Denning, 1995).

The take-grant system models a safety and protection system which consists of a set of states and state transitions. The connections between the nodes of the system are shown by the directed graph. The nodes are illustrative as well as representative of the objects or subjects of the model (Denning, 1995).

f. Mandatory Access Control

MAC is considered as the most technical and strictest of all control levels (Techotopia, 2009) as a result of this feature MAC is mainly used by any form of government. MAC is a security model that prevents the tendency or ability of any resource owners have to deny or grant access to resource object in any given file. The criteria for MAS are usually defined by the system administrator. The access criteria are imposed by the OS or the security kernel which cannot be altered or manipulated by any user.

MAC is used both in the military and government agencies. It works by assigning a classification label to each file object. These classifications include top secret, secret and confidential. Whenever a user or device intends to access a resource, the security kernel and OS will confirm the credential of the entity to know if access permission will be allowed. To keep the users and

the objects up to date, MAC requires adequate and careful planning as well as continuous scheduling.

MAC can be compared with lower-level DAC which permits individual owners of resources to assign security controls and make their own policies.

g. Discretionary Access Control

Relating to computer security, discretionary access control (DAC) is a type of access control defined by the Trusted Computer System Evaluation Criteria "as a means of restricting access to objects based on the identity of subjects and/or groups to which they belong. The controls are discretionary in the sense that a subject with certain access permission is capable of passing that permission, often indirectly, on to any other subject (unless restrained by mandatory access control)".

This access control model is commonly discussed in contrast to mandatory access control (MAC, sometimes termed non-discretionary access control). Occasionally a system as a whole is said to have "discretionary" or "purely discretionary" access control as a way of saying that the system lacks mandatory access control. On the other hand, systems can be said to implement both MAC and DAC simultaneously, where DAC refers to one category of access controls that subjects can transfer among each other, and MAC refers to a second category of access controls that imposes constraints upon the first.

Research Questions

To investigate and address the challenges posed by inadequate security, unreliable and inefficient access control of conventional medical information, the following research questions were articulated:

- What are the notable consequences usually emanating from vulnerable conventional medical records?
- How can we ensure the protection and security of conventional medical information from any form of vulnerability by using a flexible columned-based approach?

The first research question has been attended to at both the introduction and literature review sections while the second research question has been addressed by the FCBAC architecture framework presented.

The diagram shown in Figure 3 illustrates the functionality of the secured FCBAC-CMR system. The implementation of the system starts out with the System Security Administrator. The administrator creates security policies for each relation, row and most importantly sensitive columns in the database. These policies are, of course, created as described by the clients (system owners).

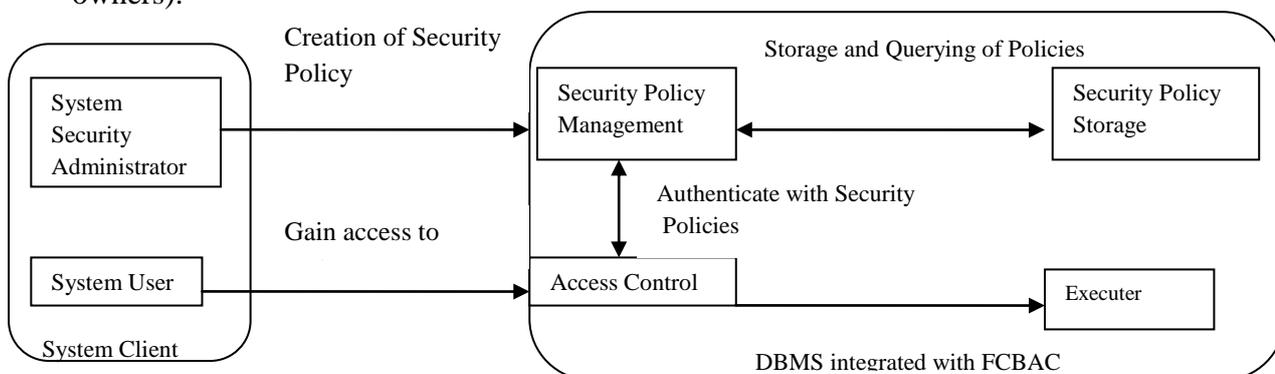


Figure 3: proposed architecture for FCBAC-CMR

The policies are stored in the database and when a sensitive column is requested by a system user, the policies defined for that column (if any) are called. Information returned to the requesting user, depends greatly on these policies and if any restrictions are made on that column for that particular user, such restrictions are respected and no results are returned. Other columns with no restrictions or valid requests are however returned to the requesting user as results of the user's query or executed depending on the query sent.

Hospital Workers' Roles and Permission

Few of the roles and permissions used for the initial implementation of the architecture are listed below:

1. Doctor : Add, Update and Delete Patient Records
2. Nurse: Update and View Patient Records
3. Pharmacist: Update and View Patient Records
4. Counsellor: View Patient Records
5. Patient : Update and View own Record
6. Insurance Companies and other External bodies: View Client Records

FCBAC-CMR Scheme

Our Dynamic Column Based Access Control Scheme comprises of these components:

- Users = {U_ID| U_ID is the identifier of a user in the system}
- Roles = {RL_ID| RL_ID is the identifier of a role in the system}
- Sensitive Columns (C) = {T₁.c₁, T₁.c₂, T₁.c₃... T₁.c_{m1}, T₂.c₁, T₂.c₂... T₂.c_{m2}... T_n.c_{mn}| T_i represents the relations or tables in the system database and set {T_i.c₁, T_i.c₂... T_n.c_{mi}} refers to columns in tables of the database, where 1 ≤ i ≤ n and m,n ∈ N}
- Operations = { SELECT, UPDATE, DELETE }

Now relating these components, we have:

1. User-Role Assignment (U-RL): U-RL= { (RL, {u₁... u_n}) | RL ∈ Roles, and u_i ∈ Users, where 1 ≤ i ≤ n }
2. Permissions (P) : P = {(c_i, fil_t) | c_i ∈ C, and fil_t ∈ FIL where FIL is a set of filters. fil_t represents a predicate in an SQL statement that results in "true" or "false" }. (c_i, fil_t) defines a permission that indicates that tuples satisfying predicate fil_t accessible over column c_i.
3. Permission-Operation Relation (POR): POR = {(p_i, o_g... o_j) | p_i ∈ P, o_i ∈ Operations}. POR defines the operation set a given permission allows.
4. User-Role-Permission-Operation Relation (URPO): URPO: (UURL) → PO.
URPO: {(s, (c,f), o) | s ∈ UURL, (a,f) ∈ P, and o ∈ 2^{operations}}

Implementing FCBAC-CMR in MySQL Database

A database of CMR records is used to depict a partial implementation of this scheme. This database contains 6 patients and 3 doctors. Few of the screenshots obtained are shown below.

```

Microsoft Windows [Version 6.2.9200]
(c) 2012 Microsoft Corporation. All rights reserved.

C:\Users\Mholu>mysql -uroot -pprincessa
Welcome to the MySQL monitor.  Commands end with ; or \g.
Your MySQL connection id is 7
Server version: 5.5.33 MySQL Community Server (GPL)

Copyright (c) 2000, 2013, Oracle and/or its affiliates. All rights reserved.

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affiliates. Other names may be trademarks of their respective
owners.

Type 'help;' or '\h' for help. Type '\c' to clear the current input statement.

mysql> use emr;
Database changed
mysql> select * from patients;
+----+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| PatientId | FirstName | LastName | DocID | Disease | Phone | age | address | LastConsultationDate | Sex |
+----+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| 1 | Bimbo | Akintola | 72 | Malaria | 80657877 | 14 | Gbagada, Lagos | March 31, 2012 | F |
| 2 | Sope | Morolakin | 12 | Typhoid | 80657689 | 43 | Ikeja, Lagos | July 12, 2009 | M |
| 3 | Bisola | Adesakin | 107 | Fever | 80455689 | 34 | Ikorodu, Lagos | April 12, 2014 | F |
| 4 | Uche | Ezenwa | 12 | Malaria | 806989777 | 19 | Akoka, Lagos | January 09, 2008 | M |
| 5 | Carol | White | 72 | Chicken Pox | 80234577 | 29 | Lekki Phase 1, Lagos | May 29, 2008 | F |
| 6 | Dasola | Pepple | 107 | Typhoid | 80298877 | 16 | Bariga, Lagos | May 06, 2014 | F |
+----+-----+-----+-----+-----+-----+-----+-----+-----+-----+
6 rows in set (0.00 sec)

mysql>
    
```

Figure 4: record of all patients in the system (queried by root user).

The root user is the only user allowed access to records of all patients. However, in this system, doctors are only allowed to view their patients. Some columns (age, sex) are also restricted from view of doctors. This is done by creating what are known in MYSQL as views for each doctor. This view disables the selection of other patients that are not handled by a particular doctor. So whenever a doctor queries patients, only patients handled by this doctor are returned. As shown below, doctors with ID 12, 72 and 107 can only view patients assigned to them.

```

C:\Users\Mholu>mysql -u12 -pprince
Welcome to the MySQL monitor.  Commands end with ; or \g.
Your MySQL connection id is 11
Server version: 5.5.33 MySQL Community Server (GPL)

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owners.

Type 'help;' or '\h' for help. Type '\c' to clear the current input statement.

mysql> use emr;
Database changed
mysql> select * from docview;
+----+-----+-----+-----+-----+
| PID | FirstName | LastName | Disease | Address |
+----+-----+-----+-----+-----+
| 2 | Sope | Morolakin | Typhoid | Ikeja, Lagos |
| 4 | Uche | Ezenwa | Malaria | Akoka, Lagos |
+----+-----+-----+-----+-----+
2 rows in set (0.02 sec)

mysql>
    
```

Figure 5: Doctor with ID 12 query result.

```

C:\Users\Mholu>mysql -u72 -pprince
Welcome to the MySQL monitor.  Commands end with ; or \g.
Your MySQL connection id is 12
Server version: 5.5.33 MySQL Community Server (GPL)

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owners.

Type 'help;' or '\h' for help. Type '\c' to clear the current input statement.

mysql> use emr;
Database changed
mysql> select * from docview;
+----+-----+-----+-----+-----+
| PID | FirstName | LastName | Disease | Address |
+----+-----+-----+-----+-----+
| 1 | Bimbo | Akintola | Malaria | Gbagada, Lagos |
| 5 | Carol | White | Chicken Pox | Lekki Phase 1, Lagos |
+----+-----+-----+-----+-----+
    
```

Fig 6: Doctor with ID 72 Query Result. Only patients handled by this doctor are returned.

```

C:\Users\Mholu>mysql -u107 -pprince
Welcome to the MySQL monitor.  Commands end with ; or \g.
Your MySQL connection id is 13
Server version: 5.5.33 MySQL Community Server (GPL)

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affiliates. Other names may be trademarks of their respective
owners.

Type 'help;' or '\h' for help. Type '\c' to clear the current input statement.

mysql> use emr;
Database changed
mysql> select * from docview;
+----+-----+-----+-----+-----+
| PID | FirstName | LastName | Disease | Address |
+----+-----+-----+-----+-----+
| 3   | Bisola   | Adesakin | Fever   | Ikorodu, Lagos |
| 6   | Dasola   | Pepple   | Typhoid | Bariga, Lagos |
+----+-----+-----+-----+-----+
2 rows in set (0.00 sec)

```

Fig 7: Doctor with ID 107 Query Result. Only patients handled by this doctor are returned.

The details of the implementation shall be well demonstrated during the oral presentation.

CONCLUSION

In this paper we propose, a Flexible Column-Based Access Control (FC-BAC) Model mainly to achieve effective and reliable access control in a CMR. Though, this research is at the initial stage of implementation. We plan to investigate further by carrying further implementation by using Oracle 10g in order to obtain a more reliable result. With little experimentation carried out so far, it is believed that a real life implementation of this proposed architecture will assist towards improving the security of health related information.

REFERENCES

- J. U. M.A. Harrison, W.L. Ruzzo, "Protection in operating systems," Communications of the ACM, vol. 19, no. 8, pp.461–471, 1976.
- L. L. D. Bell, "Secure computer systems: Mathematical foundations," The Mitre Corp., Bedford, Technical Report M74-244s, 1973.
- R. S. T.F. Lunt, D.E. Denning, "The seaview security model," IEEE Transactions on Software Engineering, vol. 16, no. 6, pp. 218–233, 1990.
- R. S. S. Jajodia, "Towards a multilevel secure relational data model," ACM SIGMOD Record, vol. 20, no. 2, pp. 50–59, 1991.
- N. L. J.W. Byun, E. Bertino, "Purpose based access control of complex data for privacy protection," in Proceedings of 10th ACM symposium on Access control models and technologies (SACMAT). ACM Press, 2005, pp. 102–110.
- N. Z. N. Yang, H. Barringer, "A purpose-based access control model," in Proceedings of 3rd International Symposium on Information Assurance and Security (IAS). ACM Press, 2007, pp. 143–148.
- H. H. J. Jin, G.J. Ahn, "Patient-centric authorization framework for sharing electronic health records," in Proceedings of 14th ACM Symposium on Access Control Models and Technologies (SACMAT). ACM Press, 2009, pp. 125–134.
- (2010) Homepage of integrating the healthcare enterprise (ihe). [Online]. Available: <http://www.ihe.net>
- (2010) Homepage of project epsos. [Online]. Available: <http://www.epsos.eu>
- Blake, S. Q. (2000, May 17). *New Page 1*. Retrieved July 23, 2014, from Indiana University Of Pennsylvania: <http://www.lib.iup.edu/comscisec/sanspapers/blake.htm>
- Denning. (1995, May 4). Take-Grant Systems. *Cryptography and Data Security*.
- Ellen, N., & Rouse, M. (2006, January). *TechTarget*. Retrieved August 7, 2014, from TechTarget: <http://searchsoftwarequality.techtarget.com/definition/access-control-list>

- Ge, X., Polack, F., & Laleau, R. (n.d.). Secure Databases: an Analysis of Clark-Wilson Model in a Database Environment. 5-6.
- Microsoft. (2012, December 5). *Understanding Role Based Access Control: Exchange 2013 Help*. Retrieved July 23, 2014, from Exchange: <http://technet.microsoft.com/en-us/library/dd298183%28v=exchg.150%29.aspx>
- Microsoft. (2014). *Windows Dev Center-Desktop*. Retrieved August 7, 2014, from Microsoft: <http://msdn.microsoft.com/en-us/library/windows/desktop/aa374872%28v=vs.85%29.aspx>
- Oracle. (2010, August). *Introducing the Role-Based Access Control Model-Oracle Identity Analytics User's Guide*. Retrieved July 23, 2014, from Oracle: http://docs.oracle.com/cd/E27119_01/doc.11113/e23125/usersguideprintable11.html#scrolltoc
- Sandhu, R. S. (1993, November). Lattice-Based Access Control Models. *IEEE Computer*, 26, 1-2.
- Sandhu, R. S., Coyne, E. J., Feinstein, H. L., & Youman, C. E. (1996, February). Role Based Access Control Models. 38-39.
- Sandhu, R. S., Coyne, E. J., Feinstein, H. L., & Youman, C. E. (2014, July 8). *Role Based Access Control and Role Based Security*. Retrieved July 23, 2014, from NIST: <http://csrc.nist.gov/groups/SNS/rbac/>
- Techtopia. (2009, July). *Mandatory, Discretionary, Role and Rule Based Access Control*. Retrieved August 7, 2014, from Techtopia: http://www.techtopia.com/index.php/Mandatory,_Discretionary,_Role_and_Rule_Based_Access_Control
- Zhao, G., & Chadwick, D. W. (2008). On the Modeling of Bell-LaPadula Security Policies using RBAC. *Workshop on Enabling Technologies: Infrastructure for Collaborative Enterprises, WETICE '08* (pp. 257-262). Rome: IEEE.
- McLean, J. (2008). *The Algebra of Security*. *IEEE Symposium on Security and Privacy* (p. 2). Oakland, CA: IEEE Computer Society.

KINETICS OF THE REACTIONS OF 2,4-DINITROFLUOROBEZENE WITH SOME PRIMARY AMINES IN TOLUENE AND TOLUENE-ETHANOL MIXTURES

A. I. Babatunde, N. A. Adebare, A. D. Adesina & A. M. Olusegun

Department of Chemistry, University of Lagos, Akoka, Lagos.

ABSTRACT

The kinetics of the reactions of 2,4-dinitrofluorobenzene (DNFB) with benzylamine, n-butylamine, cyclohexylamine and isopropylamine respectively were investigated. Kinetic measurements were made spectrophotometrically at the absorption maxima of the products of reaction. Rate constants were calculated from absorbance data by standard methods. The reactions of benzylamine, n-butylamine and cyclohexylamine were insensitive to amine concentrations while that of isopropylamine was base-catalysed. The base catalysis of the reaction involving the primary amine, isopropylamine is attributed to steric compression in the intermediate complex involving the amine, the reversion to reactants of which would produce charge neutralization and relief from strain, thereby lowering k_2/k_{-1} ratio. The addition of small amounts of ethanol to toluene medium in the reactions of DNFB with all the amines produced moderate rate increase contrary to expectation. The unusual increase in rate is attributed to an enhanced electrophilicity of the carbon atom at the reaction centre due to solute - solvent interaction of the leaving group, fluoride ion and hydrogen bond donor, ethanol in the first step of reaction. The mechanism of the reactions studied are rationalized in terms of the cyclic transition state involving four-membered ring for uncatalysed reactions and six-membered ring for the reaction catalysed by one molecule of amine.

Keywords: Nucleophilicity, Zwitterionic intermediate, Base catalysis, Solvent, Mechanism

INTRODUCTION

The kinetic studies of nucleophilic aromatic substitution are still an area of active research as they play a key role in the synthesis of chemical compounds for therapeutic usage. The widely accepted mechanism for nucleophilic aromatic substitution (S_NAr mechanism) is the addition - elimination mechanism involving the formation of intermediate complex, the formation or decomposition of which may be rate determining depending on the nature of the substrate, the leaving group capability, the nucleophile and most often the solvent (Terrier, 1991; Crampton et al., 2006; Isanbor and Babatunde, 2009; in Sun Koo, 2010). Solvents have been found to play a major role in many chemical and physical processes (reaction rates, selectivity, chemical equilibrium, position and intensity of spectral absorption bands) (Reichadt, 2003; Mohammad et al., 2011). The mechanism of S_NAr which is fairly well established in polar protic and polar aprotic solvents is subject to controversy in non-polar aprotic solvents due to anomalous kinetics such as quadratic dependence of reaction rate on nucleophile concentration and inverse temperature effects observed for reactions in the latter (Nudelman and Palleros, 1983; Banjoko and Bayeroju, 1988; Hirst, 1994). The mechanisms

proposed to rationalize the unusual observations for S_NAr in these solvents include the cyclic transition state (Banjoko and Babatunde, 2004) and dimer mechanism (Nudelman and Palleros, 1985). Kinetic studies involving added hydrogen bond donor solvent (HBD) at low concentrations to inert solvents have provided remarkable effects that could lead to better understanding of the mechanism of S_NAr in these media. Of particular interest is the observation of rate diminution in toluene and benzene at low concentration of HBD, methanol, for some S_NAr involving activated phenyl phenyl ethers and anisoles with primary and secondary amines.

In contrast, continuous rate increase was observed for the base catalysed reaction of 2,4,6-trinitro phenyl phenyl ether with aniline and that of 2,4-dinitrofluorobenzene with piperidine in similar mixed solvents. To gain further understanding of S_NAr mechanism in non-polar aprotic solvent and in particular the conflicting effect of HBD addition in such media, the kinetic study of 2,4-dinitrofluorobenzene with some primary amines were investigated.

METHODS

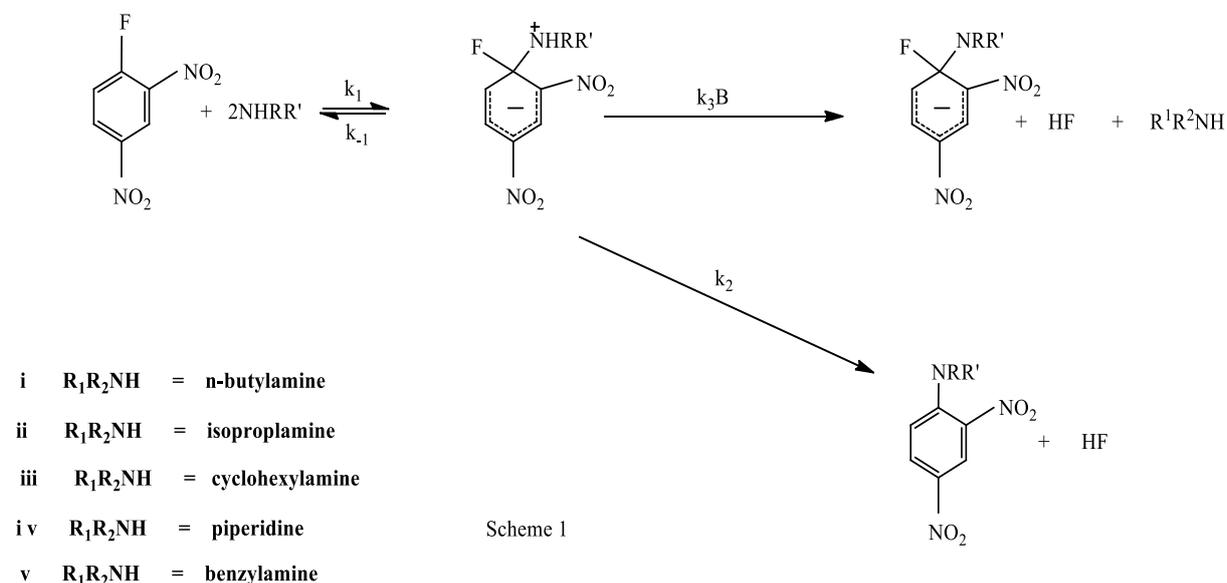
DNFB, amines and toluene were the purest available commercial samples. Kinetic measurements were made spectrophotometrically at the absorption maxima of the products of reaction using Varian Cary 50 or 100 UV-Vis spectrophotometers. Rate constants were measured at 30 °C under pseudo-first-order conditions with substrate concentrations of 1×10^{-4} - 1×10^{-5} mol dm⁻³ and were calculated by standard methods. Values are precise to $\pm 3\%$.

RESULTS AND DISCUSSION

The reactions of 2,4-dinitrofluorobenzene (DNFB) with the amines in toluene gave the expected products of substitution in > 95% yield. Kinetic measurements were made spectrophotometrically with the concentration of the amine in large excess of the substrate concentration and first-order kinetics were observed. Division of the pseudo-first-order coefficient by the appropriate concentration of the amine gave the second – order rate coefficient, k_A , as presented in Tables 1. The general substitution processes are interpreted by Scheme 1. The application of steady - state hypothesis to the mechanism depicted in Scheme 1 gives equation (1) when the amine acts both as the nucleophile and as the catalysing base.

$$k_A = \frac{k_1 k_2 + k_1 k_3 [B]}{k_{-1} + k_2 + k_3 [B]} \quad (1)$$

Both the formation of the intermediate and its decomposition can be rate determining. When the condition $k_2 + k_3^B [B] \gg k_{-1}$ holds, equation (1) reduces to $k_A = k_1$ such that the formation of the intermediate is rate limiting, otherwise the reaction proceeds through base catalysis.

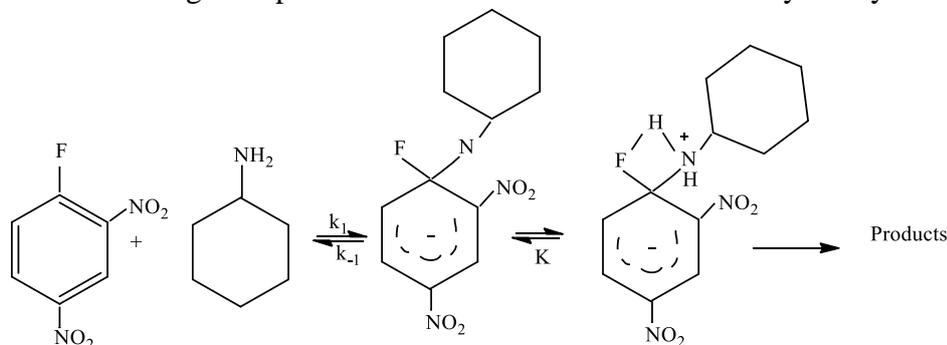


The values of second-order rate constants k_A for the reactions of DNFB with n-butylamine, benzylamine and cyclohexylamine in pure toluene were found to be nearly insensitive to the amine concentrations. The plot of k_A against amine concentration for benzylamine gave catalytic effectiveness (k_3/k_2) value of 29.27. Similar plots for n-butylamine and cyclohexylamine also gave low values of catalytic effectiveness. The implication of this is that these reactions are not base catalysed in line with Bunnett's deduction. For the reactions of DNFB with n-butylamine, benzylamine and cyclohexylamine, the condition of $k_{-1} \ll k_2 + k_3[B]$ holds for equation (1), therefore, equation (1) simplifies to equation (2).

$$k_A = k_1 \quad (2)$$

BASE CATALYSIS

One of the important factors associated with the occurrence of base catalysis in S_NAr is the ratio of k_2 to k_{-1} (k_2/k_{-1}). Reactions with $k_2/k_{-1} \ll 1$ are base catalysed while those with $k_2/k_{-1} \gg 1$ are not. Extensive kinetic studies have shown that k_2/k_{-1} ratio is frequently much lower for secondary amines compared with primary amines of comparable basicity, the consequent of which is that the reactions with the primary amines are often not base catalysed. In the present investigation, only the reaction of isopropylamine with DNFB is base catalysed while those of n-butylamine, benzylamine and cyclohexylamine with the same substrate were not. There is general agreement that the decomposition of intermediate complex to give products in an uncatalysed S_NAr reaction occurs through intramolecular hydrogen bonding involving a four membered ring as depicted in Scheme 2 for the reaction of cyclohexylamine with DNFB.



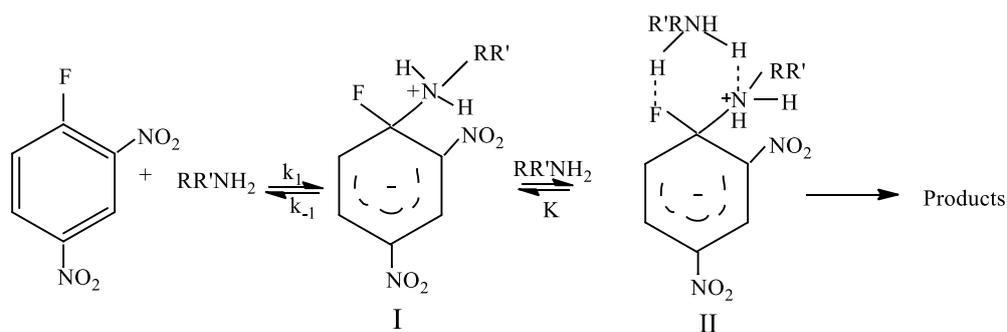
Scheme 2

The reactions of n-butylamine and benzylamine respectively, with DNFB in toluene can be rationalized using the above mechanism. These reactions are not base catalysed and the rate determining step is the first step involving the attack of nucleophile on the substrate. The order of first-order rate constant (Table 1) in the reactions is n-butylamine \gg benzylamine \gg cyclohexylamine. The pKa of these amines are relatively the same and the variation in their rate of reactions parallels the steric factors in the molecules which have been shown to decrease in the order n-butylamine \gg benzylamine \gg cyclohexylamine. The reaction of DNFB with isopropylamine in pure toluene is base catalysed where the condition of $k_{-1} \gg k_2 + k_3[B]$ holds for equation (1) to give equation (3).

$$k_A = \frac{k_1 k_2}{k_{-1}} + \frac{k_1 k_3 [B]}{k_{-1}} \quad (3)$$

The plot of k_A against amine concentration gave a linear graph shown in Figure 1. The catalytic effectiveness (k_3/k_2) calculated from the slope and intercept has a value of 119. The fluoride ion

is not particularly a poor leaving group in protic solvent but becomes so in non-polar aprotic solvent due to the high demand for solvation of the ion which cannot be provided by the solvent. The low value of k_2/k_{-1} ratio for isopropylamine can be attributed to steric compressions in the intermediate complex, I (Scheme 3). The reversion of the intermediate complex to reactants leads to a charge neutralization, thus k_{-1} is expected to increase strongly in non polar solvent like toluene, reducing the k_2/k_{-1} ratio unless a compensating effect of larger magnitude operates on k_2 . In the base catalysed step, another amine molecule assists the departure of the leaving group through hydrogen bonded transition state, II to give the final product. The cyclic transition state presents an alternative route for the decomposition of zwitterionic intermediate involved in S_NAr reactions without aggravating the level of electronic charges which cannot be supported in a non-polar medium like toluene. The concept has been used to rationalize the anomalous kinetics often observed for S_NAr reactions in non-polar aprotic solvents (Banjoko and Ezeani, 1982; Emokpae and Atazie, 2005).

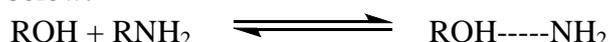


RR'NH₂ = isopropylamine

Scheme 3

Solvent Effect

The addition of small amounts of ethanol to toluene medium for the reactions of DNFB with all the studied amines produced moderate increase in reaction rates and the results are presented in Table 2. Many S_NAr reactions in non-polar and HBD mixed solvents have been found to display diminution in rate at low concentration of the latter when the leaving group on substrates were alkoxide and phenoxide ions (Nudelman and Palleros, 1994; Banjoko and Bbatunde, 2004). The diminution in rate observed by Nudelman and Palleros in the reaction of 2,6-dinitroanisole with cyclohexylamine in toluene - methanol mixtures was attributed to solute - solvent interaction in which the nucleophilicity of the amine is lowered. Similar observation by Banjoko and Babatunde (2004) of rate decrease in the reactions of phenyl-2,4,6-trinitrophenyl ether with cyclohexylamine and piperidine in toluene-methanol mixtures was interpreted on the basis of solute - solvent interaction. The formation of aggregate via hydrogen bonding between amines and methanol has been widely studied (Kollama and Allen, 1971). The methanol molecule acts as a proton donor to the amine resulting in the formation of aggregate of reduced nucleophilicity shown below.



It has been suggested (Javad et al., 2011; Habibi-Yangjeh, 2004; Macini et al., 2002) that in mixed solvents, solute - solvent interactions are much more complex than solvent - solvent interactions because of the possibility of preferential solvation by any of the solvent in the mixture and on the other hand, solvent - solvent interactions can strongly affect solute - solvent interactions. The amine - methanol aggregate formation in which the nucleophilicity of amine is unfavoured should result in rate decrease in S_NAr reactions, particularly in uncatalysed reaction where the first step is rate determining. Contrary to expectation, the addition of small amounts of

ethanol to toluene medium in the reaction of DNFB with n-butylamine, cyclohexylamine and benzylamine respectively produces moderate rate increase in the present study. In all these reactions, the first step is rate determining and whatever effect that is responsible for rate increase must be operational in that same step. To rationalise the observation in we suggest substrate - ethanol interaction in the form of hydrogen bond formation. This effect could strongly enhance the electrophilicity of carbon at the reaction center, hence, an increased rate. There is therefore an interplay of two factors of opposite effects in the first step of the reaction. The first being solute - solvent interaction of ethanol- amine and the second, solute - solvent interaction of fluorine (substrate) - ethanol. It is reasonable to assume the predominance of fluorine - hydrogen bond over nitrogen - hydrogen bond with the resultant moderate increase in reaction rate. This effect may not be observed when there is weak hydrogen bond or when its formation is sterically hindered.

CONCLUSION

Addition of hydrogen-bond donor (HBD) solvent, ethanol to toluene medium in S_NAr reactions of n-butylamine, cyclohexylamine, benzylamine and isopropylamine respectively with DNFB produced moderate rate increase. Only the reaction of isopropylamine is base catalysed while others are uncatalysed. The observed increase in rate is attributed to an enhanced electrophilicity of the carbon atom in reaction center due to solute - solvent interaction of the leaving group fluorine and ethanol.

REFERENCES

- Aziz Habibi-Yangjeh, (2004). A model for correlation of various solvatochromic parameters with composition in aqueous and organic binary solvent systems. *Bull. Korean Chem. Soc.*, Vol. 25, No. 8, 1165-1170.
- O. Banjoko, and A. I. Babatunde, (2004). Rationalization of the conflicting effects of hydrogen bond donor solvent on nucleophilic aromatic substitution reactions in non-polar aprotic solvent: reactions of phenyl 2,4,6-trinitrophenyl ether with primary and secondary amines in benzene-methanol mixtures. *Tetrahedron*, 60, 4645 – 4654.
- O. Banjoko and A. I. Bayeroju, (1988). Catalysis of nucleophilic aromatic substitution reactions in mixed solvents. Part 1. Reaction of phenyl-2,4,6-trinitrophenyl ether in benzene-methanol mixtures: strong evidence against dimer mechanism. *J. Chem. Soc. Perkin Trans. 2*, 1853-1857.
- M. R. Crampton, T. A. Emokpae and C. Isanbor, (2006). Electronic and steric effects in the S_NAr reactions of substituted anilines with 2,4-dinitrophenyl-2,4,6-trinitrophenyl ether in acetonitrile. *J. Phys. Org. Chem.*, 19, 75-80.
- T. A. Emokpae and N. V. Atasi, (2005). The influence of some steric and electronic effects on the mechanism of aromatic nucleophilic substitution reactions in non-polar solvent. *Int. J. Chem. Kinet.* 37, 744-750.
- J. Hirst, (1994). Mechanism of aromatic nucleophilic substitution reactions by amines in solvents of low relative permittivity, *J. Phys. Org. Chem.*, Vol. 7. No 2, 68-79.
- C. Isanbor and A. I. Babatunde, (2009). Kinetics of S_NAr reactions of 1-phenoxy-nitrobenzenes with aliphatic amines in toluene: ring substituent and solvent effects on reaction pathways. *J. Phys. Org. Chem.*, 22, 1078-1085.
- Javad Jamali - Paghaleh, Ali Reza Harifi - Mood and Mohammad Reza Gholami, (2011), Reaction Kinetics Investigation of 1-Fluoro-2,4-dinitrobenzene with Substituted Anilines in Ethyl acetate - Methanol Mixtures Using Linear and Nonlinear Free Energy Relationships, *J. Phys. Org. Chem.*, 24, 1095-1100

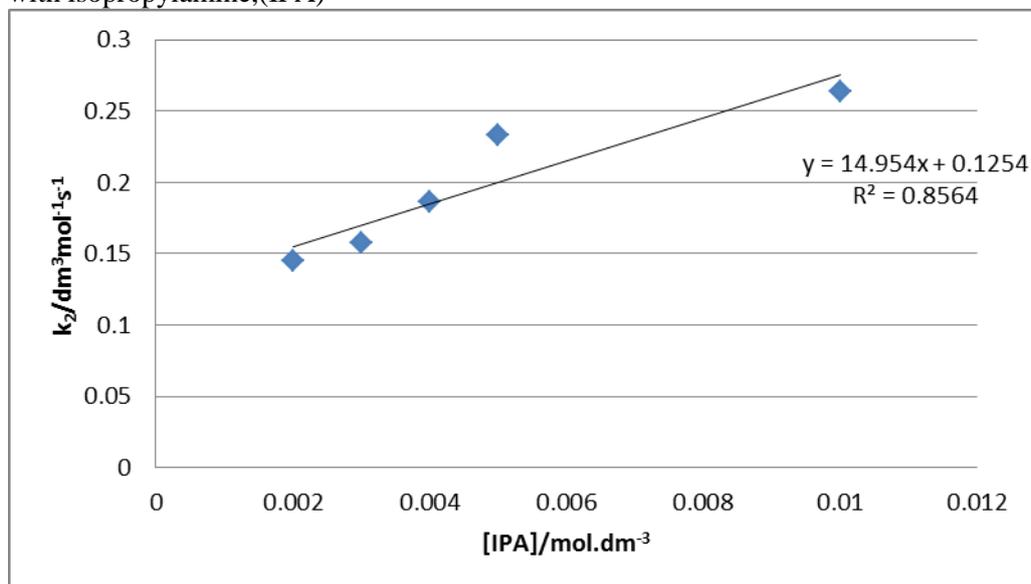
- P. M. Macini, G. G. Fortunato, C. Adam, L. R. Vottero and A. J. Terenzani, (2002). Specific and non-specific solvent effects on aromatic nucleophilic substitution. kinetics of the reaction of 1-fluoro-2,6-dinitrobenzene in binary solvent mixtures. *J. Phys. Org. Chem.*, 15, 258-269.
- N. Nudelman, N. Sbarbati and D. Palleros, (1983). Reactions of nitroanisoles. 4. Reactions of 2,4- and 2,6-dinitroanisole with cyclohexylamine. Evidence of a "dimer" nucleophile, *J. Org. Chem.*, 48, 1607-1612.
- C. Reichadt, (2003). Solvent and solvent effects in Organic Chemistry, 3rd edn, Wiley VCH, Weinheim.
- F. Terrier, (1991), Nucleophilic Aromatic Displacement. The Influence of Nitro Group. New York: VCH.
- Young Sun Kim, Hojune Choi, Kiyull Yang, Jong Keun Park and In Sun Koo. (2010), Kinetics and Mechanism of Nucleophilic Substitution Reaction of 4 - Substituted - 2,6 - dinitrobenzene with Benzylamines in MeOH - MeCN Mixtures, *Bull. Korean Chem. Soc.*, Vol. 31, No 11, 3279 - 3282.
- Young Sun Kim, Hojune Choi, Kiyull Yang, Jong Keun Park and In Sun Koo, (2010). Kinetics and mechanism of nucleophilic substitution reactions of 4-substituted-2,6-dinitrochlorobenzene with benzylamines in Meoh - MeCN mixtures, *Korean Chem. Soc.* Vol. 31, No. 11, 327
- Table 1. Kinetic data for the reaction of 2,4-dinitrofluorobenzene with n-butylamine (nBTA), benzylamine (BEA), cyclohexylamine (CHA) and isopropylamine (ISPA) in Toluene at 30°C

Table 2. Kinetic data for the reaction of 2,4-dinitrofluorobenzene with the studied amines in Toluene – Ethanol mixtures at 30°C.

[Amine] (mol dm ⁻³)	k ₂ (dm ³ mol ⁻¹ s ⁻¹)			
	CHA	nBTA	BEA	ISPA
0.001			0.0621	
0.002		0.327	0.0691	0.145
0.003		0.334	0.0702	0.158
0.004		0.342		0.186
0.005	0.053	0.400	0.0798	0.233
0.0075	0.054			
0.010	0.061		0.0804	0.264
0.015	0.063			
0.02	0.066			
0.03	0.073			

[Amine] (mol dm ⁻³)	Ethanol %	n-butylamine	Piperidine	Benzylamine	Isopropylamine
0.003	0.0	1.002	0.053	0.211	0.474
0.003	0.6	1.435	0.081	0.690	
0.003	0.8	1.667	0.089	0.707	0.386
0.003	1.0	2.018	0.071	0.766	0.346
0.003	2.0	2.213	0.094	0.803	0.683

Figure1 : The plot of k_A against amine concentration for the reaction of 2,4-dinitrofluorobenzene with isopropylamine, (IPA)



THE INHIBITIVE EFFECTS OF ANILINE AND SOME SUBSTITUTED ANILINES ON ACID CORROSION OF ALUMINIUM IN 1 M HCl SOLUTION

A. I. Babatunde, M. O. John, Ogunbanwo, C. M. & I. M. Akinnusi

Department of Chemistry, University of Lagos, Akoka, Lagos
ibitoniola@yahoo.com

ABSTRACT

The inhibitive effects of aniline, p-nitroaniline (PNA), m-nitroaniline (MNA), p-aminoacetophenone (PAAP), m-aminoacetophenone (MAAP) and m-anisidine (MASD) on acid corrosion of aluminium in 1 M HCl solution were investigated using chemical technique. All the additives displayed impressive inhibitory effects on acid corrosion of aluminium in the acid medium except PNA and MNA. The reduced protection efficiencies of PNA and MNA are attributable in one part to the reduced nucleophilicity of the amines by electron withdrawing capability of nitro group and on the other part, the partial reduction of same in acid with resultant heat of hydrogenation that aids the desorption of inhibitor molecules from aluminium metal surface. The inhibition efficiencies of the tested compound are attributed to the adsorption of their molecules on aluminium surface and the adsorption was found to obey kinetic/thermodynamic El-Awady adsorption isotherm. The results from the analysis of kinetic/thermodynamic parameters from the latter revealed that the mode of adsorption of inhibitors is physisorption, however, the physisorption of PAAP may be laced with chemisorption. It is suggested that each molecule of inhibitor occupies more than one active site.

Keywords: Adsorption isotherm, Surface coverage, Substituent effect, Physisorption, Corrodant

INTRODUCTION

Aluminum has been found very suitable for usage in various fields due to its special characteristics such as good appearance, low cost, excellent electrical and thermal conductivities, low density, low cost and good appearance. It is particularly suitable for neutral or oxidizing substances such as paraffin, alcohols, nitric acid, hydrogen peroxide, etc (Safak et al., 2012; Sherif and Park, 2005; Monsaviferal et al., 2013; Meng et al., 2009). The metal and its alloys are generally known to be good corrosion resistant materials, however, they still suffer from different forms of corrosion depending on the service environment.

The use of corrosion inhibitors amidst several other options for controlling the corrosion of the metal is one of the best methods for protecting metals against corrosion. Most of the well known acid inhibitors are organic compounds that contain nitrogen, sulphur, oxygen and multiple bonds in the molecules through which they are absorbed on the metal surface (Martinez and Stern, 2002). Research on organic corrosion inhibitors have extended to the study of the relationship of inhibitor structure to its adsorption properties and mechanisms of adsorption. The adsorption of chemical compound are influenced by the electronic structure of the inhibiting molecules, steric factors, aromaticity, electron density at the donor atoms and the presence of functional groups (Bentisi et al., 1999; McCafferty et al., 1970; Bentiss et al., 2005; El - Taib and Heikal, 1980; Ekpe et al., 1995; Metikos et al.1994).

The present study is aimed at investigating the electronic and steric effects of substituents on aniline derivatives in the inhibition of aluminium corrosion in 1M HCl solution using weight loss technique.

METHODS

Concentrated HCl (37%) and aniline derivatives were obtained as the purest commercial samples.

Weight - Loss Measurements. The weight - loss method of monitoring corrosion rate has been found suitable due to its simplicity and reliability (Popova et al., 2003). The weight - loss measurements were carried out with aluminium sheets which were mechanically press - cut into 3 cm by 2 cm coupons of 0.38mm thickness. The corrodant of 1 M HCl solution was prepared by dilution from analytical grade concentrated HCl of 37%. The coupons were used as supplied without further polishing. However, they were degreased in absolute ethanol, rinsed with double - distilled water and dried in acetone. The samples were immersed in the corrosive medium (80 cm³ of 1 M HCl) with and without the tested compounds. After 90 minutes, the samples were removed, washed with double - distilled water and dried. All runs were done in duplicate. The weight loss was calculated in grams as the difference between the initial weight prior to immersion, and weight after removal of the corrosion product.

The percentage inhibition of each additive on the corrosion of aluminum was calculated at the different times using equation 1:

$$\% \text{Inhibition} = \frac{W_c - W_{inh}}{W_c} \times 100 \quad (1)$$

Where W_c and W_{inh} are the uninhibited and inhibited weight losses, respectively.

RESULTS AND DISCUSSION

Effect of concentration of inhibitors on inhibition efficiency

The inhibition efficiencies for all studied compounds increase with increase in inhibitor concentration except for para- and meta-nitroaniline as shown in Table 1. Similar increase in inhibition efficiency with inhibitor concentration for organic molecules in the inhibition of metal corrosion are extensively reported in literature (Oguize, 2007; Ekpe et al., 1995; Fouda and Ellithy, 2009; Lagrenee et al., 2001; Sorkhabi, 2005; Safak, 2012). The inhibition of aluminum corrosion in the present study is attributed to the adsorption of inhibitor molecules on the metal surface thereby reducing the level of interaction between the metal surface and acidic medium.

The order of increase in inhibition efficiency for studied inhibitors as clearly reflected in Figure 1 is p-aminoacetophenine (PAAP) > m-aminoacetophenone (MAAP) > aniline > m-anisidine (MASD) > m-nitroaniline (MNA) > p-nitroaniline (PNA). The efficiency of an organic compound as a successful inhibitor has been shown to be dependent on its ability to be adsorbed on the metal surface which in turn depends on the electronic structure of the molecules due to the presence of appropriate functional groups, aromaticity, electron density at the donor atoms and orbital character of donating electrons. Table 1 shows that aniline and its derivatives exhibit excellent to fair inhibition of aluminium corrosion in 1 M HCl solution. The ability of aniline and its derivatives to inhibit the corrosion of aluminium is attributable to the basicity of the amino group in the compounds. Substituted anilines have different basicities depending on the electronic and steric effects of the substituent groups. Electron withdrawing group at para position decreases the basicity of aniline and this is reflected in the relatively lower inhibition efficiency of para- nitroaniline as compared with aniline. Apart from the inductive effect of nitrogen on aniline, the nitro compound is also partially reduced in acid medium.

It is worthy of note that para-aminoacetophenone inhibit the corrosion of aluminium remarkably better than aniline despite the presence of electropositive carbonyl carbon. One reasonable explanation for the unexpected observation could be that hyperconjugative effect of the methyl group adjacent to the electropositive carbon, promote the availability of carbonyl oxygen for

interaction with active center on the metal surface. Moreover, it has been suggested by many authors that adsorption of surface active organic compounds increase with increase of molecular weight (Rajeev et al.; 2012).

It is interesting to note that the meta-anisidine did not inhibit the corrosion of aluminium as much as aniline.

Adsorption parameters

It has been established that adsorption of molecules on metal surface is responsible for corrosion inhibition by organic molecules. The mode of adsorption and the adsorption isotherm that best describe experimental data are important in any corrosion study. The adsorption isotherm that best fit the surface coverage of molecules on metal surface provides important information on the interaction of molecules with metal surface.

Surface coverage (Θ) can be obtained using equation (2)

$$\Theta = \frac{IE (\%)}{100} \quad (2)$$

The application of Langmuir adsorption isotherm for the adsorption process did not give a satisfactory fitting but a better result was obtained using kinetic/thermodynamic isotherm of El-Awady as given in equation (3)

$$\log \frac{\Theta}{1 - \Theta} = \log K + y \log C \quad (3)$$

where C is the inhibitor concentration, Θ is the fraction of the metal surface covered with inhibitor molecule and K_{ads} is the equilibrium constant for the adsorption process. In El-Awady model, the number of active sites, y is included. Values of $1/y$ less than one implies multilayer adsorption while a value of $1/y$ greater than unity suggests that a given inhibitor molecule occupies more than one active site. The fitting of experimental data to El-Awady isotherm gave good correlation for aniline, para-aminoacetophenone and meta-aminoacetophenone and the calculated parameters are presented in Table 2.

The equilibrium constant for adsorption is related to the standard free energy of adsorption by equation (4)

$$K_{ads} = \frac{1}{55.5} \cdot \exp \left(\frac{-\Delta G_{ads}^{\circ}}{RT} \right) \quad (4)$$

where R is universal gas constant, T is the absolute temperature and 55.5 is the molar concentration of water in solution in mol dm^{-3} . The values of K_{ads} and ΔG_{ads}° for aniline are presented in Table 2. The negative value of ΔG_{ads}° is an indication of spontaneous adsorption of the molecules on metal surface. There is general agreement that values of ΔG_{ads}° of up to -20 kJ/mol signify physisorption in which charged adsorbate molecules are attracted to charged metallic surface, while values around -40 kJ/mol are attributed to chemisorption in which dative bonds are formed between inhibitor molecules and empty orbitals on metal surface. The values of ΔG_{ads}° for the inhibitors used in the present study ranged from 17.43 to 21.22 kJ mol^{-1} . The inhibition of aluminium corrosion by aniline and meta-aminoacetophenone can be said to be by physisorption while that of para-aminoacetophenone could be by mixed physisorption and chemisorption.

CONCLUSION

From the present study, it is concluded that:

- (i) All the tested compounds inhibit the corrosion of aluminium in 1 M HCl to different extents depending on the type of substituent present on the phenyl ring of amines.
- (ii) The thermodynamic adsorption parameters obtained support physisorption mode of adsorption for MNA, PNA, and MASD, MAAP but a mixture of physical and chemical adsorption for PAAP.
- (ii) Each inhibitor molecule interacted with more than one active sites.

REFERENCES

- F. Bentisi, M. Lebrini, M. Lagrenee, M. Traisnel, and J. C. Hornez, (1999). The corrosion inhibition of mild steel in acidic media by a new triazole derivative. *Corrosion Science*, 41, 789 - 803.
- F. Bentiss, M. Lebrini, and M. Lagrenee, (2005). Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/ 2,5 – bis (n-thienyl) -1,3,4-thiadiazoles/hydrochloric acid system. *Corrosion Science*, 47, 2915-2931.
- U.J.Ekpe, U.J. Ibok, B.I Ita, O.E. Offiong and E.E. Ebenzo, (1995). Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid. *Materials Chemistry and Physics*, 40, 87-93.
- A. S. Fouda and A. S. Ellithy, (2009). Inhibition effect of 4 - phenylthiazole derivatives on corrosion of 304 L stainless steel in HCl solution. *Corrosion Science*, 51, 868-875.
- E. McCafferty, V. Pravadic and A. C. Zettlemoyer, (1970). Dielectric behavior of adsorbed water films on the α -Fe₂O₃ surface. *Transactions of the Faraday Society*, 66, 1720-1731.
- G. Meng, L. Wei, T. Zhang, Y. Shao, F. Wang, C. Dong and X. Li, (2009). Effect of microcrystallization on pitting corrosion of pure aluminium. *Corrosion science* 51, 2151 – 2157.
- M. Metikos-Hukovic, Z.Grubic and E.Stupnisek-Lisae, (1994). Organic corrosion inhibitors for aluminium in perchloric acid. *Corrosion*, 50, 146-151.
- S. M. Monsaviferal, P.M. M, Nouri, M. M. Attar and B. Ramezanzadah, (2013). The effects of Zinc aluminium polyphosphate (ZPA) and Zinc aluminium polyphosphate (ZAPP) mixtures on corrosion inhibition performance of epoxy/polyamide coating, *J. Ind. Eng. Chem.* 19, 1031-1039.
- P. M. Niamien, H. A. Kouassi, A. T. Trokourey, F. K. Essy, D. Sissouma and Y. Bokra, (2012). Copper corrosion inhibition in 1 M HNO₃ by two benzimidazole derivatives. *International Scholar Network Material Science*, 1-5.
- E. E. Oguzie, (2007). Corrosion inhibition of aluminium in acid and alkaline media by *Sansevieria trifasciata* extract. *Corrosion Science*, 49, 1527-1539.
- A. Popova, E. Sokoloya, S. Raicheva and M. Christoy, (2003). AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives. *Corrosion Science*, 45, 33 - 58.
- P. Rajeev, A.O. Surendranathan, Ch. S.N. Murthy (2012). Corrosion mitigation of the oil well steels using organic inhibitors- A review. *Journal of material and environmental science* 3(5), 856- 869.
- S. Safak, B. Dran, A. Yurt and G. Turoglu, (2001). Schiff bases as inhibitor for aluminium in HCl solution. *Corrosion Science*, 54, 251-259.
- S. Safak, B. Duran, A. Yurt, G. Turkoglu, (2012). Schiff bases as corrosion inhibitor for aluminium in HCl solution. *Corrosion Science* 54, 251 – 259.
- E. M. Sherif and S. m. Park, (2005). Effects of 1, 5 – naphthalenediol on aluminium corrosion as a corrosion inhibitor in 0.5M NaCl. *Journal of Electrochemical society* 152, B205.

- H. A. Sorkhabi, Z. Ghasemi and D. Seifzadeh, (2005). The inhibition effect of some amino acids towards the corrosion of aluminium in 1 M HCl + 1 M H₂SO₄ solution. *Appl. Surf. Sci.*, 247, 408-418.
- F. El-Taib Heakal and S. Haruyama, (1980). Impedance studies of the inhibitive effect of benzotriazole on the corrosion of Copper in Sodium Chloride medium. *Corrosion Science*, 20, 887 – 898.

Table 1. Values of inhibition efficiency at different concentration for different inhibitors for the corrosion of aluminium in 1 M HCl solution at 30 °C after 90 minutes.

[inhibitor] (M)	Aniline	PAAP	MAAP	Meta Anisidine	MNA	PNA
7.5 x 10 ⁻⁴	20.90	65.50	43.30	12.01	15.98	10.79
1.0 x 10 ⁻³	25.30	70.70	46.30	21.86	11.46	7.00
2.0 x 10 ⁻³	30.70	74.90	54.00	28.85	7.88	5.02
3.0 x 10 ⁻³	38.8	80.90	60.40	49.22	5.59	4.58

Table 2. Calculated parameters from El-Awady isotherm.

[inhibitor] (M)	K _{ads}	ΔG _{ads} ^o	1/y	R ²
Aniline	18.36	-17.43 kJ mol ⁻¹	1.70	0.977
PAAP	82.60	-21.22 kJ mol ⁻¹	1.92	0.951
MAAP	25.46	-18.38 kJ mol ⁻¹	2.04	0.992

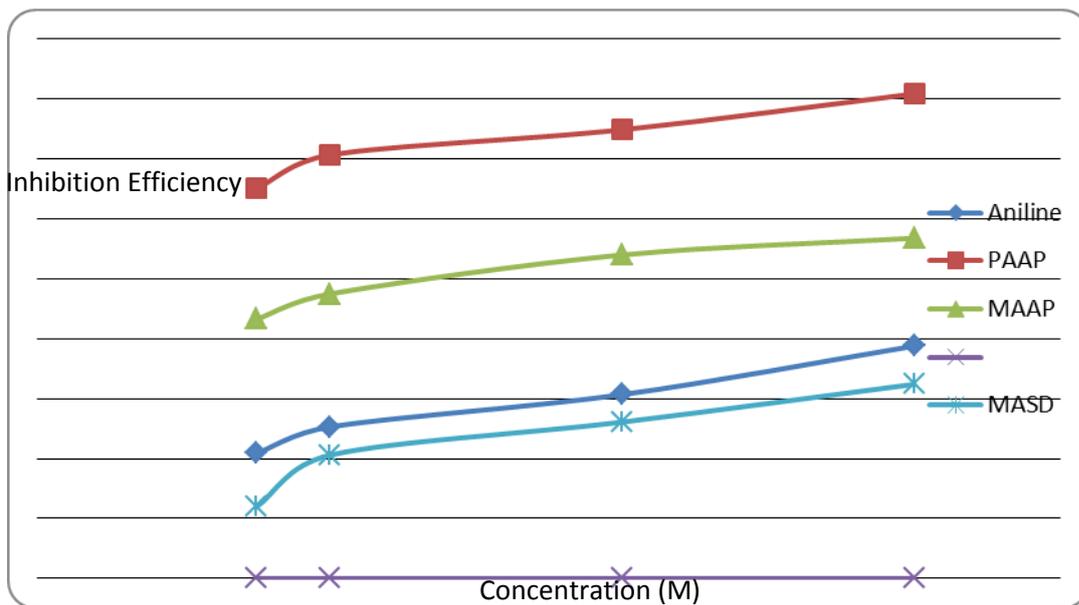


Figure 1. Plot of inhibition efficiency against inhibitor concentration for the corrosion of aluminium in 1M HCl solution containing different inhibitors at 30 °C after 90 minutes.

PAAP = para-aminoacetophenono; MAAP = meta-aminoacetophenone; MASD = meta-anisidine

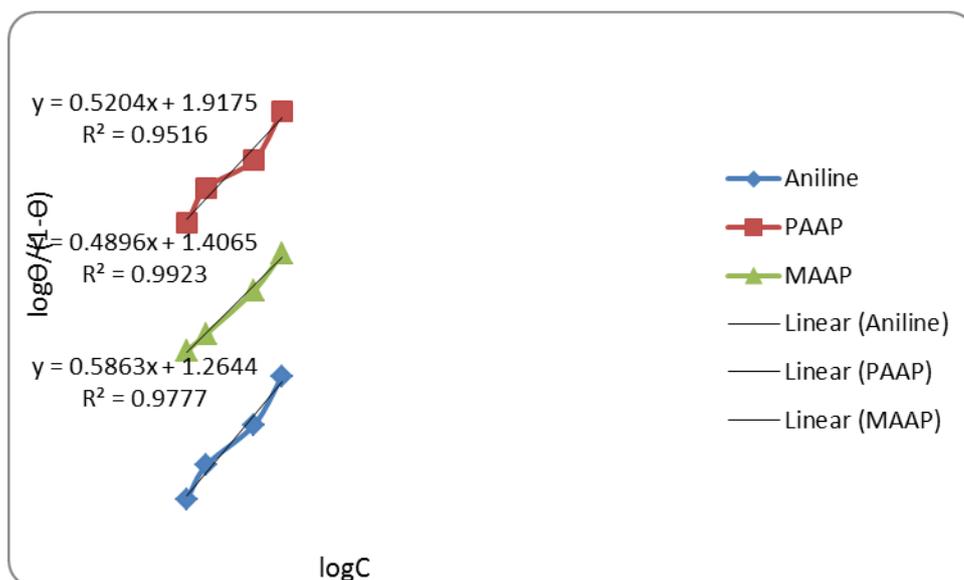


Figure 2. Langmuir adsorption isotherm for the corrosion of aluminium in 1M HCl solution containing different inhibitors at 30 °C after 90 minutes.

PAAP = para-aminoacetophenono; maap = meta-aminoacetophenone;

SYNTHESIS, STRUCTURAL INVESTIGATION, AND ANTIBACTERIAL STUDIES OF COPPER (II) COMPLEXES BASED ON AMINOPHENOL LIGANDS

F. N. Ejiah ¹, T. M. Fasina *¹, N. Revaprasadu ², F.T Ogunsola ³ & O.B. Familoni ¹

¹ Department of Chemistry, Faculty of Science, University of Lagos, Nigeria.

² Department of Chemistry, University of Zululand, South Africa

³ Department of Medical Microbiology, College of Medicine, University of Lagos, Nigeria.
tfasina@unilag.edu.ng, fejjiah@unilag.edu.ng

Abstract

The present study was carried out to investigate the effect of position of substituent on the antibacterial activities of the ligands and its metal complexes. A new series of copper(II) complexes (2-(2-hydroxybenzylideneamino)phenol)copper(II) (CuA), (3-(2-hydroxybenzylideneamino) phenol)copper(II) (CuB), (4-(2-hydroxybenzylideneamino) phenol)copper(II) (CuC) of Schiff base 2-hydroxybenzylidene-2-aminophenol (A), 2-hydroxybenzylidene-3-aminophenol (B), 2-hydroxybenzylidene-4-aminophenol (C) were synthesized and characterized on the basis of physical properties, elemental analysis, spectral (FT-IR, ¹H NMR, UV-Vis) and magnetic susceptibility measurements. The Schiff bases behave as bidentate ligands coordinating to metal through imine nitrogen and hydroxyl oxygen. All the complexes have square-planer geometry. The ligands as well as their metal complexes were evaluated for antibacterial activity against several bacterial strains, such as *E. coli*, *S. aureus*, *P. aeruginosa*, *B. cereus*, *E. faecalis* and *K. pneumonia*. It was found that metal complexes are more potent as compared to uncomplexed ligands.

Keywords: Antimicrobial agents, Copper (II), metal complex, Schiff base, aminophenol.

INTRODUCTION

Schiff bases obtained from salicylaldehyde and their metal complexes show a wide spectrum of antimicrobial properties (1-3). Antimicrobial activity is a property of both inorganic and organic substances, and the exploitation of such activity is a matter of considerable practical importance in the development of antiseptics, sanitizers, germicides, bactericides, sporicides, virucides and disinfectants (4). Schiff bases have played a great role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals (5). Metal complexes of Schiff bases are specifically of interest in bioinorganic chemistry because many of these complexes provide biological models in understanding the structure of biomolecules and biological processes (6). These complexes may statistically mimic the spectroscopic or other physical properties of an enzyme (7). Many researchers have studied the synthesis, characterization and structure activity relationship (SAR) of Schiff base metal complexes (8-11), but much work has not been reported on the effects of position of substituents on the Schiff base metal complexes of aminophenol derivatives. In line with this, a new series of copper (II) complexes with Schiff bases of 2-hydroxybenzylidene-2-aminophenol, A, 2-hydroxybenzylidene-3-aminophenol, B, 2-hydroxybenzylidene-4-aminophenol, C have been synthesized and characterized. Effects of position of substituents on the antimicrobial activity have been studied to determine the derivative that exhibited a better activity. This study will lay basis in further study of compounds with different derivatives in structure activity relationship. The stereochemistry of the complexes is reported for the first time.

METHODS

Materials

All reagents and solvents were of analar / spectroscopic grades and used without further purification. Ethanol, chloroform, dimethylsulfoxide, salicylaldehyde, 2-aminophenol, 3-aminophenol, 4-aminophenol, copper (II) chloride, were purchased from Aldrich-Sigma company.

Physical Measurements

Microanalytical data were obtained on a Perkin Elmer model 2400 series II CHNS/O elemental analyzer. Infrared (IR) spectra of the compounds were recorded on a Bruker FT-IR (ATR) tensor 27 spectrophotometer directly on samples of the compounds in the range 400 to 4000 cm^{-1} . $^1\text{H-NMR}$ spectra in DMSO-d_6 solution of the ligands were recorded on a Bruker Avance III 400 MHz. Chemical shifts were reported as δ relative to TMS as internal standard. Electronic absorption spectra of the compounds were recorded from 200 to 800nm on a freshly prepared CHCl_3 solution using a Cary Model 50 spectrophotometer. Melting points ($^\circ\text{C}$) were determined on a Reichert Thermovar melting-point apparatus and are uncorrected. Magnetic susceptibility measurements were made on powdered samples using a Sherwood Scientific magnetic susceptibility balance. $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as the calibrant and corrections for diamagnetism were calculated from Pascal's constants.

Synthesis of Schiff Bases

Equimolar quantities of salicylaldehyde and corresponding amine (10 mmol) were dissolved in ethanol (50ml) and stirred under reflux at 70°C for 6 h. The precipitate formed was separated by filtration, re-crystallized from ethanol, dried and stored in a desiccator.

Synthesis of Metal Complexes

An ethanolic solution (40 ml) of Schiff base (4 mmol) was mixed with an ethanolic solution (20 ml) of $\text{Cu}(\text{II})$ chloride (2 mmol). The solution was made slightly alkaline with triethylamine. The mixture was refluxed for 4 h. The solid product obtained was filtered hot, washed in ethanol and dried in vacuum.

Biological Studies

The Schiff bases and metal complexes were individually tested against a panel of standard microorganisms namely *Escherichia coli* (ATCC 8739), *Staphylococcus aureus* (ATCC 6538), *Pseudomonas aeruginosa* (ATCC 19582), *Bacillus cereus* (10702), *Enterococcus faecalis* (ATCC 29212) and *Kliformella pneumoniae* (ATCC 10031).

Disc diffusion assay

Antibacterial activity of Schiff bases and metal complexes were carried out in triplicate using the disc diffusion method (12). Molten Mueller-Hinton agar was inoculated with the bacteria suspension which had been adjusted to the 0.5 McFarland standard and poured into sterile 90 mm Petri dishes. Schiff bases and Metal complexes were dissolved in DMSO to obtain a final concentration of 10 mg/ml. Sterile Whatman No. 1 (6 mm) discs were separately impregnated with each sample to be tested and placed on the inoculated agar. The plates were incubated at 37°C for 24 h and the zones of inhibition measured at the end of the incubation period. Ampicillin was used as reference compound.

Minimum inhibitory concentration (MIC)

The minimum inhibitory concentration (MIC) of the Schiff bases and metal complexes were determined using the 96-well micro-plate dilution method (13). Serial plate concentrations of

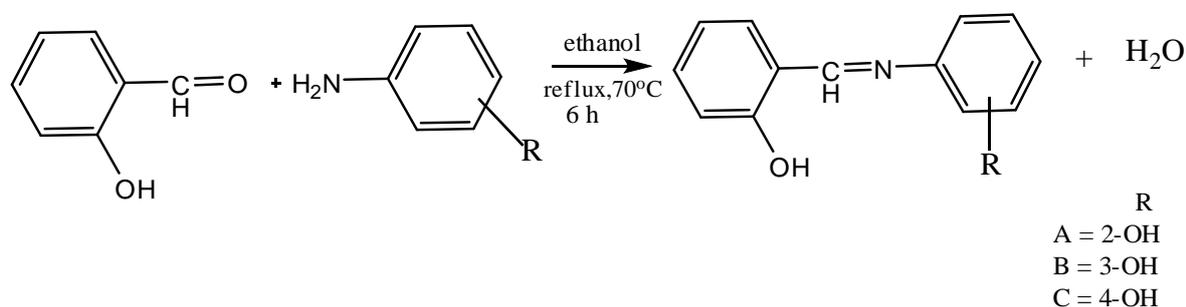
5.0, 2.5, 1.25, 0.625, 0.312, and 0.157, 0.078 and 0.039 mgmL⁻¹ were prepared for each compound. Each was inoculated with 108 cfu mL⁻¹ of 0.5 McFarland standard bacteria suspension and incubated for 24 h at 37°C. As an indicator of bacterial growth, 20 µL of 0.2 mgmL⁻¹ *p*-iodonitrotetrazolium solution (a colourless tetrazolium) was added to each well and incubated at 37°C for 30 min. Growing bacteria metabolise this salt to give a red product (formazan). Inhibition prevents this conversion resulting in a clear well. MIC values were recorded as the lowest concentration of compound preventing bacterial growth.

RESULTS AND DISCUSSION

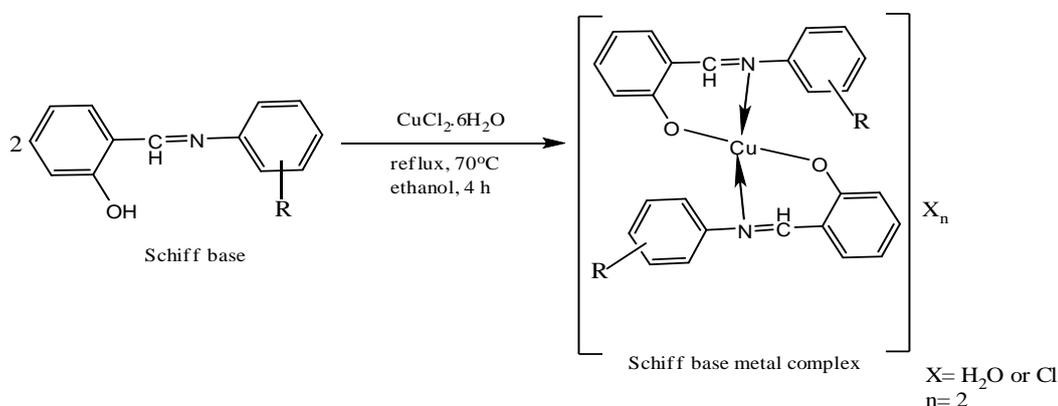
Synthesis

The Schiff base ligands were prepared by the reaction of salicylaldehyde and aminophenol in a 1:1 ratio stoichiometry as illustrated in **Scheme 1** below. Analytical and physical data is represented in **Table I**. The compounds were isolated in good yield. ¹H NMR data revealed that the Schiff bases were isolated while microanalysis confirmed the purity of the ligand.

Treatment of the ligands A, B and C with Cu(II) chloride yields complexes (**Scheme 2**) corresponding to the general formula [CuL(X)_n] where L = A, B or C, X = H₂O or Cl and n = 2. The analytical data show that the metal to ligand ratio is 2:1. The complexes were soluble in common organic solvents; chloroform, DMF, DMSO.



Scheme 1: Synthetic route to Schiff bases A – C



Scheme 2: Synthetic route to Schiff base metal complexes CuA –CuC

Table I: Physical properties and analytical data of synthesized compounds

Compound	Formula weight	Yield %	Color	M.pt °C	Micro-analytical data found(cald)		
					%C	%H	%N
A	C ₁₃ H ₁₁ NO ₂	74	Red	146-147	73.43(73.23)	6.44(6.57)	5.10(5.20)
CuA	C ₂₆ H ₂₀ Cl ₂ CuN ₂ O ₄	57	Green	Decomp>293	56.43(55.87)	2.96(3.61)	4.89(5.01)
B	C ₁₃ H ₁₁ NO ₂	71	Orange	82-83	73.01(73.23)	5.16(5.20)	6.57(6.57)
CuB	C ₂₆ H ₂₂ Cl ₂ CuN ₂ O ₄	61	Brown	Decomp>250	55.32(55.67)	3.97(3.95)	5.54(4.99)
C	C ₁₃ H ₁₁ NO ₂	65	Orange	98-99	73.23(73.23)	5.11(5.20)	6.61(6.57)
CuC	C ₂₆ H ₂₄ CuN ₂ O ₆	79	Brown	decomp>273	60.32(59.59)	4.95(4.62)	5.71(5.35)

Infra-red Spectroscopy

In order to study the binding mode of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. IR spectra bands of the ligands and their metal complexes are presented in **Table II**.

Table II: IR and ¹H-NMR spectra data of synthesized compounds

Compound	ν(C=N)	ν(C-O)	ν(O-H)	ν(Cu-N)	ν(Cu-O)	Chemical shift δ (ppm)	
						HC=N	OH
A	1616	1287	3040	-	-	8.69	9.11
CuA	1612	1268	3050	487	536	-	-
B	1584	1225	3294	-	-	8.38	8.77
CuB	1581	1190	-	442	532	-	-
C	1607	1272	3104	-	-	8.36	8.78
CuC	1601	1266	3204	513	540	-	-

Infrared spectra of the Schiff base ligands, A, B and C shows characteristics absorption bands in the 1616, 1584 and 1607 cm⁻¹ regions, assignable to C=N. These bands due to the azomethine nitrogens of the Schiff base underwent a shift to lower frequency 1612, 1581 and 1601 cm⁻¹ upon complexation, indicating the involvement of nitrogen of the azomethine group in coordination (14). The C-O band which occur at 1287, 1225 cm⁻¹ for the ligand A, B was moved to lower frequencies 1268, 1190 cm⁻¹ (CuA and CuB) after complexation which indicates that the shifts are due to the coordination of the phenolic oxygen of the ligand to the metal ion (15), it can be concluded that the Schiff base is a bidentate ligands coordinating *via* the azomethine N and the phenolic O. The broad band at 3204 cm⁻¹ for CuC complex indicates the presence of coordinated water molecule. The new bands observed in the complexes in the region 442-513 and 532-536 cm⁻¹ were assigned to Cu – N and Cu – O bonds respectively (16).

3.3 ¹H NMR Spectra

The ¹H NMR spectrum of the ligands (A, B and C) in DMSO show signal at 8.36, 8.38, 8.69 ppm (s, 1H, N=C-H) assigned to the azomethine protons. The peaks at 8.77, 8.78, 9.11 ppm is attributed to phenolic protons (s, 1H, phenolic –OH) respectively.

3.4 Magnetic Susceptibility Measurements and Electronic Absorption Spectra

The electronic spectra and magnetic moments of Schiff bases and their metal complexes are presented in **Table III**. The electronic spectra of the free ligands and its metal complexes were studied in chloroform solution. In all the spectra of the ligand, three absorption bands appear in the region 240-268nm, 270-303nm and 343-355nm assigned to π→π* and n→π*. Electronic

spectra of Cu(II) complexes showed absorption bands in the region 306-328nm assigned to charge transfer (CT) and 391 – 446 nm due to d→d transitions attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition of four coordinate, square-planar geometry. This d-d transition is in the region of that observed for structurally well characterized complexes of copper(II) N-alkylsalicyladiminates with square planar geometry(17). This was further corroborated with the magnetic moments values of 1.76-1.88 B.M which falls within the range normally observed for one unpaired electron of Cu^{2+} complexes with square-planar geometry (18).

Table III: Magnetic moments and electronic spectra data (nm) of Schiff bases and their metal complexes

Compound	Ligand Transitions			d→d Transitions	μ_{eff} . B.M
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	CT		
A	240, 270	355		-	-
CuA			306	420,446	1.79
B	242, 270	343		-	-
CuB			329	422	1.88
C	268, 303	346		-	-
CuC			308	391	1.76

3.5 Antibacterial Activity

Antibacterial activity of the ligands and complexes were tested *in-vitro* against six human pathogenic bacteria. The activities were compared with that of ampicillin. The compounds were tested at a concentration of 10mg/ml in DMSO using the paper disc diffusion method. The growth inhibitory zones were measured in diameter and the results are presented in **Table IV** and **Figure I**. The complexes showed comparable activity with the reference compound ampicillin.

Table IV: Diameter of zones of inhibition of bacteria in different compounds (mm)

Bacterial strain	A	CuA	B	CuB	C	CuC	Ampicillin
<i>S.aureus</i> (ATCC 6538)	10	13	10	10	10	10	13
<i>E.faecalis</i> (ATCC 29212)	7	11	0	10	0	9	11
<i>B.cereus</i> (ATCC 10702)	10	10	10	10	0	10	14
<i>E.coli</i> (ATCC 8739)	11	13	0	11	0	11	10
<i>P.aureginosa</i> (ATCC 19582)	0	12	0	10	0	8	9
<i>K.pneumonia</i> (ATCC 10031)	0	11	0	10	0	10	11

Diameter of zones of inhibition ≥ 7 = active, diameter of zones of inhibition ≤ 6 = not recorded (low activity = 0).

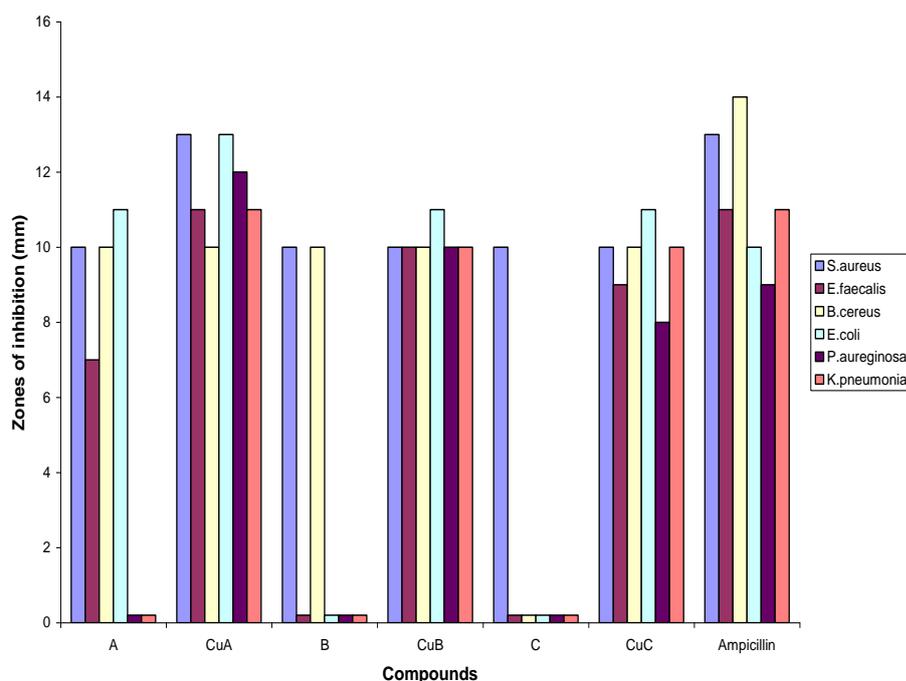


Figure 1: Histogram showing the comparative activities of the compounds

Table V: Minimum inhibitory concentration (mg/ml)

Bacterial strain	A	CuA	B	CuB	C	CuC	Ampicillin
<i>S.aureus</i> (ATCC 6538)	2.50	0.15	2.50	2.50	5.00	2.50	2.50
<i>E.faecalis</i> (ATCC 29212)	5.00	1.25	2.50	2.50	5.00	2.50	5.00
<i>B.cereus</i> (ATCC 10702)	5.00	0.62	5.00	5.00	5.00	2.50	5.00
<i>E.coli</i> (ATCC 8739)	2.50	2.50	2.50	2.50	2.50	2.50	1.25
<i>P.aureginosa</i> (ATCC 19582)	5.00	0.62	2.50	2.50	2.50	2.50	5.00
<i>K.pneumonia</i> (ATCC 10031)	2.50	0.62	2.50	2.50	2.50	2.50	2.50

The Schiff base ligands and their metal complexes, all have the capacity of inhibiting the metabolic growth of the investigated bacteria to different extent. MIC values of the all the compounds against six bacteria strains used in the study are presented in **Table V**. A minimum inhibitory concentration value of 0.28-1.27 mg/ml has been attributed with extremely strong activity while MIC values of 1.81-8.85 mg/ml are attributed with weak activities (19). The MIC result showed that the **CuA** (copper (II) complex of Schiff base 2-hydroxybenzylidene-2-aminophenol) exhibited an extremely strong activity against the tested bacteria except against *E.coli* which exhibited weak activity (19). It is known that chelation tends to make ligands act as more powerful and potent bactericidal agent and this was confirmed by the fact that the metal complexes showed enhanced antimicrobial activity against one or more strains with **CuA** remarkably showing good activity. This can be attributed to the position of substituents, **CuA** having the OH group at the *ortho* position (20-21). Increase in activity of this complex can be attributed to the ease of chelate formation between the OH group at *ortho* position to the imine nitrogen and the metal ion.

CONCLUSION

The results of this investigation support the suggested structures of the metal complexes. A square-planar geometry was predicted for all the complexes. The antibacterial (MIC) results show that the Cu(II) complexes were more active than the Schiff bases, with **CuA** complex exhibiting a very low MIC compared to the other complexes. This can be attributed to the position of the substituent (OH) at the *ortho* position. This study is of great importance as broad spectrum antimicrobial agents can be developed using the Cu(II) complexes described with particular reference to the **CuA** complex.

ACKNOWLEDGEMENT

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REFERENCES

1. Roth A, Spielberg ET, Plass W. Kit for Unsymmetric dinucleating double-Schiff-base ligands: Facile access to a versatile new ligand system and its first heterobimetallic copper-zinc complex. *Inorg. Chem.* 2007;46(11):4362-4364.
2. Wu LM, Teng HB, Feng XC, Ke XB, Zhu QF, Su JT, *et al.* Supramolecular networks in crystals of metal(II) complexes with water-soluble salicylaldehyde-2-sulfobenzoylhydrazone anion ligand. *Cryst. Growth. Des.* 2007;7(7):1337-1342.
3. Xu SP, Shi L, Lv PC, Fang RQ, Zhu HL. Synthesis and antibacterial activities of metal (II) complexes with Schiff bases derived from 3,5-diiodosalicylaldehyde. *J. Coord. Chem.* 2009;62(12):2048-2057.
4. Maurer GL, Shringapurey SK. Complexes of heavy metal ions and polyfunctional organic ligands used as antimicrobial agents. A01N 9/00 ed. United States National Research Laboratories, Cincinnati, Ohio. 1977.
5. Taylor MK, Reglinski J, Wallace D. Coordination geometry of tetradentate Schiff's base nickel complexes: the effects of donors, backbone length and hydrogenation. *Polyhedron.* 2004;23(18):3201-3209.
6. Abd El-Wahab ZH, El-Sarrag MR. Derivatives of phosphate Schiff base transition metal complexes: Synthesis, studies and biological activity. *Spect. Acta A.* 2004;60(1-2):271-277.
7. Albrecht M, Hubler K, Scheiring T, Kaim W. Copper(I) and copper(II) complexes of the bidentate imidazole/thioether ligand 1-methyl-2-(methylthiomethyl)-1H-benzimidazole. *Inorg. Chim. Acta.* 1999;287(2):204-208.
8. Edward F, Elslager JB, Annette AP, Leslie MW. Synthetic schistosomicides. XVII. N-(Benzylidene and cinnamylidene)-N'-[2-(diethylamino)ethyl]-1,4-naphthalenediamines and related Schiff bases. *J. Med. Chem.* 1970;13 (4):587-592.
9. Ren S, Wang R, Komatsu K, Bonaz-Krause P, Zyrianov Y, McKenna CE, *et al.* Synthesis, biological evaluation, and quantitative structure-activity relationship analysis of new Schiff bases of hydroxysemicarbazide as potential antitumor agents. *J. Med. Chem.* 2002; 45(2):410-419.
10. Prusis P, Dambrova M, Andrianov V, Rozhkov E, Semenikhina V, Piskunova I, *et al.* Synthesis and quantitative structure-activity relationship of hydrazones of N-amino-N'-hydroxyguanidine as electron acceptors for xanthine oxidase. *J. Med. Chem.* 2004;47(12):3105-3110.
11. Liu H, Wang H, Gao F, Niu D, Lu Z. Self-assembly of copper(II) complexes with substituted aroylhydrazones and monodentate N-heterocycles: synthesis, structure and properties. *J. Coord. Chem.* 2007;60(24):2671-2678.
12. Bauer AW, Kirby WNN, Sherris JC, Turck M. Antibiotic susceptibility testing by a standardized single disk method. *Am. J. Clin. Pathol.* 1966;45(4):493-496.

13. Eloff JN. A sensitive and quick microplate method to determine the minimal inhibitory concentration of plants extracts for bacteria. *Planta Med.* 1998;64(8):711-713.
14. Aranha PE, Do Santo MP, Romera S, Dockal ER. Synthesis, characterization and spectroscopic studies of tetradentate Schiff base chromium (III) complexes. *Polyhedron.* 2007;26(7):1373-1382.
15. Abd-Elsa MM. Spectroscopic characterization of some tetradentate Schiff bases and their complexes with nickel, copper and zinc. *J. Chin. Chem. Soc.* 2001;48 (2):153-158.
16. Percy GC, Thornton D. N-aryl salicylaldimine complexes: Infrared and PMR spectra of the ligands and vibrational frequencies of their metal(II) chelates. *J. Inor. Nuclear.Chem.* 1972;34(11):3357-3367.
17. Bu XR, Jackson CR, Derveer DV, You XZ, Meng QJ, Wang RX. New copper(II) complexes incorporating unsymmetrical tetradentate ligands with *cis*-N₂O₂ chromophores: synthesis, molecular structure, substituent effect and thermal stability. *Polyhedron.* 1997;16(17):2991-3001.
18. Lever ABP. *Inorg. electronic spectroscopy*, Elsevier, New York 1968.
19. Aligiannis N, Kalpoutzakis E, Mitaku S, Chinou IB. Composition and antimicrobial activity of the essential oils of two origanum species. *J. Agric. Food. Chem.* 2001;49(9):4168-4170
20. Jubie S, Gowramma B, Nitin KM, Jawahar N, Kalirajan R, Gomathy S. Synthesis and biological evaluation of some 3-(methoxy phenyl)-2-aryl thiazolidin-4-one derivative. *Ind. J. Pharma Sci.* 2009; 1(1):32-38.
21. Devprakash B, Udaykumar A. A complete review of thiazolidine-4-ones. *J. Pharm. Res.* 2011;4(7): 2436-2440.

PREDICTING THE OCCURRENCE OF RAINFALL USING IMPROVED RADIAL BASIS FUNCTION NEURAL NETWORK

Isimeto, R.¹; Fasina, E.P.²; Alienyi, C.D.³ & Uwadia, C.O.⁴

^{1,2,4} Department of Computer Sciences, University of Lagos.

³ Department of Chemical Engineering, University of Lagos.

risimeto@unilag.edu.ng

ABSTRACT

Undoubtedly, rainfall prediction plays a vital role in helping people plan their daily activities. Farmers, commuters, construction companies among others always get affected by the occurrence or non-occurrence of rainfall. Statistical rainfall forecasting has been proven to be a major challenge in climatic research. This is in part due to random fluctuations involved in the process and the dynamic nature of climate phenomena.

The aim of this paper is to develop a Radial Basis Function Neural Network model based on a convex cost function, for rainfall forecasting. Weather data consisting of 7776 daily observations of temperature, rainfall, air pressure, relative humidity, wind speed and wind direction were collected from the Nigerian Meteorological Agency (NIMET). The network was trained by both Conjugate Gradient Descent (CGD) and Particle Swarm Optimization (PSO) algorithms with a software application designed specifically for this work. This model predicts the occurrence of rainfall in a day with 72.69% accuracy, given weather information about the previous day. Also, we show that CGD outperforms PSO when a convex cost function is used.

Keywords: Radial, Neural Network, Rainfall Forecasting, Conjugate Gradient Descent, Particle Swarm Optimization.

INTRODUCTION

Weather is a term that encompasses phenomena in the atmosphere of a planet. It is constituted by different phenomena or elements such as temperature, rainfall, wind speed, humidity, atmospheric pressure, etc; which are measured either by special instruments or are observed by a meteorologist. A basic assumption is by viewing the weather phenomenon as a mixture of a certain number of signals with independently stable activity. The weather changes due to the changes in the mixing patterns of these stable activities over time (Basak, 2004).

Attempts to formally forecast weather has a long history starting with (Bjerknes, 1904). (Bjerknes, 1904) discussed the probability of weather prediction from the perspective of scientific determinism and he realized that the laws of physics provided the basis of weather prediction. According to Bjerknes, an accurate forecast of the weather can be made given sufficient knowledge of the atmosphere initial conditions, and sufficient means of integrating the known equations of motion. Forecast models based on the equations for atmospheric dynamics do not perfectly determine weather conditions, and massive computational power is needed to make forecasts". Due to this challenge, within the last 30-40 years, researchers have proposed alternative approaches to solving the weather prediction problem. Some of these approaches are Artificial Intelligence-based approaches such as Artificial Neural Networks (ANN) (Jaruszewicz et.al, 2002); (Devi et al., 2012).

ANN offers a methodology for solving non-linear problems which are not easy to solve by traditional means. ANN has the ability to extract the relationship between the inputs and the outputs of a process, without the physics being explicitly given (Veisi et al., 2009). Hence, these characteristics of ANN makes it well suited to the problem of weather forecasting under consideration (Abd, 2009). (El-Feghi et al., 2013) used Radial Basis Function Neural Network (RBFNN) to forecast air temperature and his results showed good prediction results. (Chang et

al., 2001) develop a rainfall–runoff model for three-hour-ahead flood forecasting using RBFNN. The results show that the RBFNN can be considered as a suitable technique for predicting flood flow.

In this work, a RBFNN model is developed that uses a convex cost function. We consider using Conjugate Gradient Descent (CGD) and Particle Swarm Optimization (PSO) as training algorithm. Results from both algorithms will be compared. The sections that follow explain the model and methodology used in this paper. Finally, we present our results, discuss our findings and make our conclusion.

Radial Basis Function Neural Network (RBFNN)

Radial basis function (RBF) networks are feed-forward networks trained using a supervised training algorithm. They are typically configured with a single hidden layer of units whose activation function is selected from a class of functions called basis functions. Though very similar to back propagation in many ways, radial basis function networks possess several advantages. They do train much faster than back propagation networks.

Moody and Darken (1989) popularized the RBF networks which have proven to be a useful neural network architecture. The major difference between RBF networks and back propagation networks (that is, multi-layer perceptron trained by Back Propagation algorithm) is the behavior of the single hidden layer. Rather than using the sigmoidal or S-shaped activation function as in back propagation, the hidden units in RBF networks use a Gaussian or some other basis kernel function. Each hidden unit acts as a locally tuned processor that computes a score for the match between the input vector and its connection weights or centers. In effect, the basis units are highly specialized pattern detectors. The weights connecting the basis units to the outputs are used to take linear combinations of the hidden units to produce the final classification or output. Problems where these networks are useful include:

Function approximation, Classification, Modelling of dynamic systems and time series.

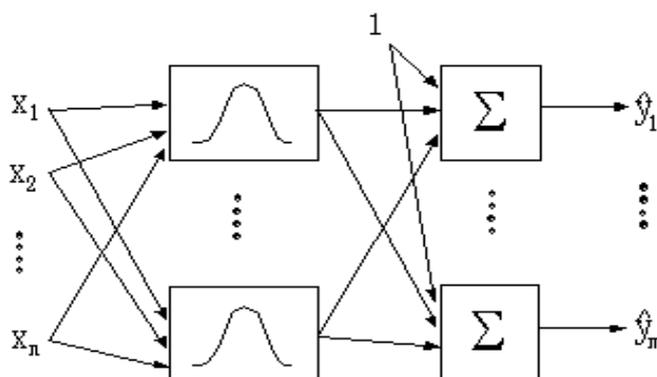


Figure 1 – The Radial Basis Neural Network Architecture

METHODS

The Model

Every RBFNN architecture has three layers and each layer is made up of one or more nodes. The input layer contains the feature nodes X expressed as:

$$X = \begin{bmatrix} x_{11} & x_{12} & \dots & x_{1d} \\ x_{21} & x_{22} & \dots & x_{2d} \\ \vdots & \vdots & \dots & \vdots \\ x_{n1} & x_{n2} & \dots & x_{nd} \end{bmatrix} \quad (1)$$

Where n represents the feature size and d the size of the data set.

The only hidden layer in RBFNN consists of J nodes. Each node in the hidden layer encapsulates two data: cluster centroid μ_j and its standard deviation σ_j . The cluster centroids are usually determined by unsupervised learning algorithm. A typical example of such algorithm is K-means. K-means algorithm clusters hyper-dimensional points into k units by minimizing the sum of squared errors between each point and its centroid. K-means suffers one limitation – the value of k must be specified. One way to tackle this problem is to try-out different k values and eventually select the one which resulted in the best classifier. This work will adopt this approach in tackling this limitation.

K-means yields J centroids positioned at each hidden nodes. The matrix representation of the centroids is:

$$C = \begin{bmatrix} c_{11} & c_{12} & \dots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \vdots & \vdots & \dots & \vdots \\ c_{j1} & c_{j2} & \dots & c_{jn} \end{bmatrix} \quad (2)$$

The centroids are critical in computing the outputs from each hidden node. This is done via kernel functions. The most commonly used are:

- Gaussian function:

$$\varphi(x) = e^{-\gamma \|x-c\|^2} \quad (3)$$

Where $\|x-c\|$ represents Euclidean distance and γ could be a constant or a function of σ

- Multi-Quadric function:

$$\varphi(x) = \sqrt{\|x-c\|^2 + \gamma^2} \quad (4)$$

- Inverse Multi-Quadric function:

$$\varphi(x) = \frac{1}{\sqrt{\|x-c\|^2 + \gamma^2}} \quad (5)$$

- Thin-plate spline function:

$$\varphi(x) = \|x-c\|^2 \log(\|x-c\|) \quad (6)$$

- Cubic function:

$$\varphi(x) = \|x-c\|^3 \quad (7)$$

- Linear:

$$\varphi(x) = \|x-c\| \quad (8)$$

The most widely used among these kernels is Gaussian function. In this work, we will however diagnose the performance of each kernel function and select the one which yields the best classifier. One or more nodes constitute the output layer. Values at each of the M output nodes are computed by:

$$y_m = w_0^m + \sum_{i=1}^J w_i^m \varphi_i(x) \quad (9)$$

where y_m is the value at output node m , w^m is a set of J number of weights used in mapping values to output node m and w_0^m is a bias term.

This work focuses on using the previous day weather data to tell whether rain falls or not the next day. This is clearly a classification problem. Consequently, we apply sigmoid function to scale the outputs from the output layer to values between 0 and 1.

$$z_m = \frac{1}{1+e^{-y_m}} \quad (10)$$

By convention, a value greater than 0.5 denote rainfall otherwise it denotes no rainfall. Getting the right set of weights that minimizes the classification error requires solving an optimization problem. The evaluation or cost function is represented as:

$$LH = \left[-\frac{1}{d} \sum_{j=1}^d \sum_{m=1}^M z_m^{obs} \log(z_m) + (1 - z_m^{obs}) \log(1 - z_m) \right] + \frac{\lambda}{2d} \sum_{j=1}^J \sum_{m=1}^M w_i \quad (11)$$

Where z_m^{obs} is the target at output node m and λ is the regularization term for controlling over-fitting.

In this work, we chose to use Log-likelihood rather than Sum of Square of Error (SSE) as the cost function. The reason is that SSE may yield a non-convex function due to the presence of a sigmoid function imbedded within it, whereas it can be mathematically shown that the log-likelihood function is a convex one. All non-convex functions contain local optimum making them unfit for gradient descent (GD) based optimization algorithm since it is not guaranteed to yield global optimum.

We will compare the performance of Conjugate Gradient Descent (CGD) against Particle Swarm Optimization (PSO) algorithms in training the weights.

Data Collection, Pre-Processing and Partitioning

Weather data were collected from the Nigerian Meteorological Agency (NIMET). The data consist of 7776 daily observations of temperature, rainfall, air pressure, relative humidity wind speed and wind direction. Our data set is made of targets and input features. The latter consists of minimum temperature T_{min} , maximum temperature T_{max} , air pressure P_{msl} at both 9:00am and 3:00pm; relative humidity RH both at 9:00am and 3:00pm; wind direction W_{dir} at both 9:00am and 3:00pm; wind speed W_{spd} at 9:00am; and the month of that day Mon . In total, there are 10 input features. The target values are nominal data indicating rain (positive or 1) or no rain (negative or 0) for the next day. We got equal number of positive and negative targets. This eliminates the need to report recall, precision or F-Score.

The data were normalized by dividing each variable by their maximum value. This process is termed feature scaling. Moreover, the data set was partitioned into training set (70%), validation set (20%) and test set (10%).

Implementation

A Matlab-based software application was built specifically for this work. This software does not depend on Matlab in-built neural network toolbox. The clustering and training algorithms were written from scratch. This choice was made because the work requires that we have full control of every variable that affects the successful implementation of RBFNN model.

The application has graphical user interface (GUI). It is designed to import data from excel and automatically pre-process them. It allows user to change training algorithm, regularization term and so on. The effect of number of hidden units, regularization term and kernel function can be diagnosed. Also, the core components of the trained classifier can be saved and used in building a commercial or open-source application that predicts future rainfall.

Number of Hidden Layer Used

The number of hidden nodes used in this work was got by experimentation. By varying the number of hidden nodes, various prediction accuracies from both training and validation sets were recorded. Figure 2 shows how these prediction accuracies vary with the number of hidden unit.

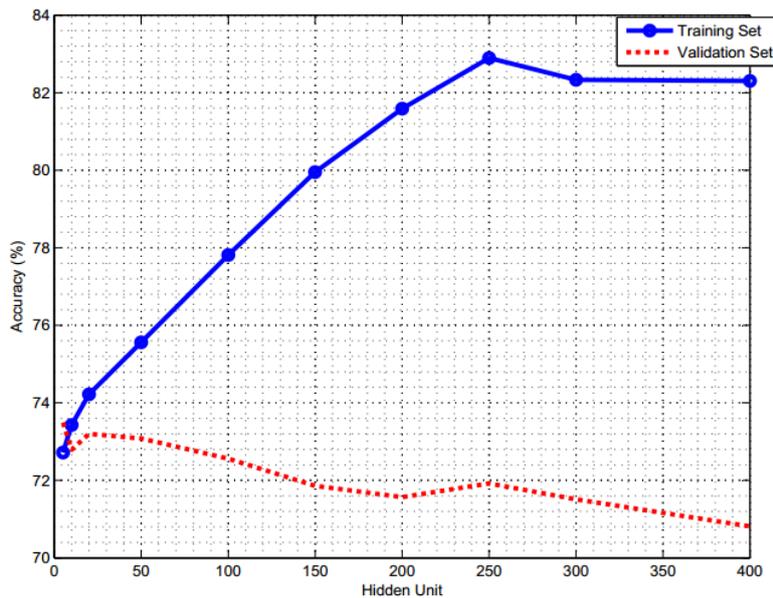


Figure 2 – Graph showing how prediction accuracy varies with number of hidden units
 This plot shows an interesting pattern. It is clear from the plot that as we increase the number of hidden units, we move from region of high bias (under-fitting) to region of high variance (over-fitting). Between these extremes, we have the desirable point (point of relatively low-bias and low variance). This point exists around hidden unit of value 20 which coincides with that used in this work.

Kernel Function Used

Similarly, the appropriate kernel function was got by experimentation. Inverse multi-quadric happens to outperform the rest from figure 3.

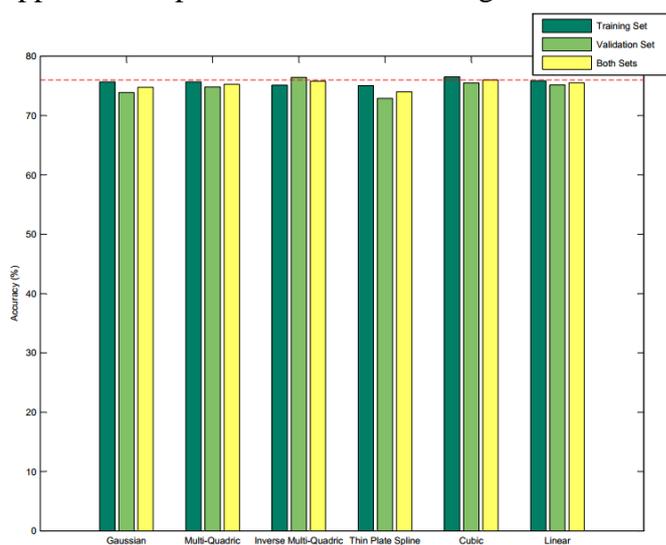


Figure 3 – Graph showing how prediction accuracy varies with various kernel functions

Regularization Term

A regularization term of 0.001 was used in this work based on the outcome we got in figure 4. There is no clear systematic pattern in figure 4. However, it is observable that the prediction accuracy of the train set diverges from that of the validation set after a regularization term of 0.1. After performing several runs, it was noticed that the prediction accuracy is not significantly affected by regularization terms.

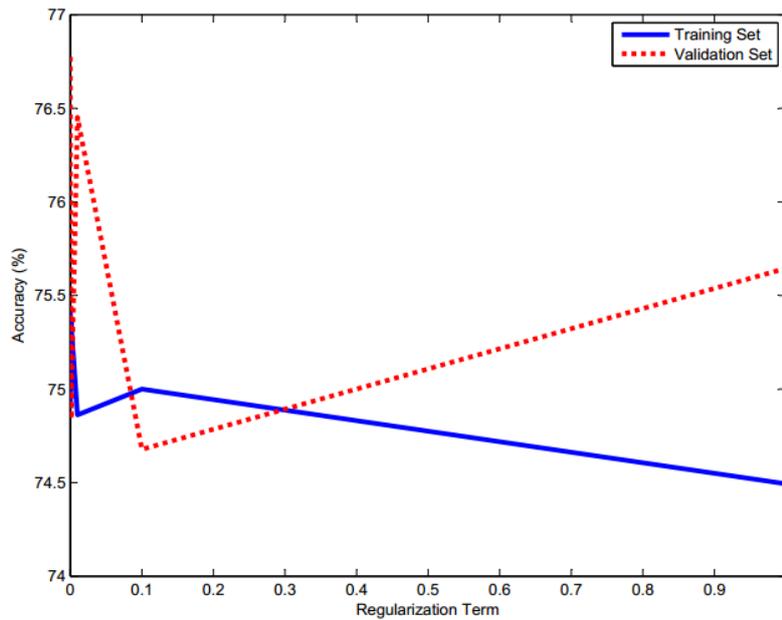


Figure 4 - Graph showing how prediction accuracy varies with regularization term

RESULT AND DISCUSSION

In this section, we present the rainfall prediction accuracy of our model. The result of training the weights with CGD and PSO is presented in table 1. Result for both training and test sets are tabulated, however we discuss that from test set since that is a representative of the unseen data.

Table 1 – Result showing the prediction accuracy using CGD and PSO training algorithms

Training Algorithm	Outcome	% Correctly classified		% Wrongly classified	
		Training Set	Test Set	Training Set	Test Set
CGD	Rain	84.01	81.54	15.99	18.46
	No Rain	66.01	63.85	33.99	36.15
	Over all	75.01	72.69	24.99	27.31
PSO	Rain	60.01	57.95	39.99	42.05
	No Rain	72.18	71.03	27.82	28.97
	Over all	66.1	64.49	33.9	35.51

Table 2 – Result showing the prediction accuracy using Log Likelihood and SSE cost functions trained by CGD

Cost Function	Outcome	% Correctly classified		% Wrongly classified	
		Training Set	Test Set	Training Set	Test Set
Log Likelihood	Rain	84.01	81.54	15.99	18.46
	No Rain	66.01	63.85	33.99	36.15
	Over all	75.01	72.69	24.99	27.31
SSE	Rain	80.01	79.49	19.92	20.51
	No Rain	69.09	65.9	30.91	34.1
	Over all	74.59	72.69	25.41	27.31

From tables 1 and 2, the following observations can be made:

1. Using CGD, there is 81.54% chance that our prediction that rain falls is true. On the contrary, CGD predicts the absence of rainfall with 63.85% accuracy.
2. PSO predicts the occurrence of rainfall with 57.95% accuracy and predicts its absence with 71.03% accuracy.
3. Overall, CGD outperforms PSO.
4. Using log likelihood as cost function outperforms that of SSE in training set only.

The reason for CGD outperforming PSO is due to the fact that an improved convex cost function was used. This implies that only one optimum exists. CGD is guaranteed to yield global minimum once the function is convex. PSO is a meta-heuristic technique that is designed to target global optimum especially when the function is non-convex. As a result, PSO is more computationally expensive than CGD and converges more slowly.

CONCLUSION

In this paper, we proposed a convex cost function for evaluating an RBFNN model for predicting the occurrence of rainfall. Rather than going for the most widely used RBFNN parameters which may not be suitable for this work, we invested substantial amount of effort in determining them experimentally.

We have shown that an improved cost function yields better prediction of rainfall based on the previous day weather information using a gradient-based optimization algorithm. The overall prediction is 72.69% which is a good one.

REFERENCES

1. Abd, M.K.(2009): Electricity load forecasting based on frameset neural network technique. *Am. J. Applied Sci.*, 6: 970-973. DOI: 0.3844/ajassp.2009.970.973
2. Basak, J. (2004): "Weather Data Mining Using Independent Component Analysis", *Journal of Machine Learning Research* 5 (2004) 239–253.
3. Bjerknes, V., Das Problem der Wettervorhersage, betrachtete vom Standpunkte der Mechanik und der physic, *Meteor. Zeit.* 21 (1904): 1-7, Translation by Y. Mintz: The problem of weather forecasting as a problem in mechanics and physics. Los Angeles, 1954. Reprinted in Shapiro and Gronas (1999) 1-4.
4. Chang, F., Liang, J., Chen, J.(2001): *Flood Forecasting Using Radial Basis Function Neural Networks*, IEEE Transactions On Systems, Man, And Cybernetics-Part C: Applications Nad Reviews, VOL. 31, NO.4, NOVEMBER 2001.
5. Devi, Ch.Jyosthna, B.Syam Prasad Reddy, K.Vagadhan Kumar, B.Musala Reddy, N.RajaNayak (2012): ANN Approach for Weather Prediction using Back Propagation, *International Journal of Engineering Trends and Technology- Volume3 Issue1- 2012*, ISSN: 2231-5381, Page 19. Available from: <http://www.internationaljournalsrsg.org>, [Accessed: 6th Nov 2013].
6. El-Feghi, I., Zubi A, S.Z., Abozgaya, A. (2013): Air Temperature Forecasting using Radial Basis Functional Artificial Neural Networks, *Recent Advances in Image, Audio and Signal Processing* ISBN : 978-960-474-350-6, https://www.academia.edu/5551974/Air_Temperature_Forecasting_using_Radial_Basis_Functional_Artificial_Neural_Networks; Accessed on 3rd Sept., 2014
7. Jaruszewicz, M. and Mandziuk, J. (2002): *Application of PCA Method to weather Prediction Task*, Proceedings of the 9th International Conference on Neural Information Processing, 2002. ICONIP '02. Volume:5.
8. Simeonov, Ivan; Kilifarev, Hristo and Ilarionov, Raycho (2006): Embedded System for Short-term weather forecasting, *International Conference on Computer Systems and Technologies- CompSySTech'06*

9. Veisi, H. and Jamzad, M., (2009): A complexity-based approach in Image Processing using neural networks, *Int. J. Sign Process*, 5: 82-92

BEHAVIOURAL EFFECTS OF TWO LARVICIDES AND RELATIONSHIP WITH CELLULAR CHANGES IN THE MOSQUITO FISH *POECILIA RETICULATA*

Joy A. Anogwih

Department of Zoology, University of Lagos, Nigeria
janogwih@unilag.edu.ng

ABSTRACT

The aim of this study was to assess the association between behavioural study and cellular damage in *Poecilia reticulata* Peter (Pisces: Poeciliidae) exposed to low concentrations of chlorpyrifos and spinosad. Results of each biomarker were related, and demonstrated the strength of the larvicides as toxicant to the fish. Gravid fish hatched their fries even at highest larvicide concentration corresponding with the absence of nucleolus and elongation of nucleus in spinosad treated fish. Chlorpyrifos was more toxic to *P. reticulata* than spinosad producing symptoms that ranged from haemorrhage to death corresponding with mitochondria rupture, and numerous dead cells including nucleus. Fish in lower spinosad concentration did not behave too differently from control, and were with minimal cellular damage characterized by increase in secretory vesicles, and mucin. Fish placed in the highest concentration of spinosad experienced reduction in feeding corresponding with ruptures in their lysosomal cells. Behavioural responses could serve as diagnostic warning signs of early, and ongoing cellular damage in exposed fish species necessary for rapid detection of toxic effects by larvicides promoting prompt intervention.

Keywords *Poecilia reticulata*, Chlorpyrifos, Biomarkers, Spinosad.

INTRODUCTION

Spinosad is a naturally derived insecticide that shows promise as a mosquito control agent. It is derived from a bacterium known as *Saccharopolyspora spinosa* Mertz and Yao.^[1] Chlorpyrifos is a synthetic organophosphorus compound, and just like spinosad, it has been successfully used against mosquito larvae species.^[2-4] These compounds when applied repeatedly to effectively control mosquito larvae often accumulate in water bodies resulting in increased exposure of non-target aquatic organisms including fish species sharing mosquito larvae habitat. The synergistic/antagonistic effects of the mixture are hardly interpreted and predicted exclusively from chemical analysis thus, the use of various histological parameters to adequately assess their non-target impacts. *Poecilia reticulata* (Pisces:Poeciliidae), commonly called guppy are natural mosquito regulating agent. Previous studies have shown non-target effects of larvicides to guppy at low concentrations using various histological biomarkers.^[5, 6]

Histological data are generated from biomarkers which are indicators of the impact of xenobiotic on different levels of biological organizations.^[7] They are used to assess damage to cell and tissue structures that are not always visible to the naked-eye. Ultrastructural changes, increased number of micronuclei (MN) cells as well as behavioural responses in organisms are examples of histological biomarkers. Behavioural changes in organisms due to exposure to chemicals usually indicate the effect of chemicals at organismal level, and therefore used to describe the trends over time.^[8] Extensive studies have been carried out on the use of abnormal behavioural responses as diagnostic endpoints for determining the sub-lethal effects of various chemicals. Drummond et al.^[9] evaluated the use of behavioural and morphological changes in fish as diagnostic endpoints for screening, and differentiating some chemicals according to their mode of action after exposing 30-day-old fathead minnows *Pimephales promelas*. Spinal deformities in fat head minnows *Pimephales promelas* and rainbow trout *Oncorhynchus mykiss* exposed to sub-

lethal concentrations of chlorpyrifos as well as loss of equilibrium, hanging vertically, rapid gill movement, gulping for air and prolonged motionless behaviour in guppies exposed to various concentrations of deltamethrin have been reported. ^[10, 11]

At no point in time were these behavioural changes linked to potential cellular damage in the organisms despite that damage to tissues usually begins as molecular malfunction within specific organelles. ^[12] Behavioural symptoms could be attributed to unobservable cellular or tissue damage which when left unattended to would degenerate to disease, chronic disorder and eventual death of organism. More often than not, mortality occurs in exposed fish before the onset of intervention simply because the initial cellular damage was ignored therefore, had progressed to advanced stage. Behavioural symptoms may be helpful in averting this problem by providing early diagnosis of new and ongoing cellular damage in aquatic organisms necessary for prompt intervention and fish survival.

Therefore, the aim of this study is to investigate behavioural changes in exposed guppy in relation to the different damage found in their cells, necessary for rapid detection and management of non-target effects by larvicides.

METHODS

Test Compound

Spinosad with active ingredient 1.25 g/kg consisting of Spinosyns A (CAS: 131929-60-7), and D (CAS: 131929-63-0) was obtained as spindor dust from Nigeria Stored Product Research Institute, Yaba (NSPRI) while commercial formulation of chlorpyrifos 48EC (Pyrinex), CAS: 3383-98-8 containing 480 g/l active ingredient was purchased from Afcott located in Lagos, Nigeria.

Preparation of Test Concentration

Low concentrations of spinosad and chlorpyrifos within the range that killed 30 to 70% population of a more susceptible larvae species: *Cx. quinquefasciatus*, but did not cause physical death of fish were selected for behavioural study. ^[5] Ultrastructural study was investigated in fish samples contained in the lowest and highest concentrations with evidences of one or more behavioural responses different from control.

Behavioural Analysis

Fishes were not fed 24 h before testing. Heterogeneous sexes of fish consisting of 18 females (gravid and non-gravid), and 9 males, in three replicates for each concentration of larvicide, and control respectively were exposed for 28 days under static renewal bioassay ^[13], and then evaluated for behavioural changes. The following concentrations of larvicides were used for spinosad, 49 μgL^{-1} , 73 μgL^{-1} and 110 μgL^{-1} ; and Chlorpyrifos, 0.4 μgL^{-1} , 0.6 μgL^{-1} and 0.8 μgL^{-1} . Gravid females were included in the highest concentrations of each larvicide as well as in the untreated dechlorinated tap water that served as control.

Behavioural changes in guppy were critically monitored throughout the experimental period, at every 24 h interval. Responses were recorded if they differed from control, and occurred in $\geq 10\%$ of the fish within each test chamber. ^[14] Control mortality was less than 5% and a fish was regarded as dead if it failed to move when gently probed with the edge of a glass rod.

Ultrastructural Analysis

At day 28, treated fish samples with evidence of behavioural changes as in MN test were randomly selected, and dissected to remove intestinal tissue. This was also applicable to the set of fish that served as control. Fish intestinal tissue was prepared for ultrastructural analysis. ^[6]

RESULTS AND DISCUSSION

Behavioural Symptoms In *Poecilia Reticulata*

Chlorpyrifos was more toxic to guppy than spinosad with several behavioural symptoms ranging from hypoactivity to heamorrhage that ended up in fish death. Reduced feeding was mostly found at the highest concentrations of both compounds. Fish in spinosad treatment were seen to behave not too differently from control especially at the lowest concentration where fish became hypoactive on day 3 thereafter, swam normal as in control (Table 1).

Gravid fish placed in highest concentrations of each larvicide were seen to hatch their fries however, this occurred earlier than in control indicating premature birth (Table 1).

Ultrastructural Changes in *POECILIA RETICULATA*

The severity in cellular damage increased at increasing concentration of each larvicide (Figures A-J). Control fish were with intact cytoplasmic and nuclear membrane, well-defined nucleus, and nucleolus. Other organelles were intact as in mitochondria with distinct cristae, and well defined matrices (Figures A and F). Fish placed in spinosad treatment especially at lowest concentration were found with less cellular damage than chlorpyrifos treated specimens. Ultrastructural changes namely rearranged nuclear cells, elongated nucleus, absence of nucleolus, large secretory vesicles, and mucin were found at the lowest spinosad concentration (Figures B and G). While the highest concentration of spinosad was characterized with more severe damage as pycnotic nucleus, degraded cell membrane, ruptured lysosome, electron dense cytoplasm, and fewer mitochondria with cristae (Figures C and H). Chlorpyrifos treated fish were with loss of grey area in cytosol, severally ruptured mitochondria and numerous dead cells essentially the nuclei, mitochondria and lysosomal cells (Figures D, E, I and J).

Results of individual biomarker were found to correspond with each other, and demonstrated the strength of each larvicide as toxicant to the bio-control fish agent. The presence of large secretory vesicles and mucin in guppy exposed at the lowest spinosad concentration indicates that the fish were beginning to be affected by this toxicant hence the initial hypoactive behaviour that stopped after day 3. The production of mucin and secretory cells in fish species after exposures to low concentration of deltamethrin and temephos have been reported ^[15, 16]. Although, these authors did not relate their findings with behavioural responses as in the current study. Mucus secretions by gills and intestines play a major role in the protection of these tissues from environmental impacts of xenobiotics, and have been presumed to be an initial protective response by fish to environmental effects of larvicides. ^[17-19]

Hatching of fry by gravid females though prematurely, could explain the reason for nucleus elongation, and absence of nucleolus at the lowest spinosad concentration. It is very likely that both larvicides lacked the potential to inhibit fish growth and development but more studies with higher concentrations are needed to validate this assumption.

Reduced feeding was found to characterize the highest concentrations of spinosad and chlorpyrifos, with evidence of lysosome ruptures in spinosad treated cells (Table 1; Figure C). The higher toxic effect of chlorpyrifos must have caused total destruction of lysosome beyond recognition in the picture explaining why fish exposed at this concentration also showed

reduction in feeding just as spinosad treated ones. There are over 40 heritable lysosomal storage diseases known, each being characterized by harmful accumulation of a specific substance or class of substances commonly polysaccharides or lipids that would normally be catabolized by the hydrolytic enzymes present within the lysosome or transported out of the lysosome therefore, lysosomal defects may impair digestion and recycling of cellular components that are no longer needed in the fish. ^[12]

The pattern of mitochondria rupture observed in the enteric cells of guppy was similar to those reported for pirimiphos methyl, ^[6] and could be diagnostic of organophosphorus toxicity to guppy species. Cell ruptures are signs of hypoxia and respiratory failures in organisms, ^[20] explaining why pectoral fin forward was mostly observed in this group of fish. Hypoactivity, haemorrhage and increased fish mortality in chlorpyrifos treatment may be attributed to the fewer mitochondria cristae, matrix damage, and the several mitochondria and nuclei deaths commonly found in this group of fish. The cristae are sites of oxidative phosphorylation and electron transport while the matrices are sites of Krebs cycle enzymes. ^[21] Any damage to these components would definitely lead to oxidative stress in the fish affecting their behaviour.

CONCLUSION

This study has demonstrated that behavioural changes can in addition to being a promising diagnostic tool for larvicide screening, serves as indicators of new and ongoing cellular damage invisible to the naked eye necessary for rapid diagnosis of non-target effects by larvicides. Usually, cellular damage begins as molecular malfunction within specific organelles, ^[12] and may gradually progress into a disease or chronic disorder hence the need for early intervention through behavioural monitoring. Behavioural monitoring should be made to complement other biomarkers of stress in any toxicological study to achieve a reliable and more meaningful result.

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REFERENCES

- [1] Thompson, G.D; Dutton, R; Sparks, T.C. Spinosad- a case study: an example from a natural product discovery programme. *Pest Manag. Sci.* **2000**, *56*, 696–702.
- [2] Lawal, M.O.; Samuel, O.B. Investigation of acute toxicity of Pirimiphos-Methyl (Actellic®, 25%EC) on Guppy (*Poecilia reticulata*, Peters, 1859). *Pak. J. Biol. Sci.* **2010**, *13* (8), 405–408.
- [3] Stevens, M. M.; Helliwell, S.; Hughes, P. A. Toxicity of *Bacillus thuringiensis* var *Israeliensis* formulations, spinosad and selected synthetic insecticides to *Chironomus tepperi* larvae. *J. Am. Mosq. Control Assoc.* **2005**, *21* (4), 446–450.
- [4] Hertlein, M.B.; Marvrotas, C.; Jousseuma, C.; Lysandrou, M.; Thompson, G.D.; Jany, W.; Ritchie, S.A. 2010. A review of spinosad as a natural product for larval mosquito control. *J. Am. Mosq. Control Assoc.* *26* (1), 67 – 87.
- [5] Anogwih, J. A.; Makanjuola, W.A.; Chukwu, L.O. Spinosad induced Cytogenotoxic effects on the mosquito fish, *Poecilia reticulata*. *J. Clin. Toxicol.* **2013**, *S12*,001doi: 10.4172/2161-0495.S12-001.

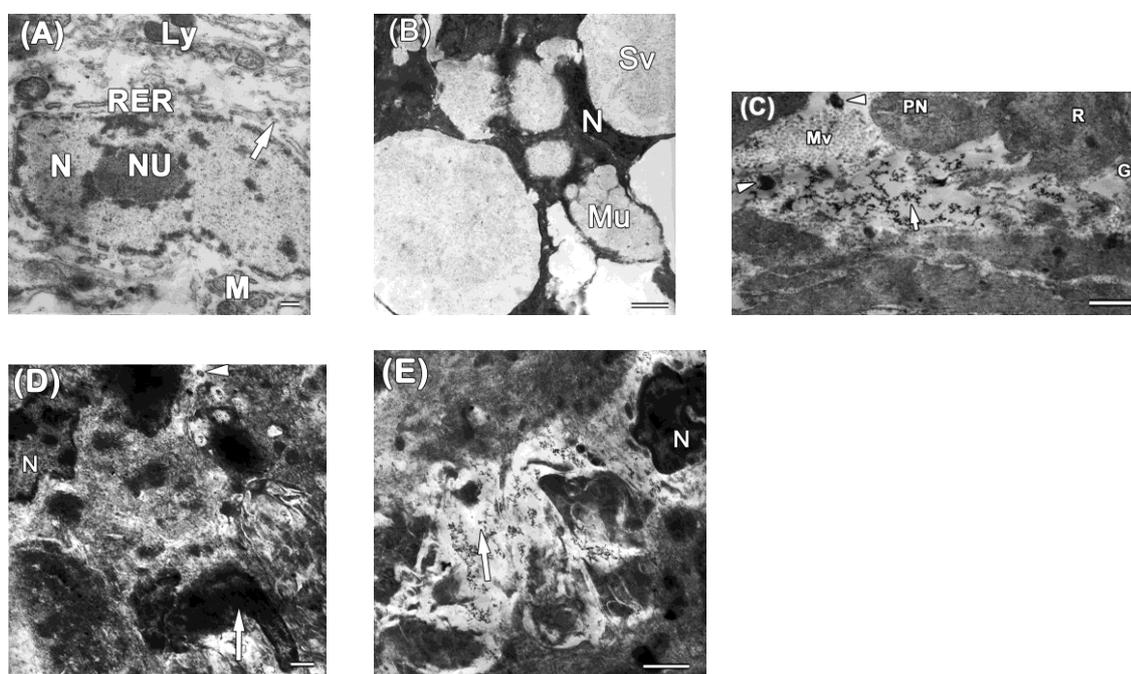
- [6] Anogwih, J.A.; Saliu, J.K.; Linton, E.W.; Makanjuola, W.A.; Chukwu, L.O. The Compatibility of spindor dust with *Poecilia reticulata* for Integrated Mosquito Larviciding. *J. Clinic. Res. Bioeth.* **2013**, *4*,157. doi:10.4172/2155-9627.1000157.
- [7] Paolini, A.; Berti, M.; Angelo, A.D.; Giansante, C. Use of histopathological indicators on Chubs (*Leuciscus cephalus*) and Brown trout (*Salmo trutta fario*) in evaluating river environments. *Veterinaria Italiana*, **2005**, *4*, 189 – 198.
- [8] Padmini, E.; Rani, M. U. Mitochondrial membrane potential is a suitable candidate for assessing pollution toxicity in fish. *Sci. Total Environ.* **2011**, *409*, 3687–3700.
- [9] Drummond, R. A.; Russom, C. L.; Gieger, D. L.; DeFoe, D. L. Behavioural and Morphological changes in fathead minnows (*Pimephales promelas*) as diagnostic endpoints for screening chemicals according to mode of action. In *Aquatic Toxicology and Environmental Fate, STP 921*; Poston, T. M., Prudy, R., Eds.; American Society for Testing and Material: Philadelphia, **1986**; *9*, 415–435.
- [10] Halcombe, G. W.; Phipps, G. L.; Tanner, D. K. The acute toxicity of Kelthane, Dursban, Disulfoton, Pydrin and Permethrin to fathead minnows: *Pimephales promelas* and rainbow trout: *Salmo gairdneri*. *Environ. Pollut.* **1982**, *29*, 167–178.
- [11] Viran, R.; Erkok, F. U.; Polat, H.; Kocak, O. Investigation of acute toxicity of deltamethrin on guppies (*Poecilia reticulata*). *Ecotoxicol. Environ. Safety* **2003**, *55*, 82–85.
- [12] Wayne, M. B.; Kleinsmith, L. J.; Hardin, J.; Greory, P. B. *The world of the cell, 7th Edition*. Pearson Benjamin Cummings: California, USA, **2009**; 789 pp.
- [13] Wester, P.W.; Canton, H.H. Histopathological effects in *Poecilia reticulata* (Guppy) exposed to methyl mercury chloride. *Toxicol. Pathol.* **1992**, *20* (1), 1–13.
- [14] Rice, P. J.; Drewes, C. D.; Klubertanz, T. M.; Bradbury, S. P.; Coats, J. R. Acute Toxicity and Behavioral effects of chlorpyrifos, permethrin, phenol, strychnine and 2, 4-dinitrophenol to 30-day-old Japanese Medaka (*Oryzias latipes*). *Environ. Toxicol. Chem.* **1997**, *16*, 696–704.
- [15] Al- Ghanbousi, R.; Ba-Omar, T. Effects of Deltamethrin on the gills of *Aphanius dispar*: A microscopic study. *Tissue and Cell*, **2012**, *44* (1), 7–14.
- [16] Ba-Omar, T.A.; Al-Jardani, S.; Victor, R. Effects of pesticide temephos on the gills of *Aphanius dispar* (Pisces: Cyprinodontidae). *Tissue and Cell*, **2011**, *43* (1), 9–38.
- [17] Sorensen, E.M. *Metal Poisoning in Fish*. CRC Press: Boca Raton, **1991**; 384pp.
- [18] Pawert, M.; Muller, E.; Triebbskorn, R. Ultrastructural changes in the fish gills as bioindicator to assess small stream pollution. *Tissue and Cell.* **1998**, *3*, 617–626.
- [19] Matey, V.; Richards, J. G.; Wang, Y.; Wood, C. M.; Rogers, J.; Davies, R.; Murray, B. W.; Chen, X. Q.; Du, J.; Brauner, C. J. The effect of hypoxia on gill morphology and ion regulatory status in the lake Quinghai scaleless carp, *Gymnocypris przewalskii*. **2008**, *J. Exp. Biol.* *211*, 1063–1074.
- [20] Richmonds, C.; Dutta, H.M. Histopathological changes induced by malathion in the gills of Bluegill, *Lepomis macrochirus*. *Bull. Environ. Contam. Toxicol.* **1989**, *43*, 123–130.
- [21] Taylor, D. J.; Green, N.P.O.; Stout, G. W. *Biological Sciences, 3rd Edition*. Cambridge University Press: UK, **1997**, 963pp.

FIGURE CAPTION

Figures A-E: TEM of Intestinal Nuclei for control and exposed fish. (FigureA): Control fish with intact Cytoplasm, Nuclear membrane, well-defined Nucleus (N) and one Nucleolus (NU). Cell organelles are intact as in Mitochondria (M); Lysosomes (Ly); Rough endoplasmic reticulum (RER); Smooth endoplasmic reticulum (arrow) **scale bar 1µm.** **(Figure B):** At 49µgL⁻¹ of spinosad, features include Electron dense cytoplasm and nucleus compared to control, elongated Nucleus (N) with rearranged chromatin, presence of large Secretory vesicles (Sv), and

Mucin (Mu), **scale bar 1 μ m. (Figure C):** Severe distortion of electron dense cytoplasm at spinosad 110 μ gL⁻¹ (arrow) characterized by Pycnotic nucleus (PN) with ruptured Lysosome (arrow heads). Golgi body (G), Microvilli (Mv), **scale bar 0.5 μ m. (Figure D):** At 0.4 μ gL⁻¹ of chlorpyrifos there was severe damage to Cytoplasm (arrow), dead cells including Nuclei (N), Smooth endoplasmic reticulum (arrow head) **scale bar 1 μ m (Figure E):** Chlorpyrifos at 0.8 μ gL⁻¹ was characterized by dead cells including Nucleus (N) and loss of grey area in cytosol (arrow), **scale bar 0.5 μ m.**

Figures F-J: TEM of Intestinal Mitochondria for control and exposed fish. (Figure F) Control fish with intact organelles including Mitochondria (M); Smooth endoplasmic reticulum (arrow head); Rough endoplasmic reticulum (arrow); free Ribosomes (Polygon shape); Lysosomes (Ly); **scale bar 200 nm. (Figure G)** At 49 μ gL⁻¹ no marked difference from control. Intact cristae in Mitochondria (M), Microbodies (Mb), Microvilli (Mv), Smooth endoplasmic reticulum (arrow), Lysosome (Ly), Lipid droplet (arrow head) **scale bar 1 μ m. (Figure H)** At 110 μ gL⁻¹ of spinosad there was marked degradation of electron dense Cytoplasm (arrow) including Mitochondria with indistinct cristae (inset), Brush border (BB), Lumen (LU), Microvilli (arrow head), **scale bar 1 μ m, Inset 0.25 μ m. (Figure I)** At 0.4 μ gL⁻¹, there was marked Mitochondria rupture (arrow head) with degenerated cytoplasmic Membrane (arrow), Smooth endoplasmic reticulum (SER) **scale bar 0.25 μ m. (Figure J)** At 0.8 μ gL⁻¹ of chlorpyrifos, Cell membrane was shrunken (arrow head), presence of numerous dead cells including Mitochondria (M) and Microbody (Mb) **scale bar 1 μ m.**



Figures A-E

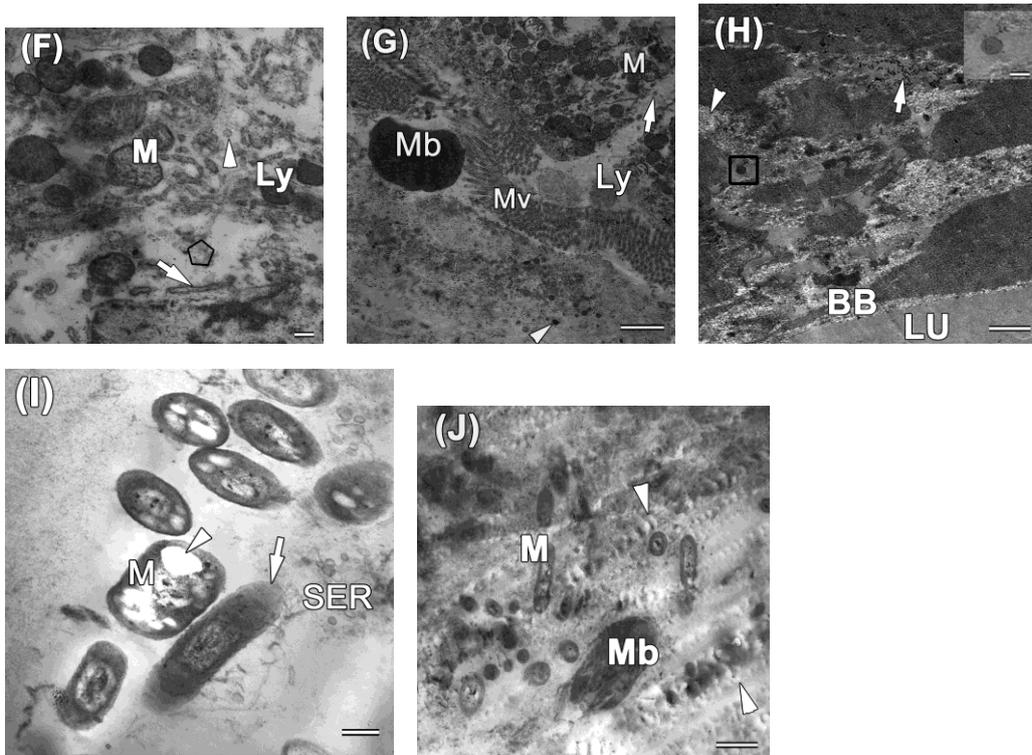


TABLE 1. Behavioural responses of *Poecilia reticulata* in the presence of larvicides.¹Responses were recorded if they differed from control and occurred in $\geq 10\%$ of the fish within each test chamber

Figures F-JDays	Behavioural symptoms	Control	Chlorpyrifos ($\mu\text{g/L}$)			Spinosad ($\mu\text{g/L}$)		
			0.4	0.6	0.8	49	73	110
1	Hyperactivity							
	Abnormal lateral flexure							
3	Hatching							^c X
	Hypoactivity					X		X
7	Haemorrhage				^b X			
14	Abnormal lateral flexure			X				
	Loss of equilibrium			X	X			
	Mortality			X	X			
	Pectoral fin forward			X	X			
	Haemorrhage		^{a,b} X	^{a,b} X	^{a,b} X			
	Hypoactivity			X	X			
	Reduced feeding		X	X	X			X
	Scoliosis				X			
	15	Loss of equilibrium			X			
	Reduced feeding			X	X			
16	Pectoral fin forward			X	X			
	Hypoactivity			X	X			
	Scoliosis			X				
	Loss of equilibrium				X			
17	Haemorrhage				^{a,b} X			
	Pectoral fin forward				X			
	Hypoactivity				X			
	Reduced feeding				X			X
	Lordosis				X			
	Mortality				X			
	20	Mortality		X	X	X		
	Hatching				^c X			
20	Lordosis				X			
	Mortality				^a X	^d X		
21	Lordosis				X	X		
	Reduced feeding				X	X		
22	Hatching	^c X						
	Mortality				^a X	X		
23	Reduced feeding				X	X		
	Mortality				^a X			
24	Reduced feeding				X	X		
	Mortality					X		
27	Reduced feeding				X	X		
	Mortality				^a X	X		

^a Male fish; ^b Operculum region; ^c Gravid Female; ^d Fries.

EFFECT OF MALARIA AND MALARIA-TYPHOID CO-INFECTION ON SELECTED LIVER FUNCTION INDICES

Kayode A.A.A* Kayode O.T & Eli O.S

Department of Chemical Sciences, College of Natural and Applied Sciences, Bells University of Technology, Km 8 Idiroko Road, Ota Ogun State, NIGERIA.
bolakayot@gmail.com

ABSTRACT

A study on the effect of malaria and malaria-typhoid co-infection on alkaline phosphatase (ALP), aspartate aminotransferase (AST) and alanine aminotransferase (ALT) activities were carried out on blood samples from 29 malaria patients, 36 malaria-typhoid co-infected patients, and 10 apparently healthy individuals as control. In the malaria infected group, a significant increase ($P < 0.05$) was observed in ALP, ALT and AST levels as compared to the control. Also, in the malaria-typhoid co-infection group, significant increases ($P < 0.05$) were observed in the levels of these hepatic enzymes. This study suggests the possibility of alterations in the levels and activities of liver enzymes such as ALT, AST and ALP during malaria infection and malaria-typhoid co-infection.

Keywords: *Malaria, Co-infection, Febrile, Apparently healthy, Liver, Ota.*

INTRODUCTION

Malaria which is of great public health importance has emerged the most deadly parasitic disease in the tropics and sub-Saharan regions of the world¹⁻³. One –fifth of infants' death in Africa is caused by the scourge of malaria⁴. In Nigeria, approximately 0.25 million deaths of children under the age of five is caused by malaria yearly⁵. Typhoid fever which is also endemic in Africa is more severe in infants and the elderly⁶⁻⁷. Both malaria and typhoid exhibits close symptomatology and epidemiology⁸. The first case of malaria- typhoid co-infection occurred among American soldiers in 1862⁹⁻¹⁰. This study examines the effect of malaria and malaria-typhoid co-infection on some liver function indices. Our study includes only the febrile patients that have been clinically said to have malaria and malaria – typhoid co-infection from the results of their malaria and widal test respectively.

METHODS

Subjects: In-Patients and out-patients aged between 14 and 30 years with febrile illness in the University Health Centers, Bells University of Technology and Covenant University, Ota.

Settings: University Health Centers, Bells University of Technology and Covenant University, Ota, Ogun State, Nigeria.

Study site and Study population: Inpatients and outpatients of the University Health Centers, Bells University of Technology and Covenant University were examined and investigated.

Ethical Approval: All necessary approval and consent were obtained from the appropriate authorities and individuals.

Experimental Design and Treatment

A total of 130 blood samples were collected from patients with a clinical suspicion of malaria and typhoid fever and screened for malaria parasites and *S. typhi* infection.

Group 1: Patients with co-infection (36 patients)

Group 2: Patients with malaria alone (29 patients)

Control Group: A total of 10 apparently healthy individuals (from the same location with the febrile patients) were used as control.

Screening of blood samples to categorize the patients in the test group was done as follows:

- i. **Parasitological examination of blood samples:** Giemsa-stained thick and thin blood films were prepared for each sample and parasitaemia evaluated per microlitre of blood using the thick film preparation according to standard methods described by the World Health Organization ¹¹, assuming a leukocyte count of 5400 μ l⁻¹ of blood established for healthy Nigerians ¹². Films were examined microscopically for the presence of malaria parasites within red blood cells in thin films. For thick films, the ring forms, trophozoites and gametocytes were looked for. A smear was considered negative for malaria parasites if no parasites are seen after examining at least 100 microscopic fields.
- ii. **Widal test:** The Widal test was performed on all blood samples by the rapid slide titration method ¹³ using commercial antigen suspensions for the somatic (O) and flagella (H) antigens. A positive widal test was considered for any given serum sample with antibody titer of 1:160 for *S.typhimurium* antigens.
- iii. The relationship between malaria parasite count μ l⁻¹ of blood and Salmonella O and H antibody titers was determined by carrying out a correlation analysis using the Microsoft Excel computer worksheet.

DETERMINATION OF HEPATIC ENZYME ACTIVITY

Alkaline Phosphatase Activity

The assessment of alkaline phosphatase (ALP) was done according to the method of Englehardt ¹⁴. Briefly, 0.01ml of the sample was placed in a cuvette containing 0.50ml of reagent R (Buffer: Diethanolamine buffer 1mol/l, pH 9.8; MgCl₂ 0.5mmol/l; Substrate: p-nitrophenylphosphate 10mmol/l) regulated at temperature of 30^o C. The initial absorbance was read and re-read after 1, 2, and 3 minutes respectively at 405nm wavelength against air on a UV spectrophotometer.

Alanine Aminotransferase Activity

The alanine aminotransferase activity (ALT) was assayed according to the method described by Reitman and Frankel ¹⁵. Briefly, 0.1ml of serum was placed in a cuvette containing 0.5ml of solution R1 (Buffer: Phosphate buffer 100mmol/l, L-alanine 200mmol/l, α -oxoglutarate 2.0mmol/l), and 0.1ml of distilled water is added to another cuvette containing 0.5ml of R1 as reagent blank. Both preparations mixed and incubated for 30 minutes at 37^o C then 0.5ml of R2 (2, 4-dinitrophenylhydrazine 2.0mmol/l) added, mixed and left to stand for exactly 20 minutes at 25^o C before 5.0ml of NaOH is added.

The solution is mixed and the absorbance read against reagent blank after 5 minutes at 546nm wavelength using a UV spectrophotometer.

Aspartate Aminotransferase Activity

The assessment of aspartate aminotransferase activity (AST) was carried out using the method described by Reitman and Frankel ¹⁵. Briefly, 0.1ml of serum was placed in a cuvette containing 0.5ml of solution R1 (Buffer: Phosphate buffer 100mmol/l, L-aspartate 100mmol/l, α -oxoglutarate 2.0mmol/l), and 0.1ml of distilled water is added to another cuvette containing 0.5ml of R1 as reagent blank. Both preparations mixed and incubated for 30 minutes at 37^o C then 0.5ml of R2 (2, 4-dinitrophenylhydrazine 2.0mmol/l) added, mixed and left to stand for exactly 20 minutes at 25^o C before 5.0ml of NaOH is added.

The solution is mixed and the absorbance read against reagent blank after 5 minutes at 546nm wavelength using a UV spectrophotometer.

Statistical Analysis

All results were analyzed statistically using One-way Analysis of Variance (ANOVA) method.

RESULTS AND DISCUSSION

The results of this study are shown in Table 1. A significant increase ($P < 0.05$) in alkaline phosphatase activities in the blood plasma of the malaria and co-infection groups was observed when compared to the control group. The observed elevated levels corroborates with the earlier findings of White, 1992 and Nogochi, 1987,^{16 - 17} who observed higher level of alkaline phosphatase in malaria infection. Alkaline phosphatase is a membrane-bound enzyme which catalyses the hydrolysis of a number of phosphate esters and one of the major sites where it is bound to the membrane in the liver. However, in terms of pathogenesis, the host liver is among the organs affected in the early stage of falciparum malaria¹⁸ leading to significant alterations in host hepatocyte physiology and morphology¹⁹. Therefore, the observed elevation in alkaline phosphatase level is an indication that the hepatic stage of the parasite's life cycle in its host is accompanied by significant perturbation of the hepatocyte membrane leading to leakage of this enzyme out of the liver cells. This finding is in agreement with earlier findings¹⁶ that centrilobular liver damage is one of the factors involved in hepatic dysfunction in acute malaria infection, leading to hyperbilirubinaemia which is a direct consequence of the impaired drainage capacity of the liver. Considering the percentage magnitude observed in the level of alkaline phosphatase in the infected group which is more than 50% of control activity, is as high as that associated with cholestasis where the level is over twice the normal limit. Also, other disease such as liver cirrhosis is associated with a 92% increase above the normal limits of serum alkaline phosphatase²⁰⁻²¹, which is higher than what we have observed in this study. In view of these differences in the percentage increase in the alkaline phosphatase activity in malaria relative to these diseases, the etiology of the increased activity of alkaline phosphatase can be claimed to be due to the malaria infection.

The observed significant increase ($P < 0.05$) in AST and ALT activity in malaria and co-infected groups when compared to the control group coincides with some other studies²²⁻²³ on effects of AST and ALT activity in relationship with malaria which indicates an increase in their activity. Since both the liver and erythrocytes are rich sources of AST and ALT, the activities of the invading *plasmodium* and *salmonella* parasites in these organs/tissues can lead to damage to the membranes of these organs/tissues and the consequent release of AST and ALT, resulting in the observed increase in the activities of these enzymes.

The result (Table 1) clearly indicates that there is a significant difference ($p < 0.05$) in the activities of the liver enzymes (ALT, AST and ALP) in malaria parasite infected patients when compared with the non-malaria parasite infected (control) subjects. The normal healthy values for serum ALT, AST and ALP as estimated by the International Federation of Clinical Chemistry (IFCC) are in the reference ranges of 10-40, 8-20 and 38-94IU/L, respectively. The differences in the normal, healthy ranges are not unexpected. This is because the normal, healthy ranges differ from one laboratory to another²⁴. The possible reasons for such variations include environmental, nutritional status and anthropometric indices²⁵.

CONCLUSION

This study suggests the possibility of alterations in the levels and activities of liver enzymes such as ALT, AST and ALP during malaria infection and malaria-typhoid co-infection.

ACKNOWLEDGEMENT

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REFERENCES

1. Mishra S K, Mohanty S., Problems in the management of severe malaria, *J. Trop. Med.*, 1 (1), 1-10 (2003)
2. Umar R. A, Hassan S. W, Ladan M. J, Jiya Nma M, Abubakar M. K, Nata'ala U., The association of K76T Mutation in *pfprt* Gene and Chloroquine Treatment Failure in Uncomplicated *Plasmodium falciparum* Malaria in a cohort of Nigeria Children, *J. Applied Sci.*, 7, 3696- 3704 (2007)
3. Mia Shahin Md, Rawshan Ara Begum, Ah- Choy Er, Raja Datuk Zaharaton Raja Zainal Abidin and Joy acqueline Pereira., Burden of Malaria at Household Level: A Baseline Review in the Advent of Climate Change, *J. Environ. Sci. Technol.*, (2011).
4. WHO Media centre, 2010; <http://www.who.int/mediacentre/factsheets/fs094/en/>;
5. UNICEF 2009. Partnering to Roll Back Malaria in Nigeria's Bauchi State. At a glance: Nigeria. United Nations Children Fund, Abuja, Nigeria. <http://www.unicef.org/infobycountry/nigeria/49472.html>.
6. Preston, M. A and Borezy A. A., Genetic Variability and Molecular typing of shigella Sonneii strain isolated in Canada. *J. Clin. Microbiol.*, 32, 1427- 1430 (1994)
7. Gatsing D., Mbah J.A., Garba I.H., Tane P., Djemgou P., and Nji – Nkah B.F., An Antisalmonella agent from the leaves of *Glossocalyx brevipes* Benth (Monimiaceae), *Pak. J. Biol. Sci.*, 9, 84-87 (2006)
8. Brian K. C. M and Wahinuddin Sulaiman., Typhoid and malaria co-infection-an interesting finding in the investigation of a tropical fever, *Malaysia J Med Sci.*, 13, 74-5 (2006)
9. Bynum B., Typhomalaria. *Lancet*; (360)139 (2002)
10. Smith D. C., The rise and fall of Typhomalaria fever: I. Origins, *J Hist Med Allied* (1982a)
11. World Health Organization (1991). A practical handbook on severe and complicated malaria, Geneva
12. Akinsanya O., Grossman S.A., Leucocyte counts in healthy Nigerians. *Nig. Med. Journal.*, 3, 95-99 (1973)
13. Raphael S.S and Spencer F (1983) *Immunology and serology*, Lynch's medical laboratory technology, Saunders, Philadelphia
14. Englehardt A et al., *Aerztl labor*16 (42) (1970)
15. Reitman S and Frankel S., A colorimetric method for the determination of serum glutamic pyruvic transaminase, *Am.J.Clin.Pathol.*, 28, 56-63 (1957)
16. White NJ, M. Ho., The pathophysiology of malaria, *Adv. Parasitol*; 31, 84-167 (1992)
17. Nogochi T and Yamashits Y., The rabbit differs from other mammals in the tissues distribution of alkaline phosphatase isoenzymes, *Biochem. Biophys Res. Commum*; 143, 15-19 (1987)
18. Kechrid Z and Kenouz R., Determination of alkaline phosphatase activity in patients with different zinc metabolic disorders, *Turk J Med Sci*; 33, 387-391 (2003)
19. Vallee RL, Auid D.S., Zinc coordination, function, and structure of zinc enzymes and other proteins, *Biochemistry*; 29, 564-567 (1990)
20. Tietz NW., *Fundamentals of Clinical Chemistry*, W.B. Saunders Company Philadelphia, U.S.A. (1987)
21. Das B. S, Thurnham D.I., and Das D.B., Plasma α - Tocopherol, retinal, and carotenoids in children with falciparum malaria, *Am J Clin Nutri*; 640, 94-100 (1996)
22. Garba I. H and Gregory U., AST/ALT Ratio In Acute, Uncomplicated Falciparum Malaria Infection: Comparison In Relation To The AST/ALT Ratios In Diseases Of The Liver, *The Internet Journal of Tropical Medicine*. Volume 2 Number 2 (2005)
23. Sujatha R., Amsath A., and Govindarajan A., AST and ALT ratio in acute plasmodium vivax infected patients in thanjavur, nagapattinam and cudallore districts of Tamil Nadu, India, *Int. J. Rece. Sci. Res.*, 3, 069-071 (2010)

24. Pratt D.S and Kaplan M.M., Evaluation of abnormal liver-enzyme results in asymptomatic patients, 1266-1271 (2000)
25. Piton A, Poynard T., and Imbert-Bismut F., et al., Factors associated with serum Alanine transaminase activity in healthy subjects: consequences for the definition of normal values, for selection of blood donors, and for patients with chronic hepatitis C. Hepatology; **27**, 1213-1219 (1998)

Table- 1: Mean Values of the Liver Enzymes Activities

PARAMETERS GROUPS	ALKALINE PHOSPHATASE (ALP) (U/L) Mean ± S.E.M	ASPARTATE AMINOTRANSFERASE (AST) (U/L) Mean ± S.E.M	ALANINE AMINOTRANSFERASE (ALT) (U/L) Mean ± S.E.M
CO-INFECTION (GROUP 1)	4.03 ± 1.64 ⁺⁺	9.50 ± 0.33 ⁺⁺	5.58 ± 0.36 ⁺⁺
CONTROL GROUP	1.45 ± 0.26	8.80 ± 0.60	4.00 ± 0.89
MALARIA (GROUP 2)	3.99 ± 0.31 ⁺⁺	8.97 ± 0.41 ⁺⁺	5.52 ± 0.23 ⁺⁺

Values are expressed as mean ± standard error of mean. ⁺⁺ significantly different from the control group (P<0.05).

VERMIREMEDIATION OF SOILS CONTAMINATED WITH MIXTURE OF PETROLEUM PRODUCTS

Kelechi L. Njoku, Modupe O. Akinola & Catherine C. Anigbogu

Department of Cell Biology and Genetics, University of Lagos.

knjoku@unilag.edu.ng, kecynjoku@gmail.com.

ABSTRACT

The indiscriminate and frequent spillage of petroleum products into the environment calls for a serious concern. This is due to the fact that there is much environmental problems associated with petroleum oil. A biological means of cleaning up soils contaminated with petroleum products was evaluated in this study using an earthworm - *Eisenia fetida*. Soils samples contaminated with mixture of petroleum products (gasoline, diesel and spent engine oil) were analysed for the total petroleum hydrocarbon (TPH) level and content every 24 hours for 120 hours using gas chromatography technique. It was observed that at each sampling time, the soils samples without the earthworm had more quantity of TPH than the corresponding samples with the earthworms. The results showed that *E. fetida* enhances the degradation and reduction of TPH levels in soils and therefore can be used for cleaning up of soils contaminated with mixture of petroleum products.

Keywords: Vermiremediation, petroleum, contamination, earthworm

INTRODUCTION

There is a high demand of petroleum and petroleum globally as fuel and as lubricants for proper functioning of machines. Due to this high demand, petroleum products are widely transported from one location to another. This may lead to spill of the products into the soil or water with subsequent adverse effects. The need to reclaim such contaminated soils and water has led to evaluation of several remediation techniques. Hitherto, mechanical, chemical and physical methods have been employed in cleaning up site contaminated with petroleum products. However, recent studies have shown that microbes, fungi, algae, plants and earthworms have the ability to facilitate the remediation of petroleum polluted sites.

Earthworms are burrowing animals and form tunnels by literally eating their way through the soil. The distribution of earthworms in soil depends on factors like soil moisture, availability of organic matter and pH of the soil. They occur in diverse habitats specially those which are dark and moist. Earthworms perform various functions in soil. They improve the physical, chemical and biological properties of the soil to enhance its fertility. According to Dabke (2013), earthworms stimulate and accelerate microbial activity by creating favorable conditions for bacteria and improving soil aeration. According to Hickman and Reid (2008) earthworms can be directly employed within bioremediation strategies to promote biodegradation of organic contaminants. Also, earthworms have been shown to aerate and bioturbate soils and improve their nutritional status and fertility, which are variables known to limit bioremediation (Hickman and Reid 2008).

According to Sinha *et al.* (2008), vermiremediation may prove a very cost-effective and environmentally sustainable way to treat polluted soils and sites contaminated with hydrocarbons in just few weeks to months. Vermiremediation leads to significant improvement in the quality of soil and land where they inhabit (Sinha *et al.*, 2008). Dabke (2013) reported a reduction in chromium level in the soil and survival of introduced earthworms, which reproduced after soil treatment, indicating improved conditions. According to Aziz *et al.* (2013)

vermiremediation utilising *Lumbricus rubellus* has proved its potential to degrade polycyclic aromatic hydrocarbons (phenanthrene, anthracene and benzo(a)pyrene (BaP)) in 30 days of incubation. From the work of Azaripa *et al* (2013) it has been observed that microelements like sodium ion and magnesium ion as well as salts like nitrate, phosphate and can be brought to their lowest level in sheep manure and garden soil in presence of *Eudriluseugeniae*. Azaripa *et al* (2013) reported a significant reduction (50-80 %) in trace elements and soluble salts in sheep manure and garden soil in presence of *Eudriluseugeniae*. The Rajiv *et al* (2013) reported that 30-35% of organic carbon and 32-48% of phenol contents were reduced during vermicomposting after 45 days of *Eudriluseugeniae*'s activity.

This study was aimed at determining the efficacy of *Eisenia fetida* to clean up soils contaminated with mixture of petroleum products. The result of the study will assist in reclaiming soils that have been more or less abandoned or that have been degraded due to contamination from petroleum products. The contamination of the soil with mixture of petroleum products in the laboratory simulates what happens naturally in soil mechanic workshops where different forms of petroleum products can spill into same soil same time or at different times. This is typical of most developing countries where mechanic workshops are sited haphazardly in open places.

METHODS

The *Eisenia fetida* used for the study was obtained from the Zoological garden of the University of Lagos, Akoka Lagos, Nigeria. The gasoline and diesel fuels were purchased from the petrol station in Akoka Lagos and the spent engine oil was obtained from a mechanic workshop in Latunde Street, Okota Lagos. The gasoline, diesel and spent engine oil were mixed in equal proportion to obtain a homogeneous petroleum product mixture.

100g of fine sieved loam soil were added to each of 500ml beaker followed by the addition of 10ml of the petroleum mixture into each beaker. The soil-petroleum mixture was properly stirred according to the procedure outlined by Mohan *et al.*, (2011). The mixture was allowed to stay 48 hours before 10 earthworms were added to each beaker (Barkley *et al*, 2011). The control experiment had no earthworm. The experiment and the control experiments were incubated at a room at room temperature for 120 hours

Soil samples were obtained every 24 hours for 120 hours. The total petroleum hydrocarbon content of the soil were extracted using the protocols outlined by Eijsackers *et al.*, (2001) using a mixture of 70% dichloromethane and 30% n-hexane. The extract was filtered using filter paper. The filtrate was purified by the concentrate through a pasture pipette packed with anhydrous sodium sulphate.

The types and levels of total petroleum hydrocarbon in the soil samples were determined using an Agilent Technologies Interface Detector Model 5975C gas chromatography. These were done according to the manufacturer's description.

RESULTS

The types and amount of petroleum hydrocarbon present in the soils with and without *E. fetida* after different incubation times are shown in figures 1 - 5. There was a general reduction of the levels of the different hydrocarbons in the soil with the earthworm compared with the ones in the soils without earthworm. Pentadecane, 2,6,10-trimethyl and dodecane 2,6,11-trimethyl were totally removed from the soil with *E. fetida* after 24 hours incubation (figure 1). There was 100% loss of dodecane, 5,8-diethyl and tricosane after 48 hour incubation (figure 2). There was also a 100% removal of dodecane, 5,8-diethyl from the soil with *E. fetida* as compared with soil without *E. fetida* after 72 hours incubation (figure 3). In the soils incubated for 96 hours (figure 4), there was 100% lost of tridecane, tetracosane and pentadecane, 2,6,10- trimethyl in soil with *E. fetida* compared with level in soil without *E. fetida*. In the case of soils incubated for 120 hours

(figure 5), many by products were observed in soil with *E.fetida*. Also, there was 100% loss of pentadecane, 2,6,10- trimethyl and Bacchotricuneatin c/tetradecane from the soil with *E. fetida* after 120 hours incubation.

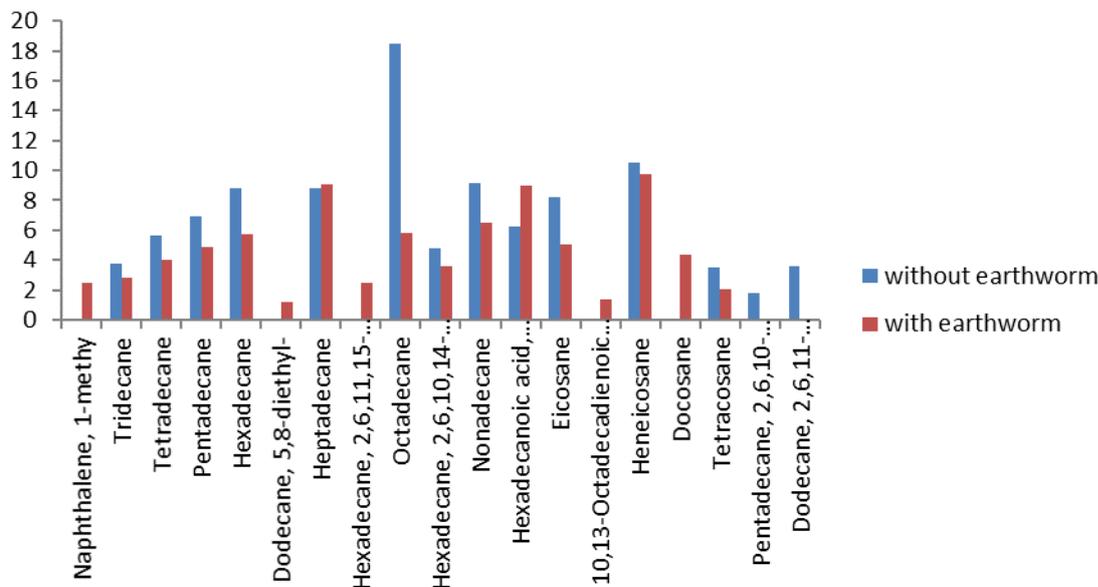


Figure 1: The types and Levels (%) of Petroleum Hydrocarbon in soil samples with and without *E. fetida* after 24 hours incubation

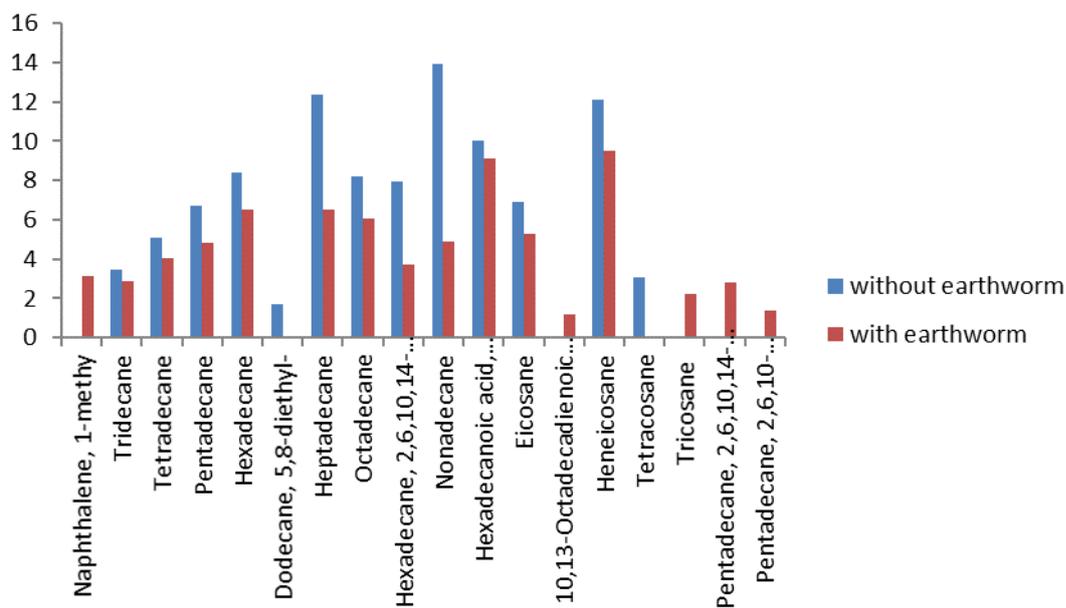


Figure 2: The types and Levels (%) of Petroleum Hydrocarbon in soil samples with and without *E. fetida* after 48 hours incubation

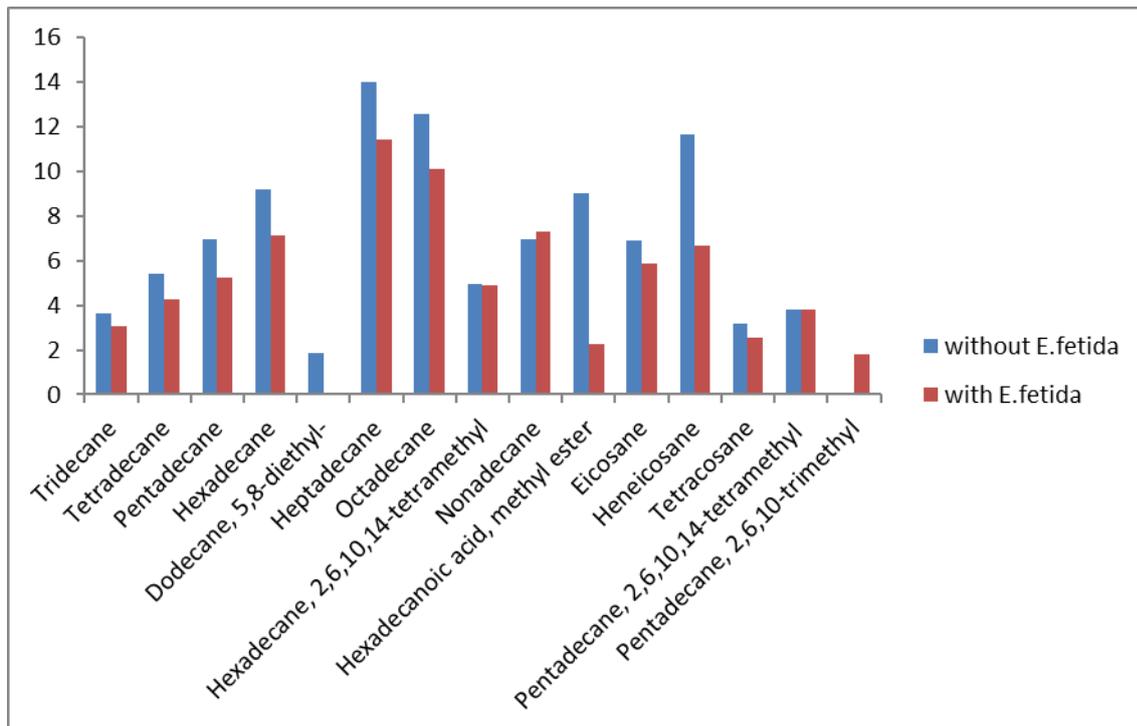


Figure 3: The types and Levels (%) of Petroleum Hydrocarbon in soil samples with and without *E. fetida* after 72 hours incubation

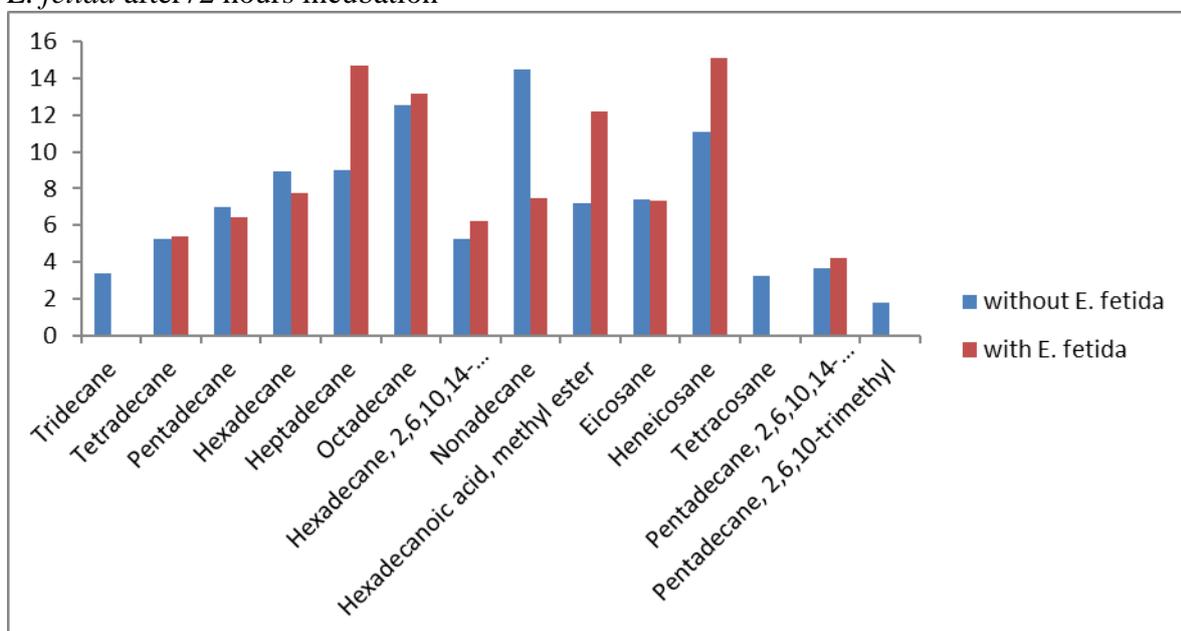


Figure 4: The types and Levels (%) of Petroleum Hydrocarbon in soil samples with and without *E. fetida* after 96 hours incubation

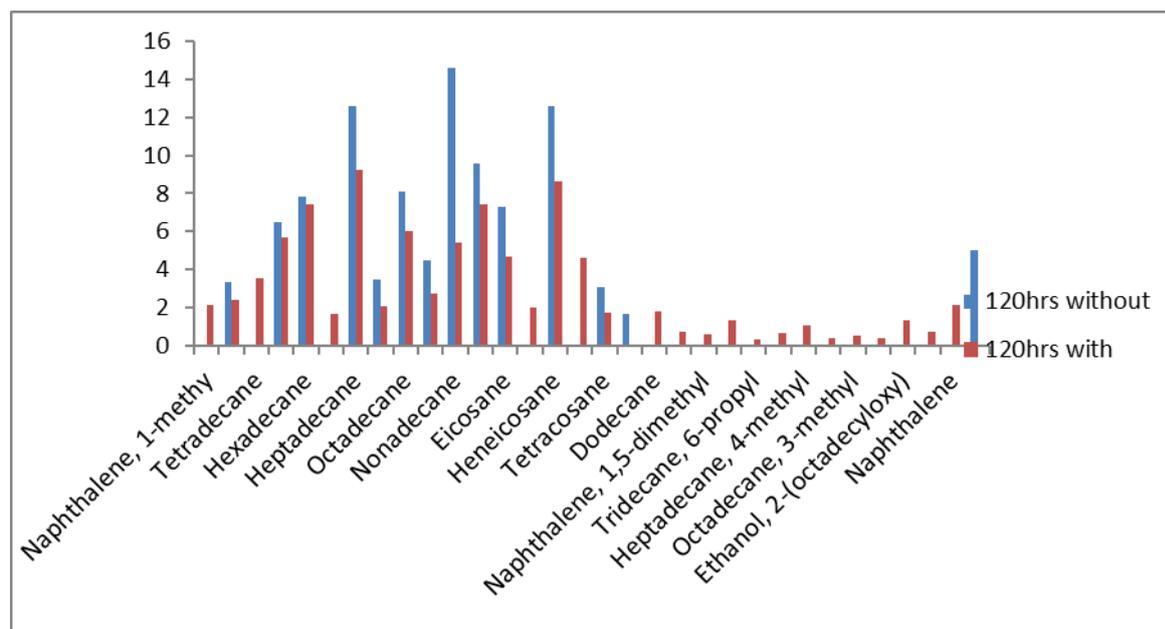


Figure 5: The types and levels (%) of Petroleum Hydrocarbon in soil samples with and without *E. fetida* after 120 hours incubation

Table 1 shows the levels of the petroleum hydrocarbons in the soil incubated for 24 hours without earthworm and in soil incubated for 120 hours with earthworm. Tridecane, tetradecane, pentadecane, octadecane, hexadecane, 2,6,10,14- tetramethyl, eicosane, heneicosane, tetracosane, and dodecane, 2, 6, 10- trimethyl were significantly reduced after 120 hours incubation with *E. fetida*

Table 1: Percentage levels of some petroleum hydrocarbons in soils incubated for 24 hours without earthworm and 120 hours with earthworm

Petroleum Hydrocarbon	24 hours without earthworm	120 hours with earthworm
Tridecane	3.73	2.4
Tetradecane	5.61	3.52
Pentadecane	6.89	5.7
Octadecane	18.44	6.03
Hexadecane,2,6,10, tetradecane	4.77	2.75
Eicosane	8.17	4.66
Heneicosane	10.48	8.64
Tetracosane	3.52	1.75
Pentadecane, 2,6,10, trimethyl	1.80	0
Dodecane, 2,6,10, trimethyl	3.57	0.75

DISCUSSION

The results of this study have shown that *E. fetida* has ability the ability to enhance the removal of petroleum hydrocarbons from soil. The total loss of some the petroleum hydrocarbons from the soil with earthworm as compared to the soils without the earthworm indicates that ability of the earthworm to remove such from soil. The reduction of the levels of the other petroleum hydrocarbons in the soils with earthworm as compared with the soils without earthworm shows the ability of the earthworm to reduce the levels of such hydrocarbons in soil. The reduction or removal of the heavy metals from the soils could be attributed to the mineralization of the

petroleum products by the earthworm. This is similar to the findings of Contreras-Ramos *et al* (2008), Tejadas and Masciandaro (2011), Aziziet *al* (2013) among others. Rajiv *et al.* (2013) reported similar trend of result as obtained in this study with reduction of 30–35% of organic carbon and 32–48% of phenol contents in soil during vermicomposting, which was achieved after 45 days of earthworm's activity. The observation of Rodriguez-Campos *et al* (2014) that accelerated removal of contaminants from soil by earthworms can be due to improvement of soil as a result of activities of earthworm and the microorganisms in their digestive track can be used to explain the possible mechanism used by *E. fetida* to remove the hydrocarbons in this study. The stimulation and increase in the activities of microorganisms which Dabke (2013) had stated as one of the functions of earthworm may account for the removal or reduction of the petroleum hydrocarbons as we observed in this study.

The presence of some petroleum hydrocarbon in the polluted soils incubated with the earthworm against their absence in soils incubated without the earthworm shows that vermiremediation of petroleum polluted soils takes through degradation. That implies that *E. fetida* enhances the degradation of petroleum in soil and those hydrocarbons are possible degradation products of petroleum.

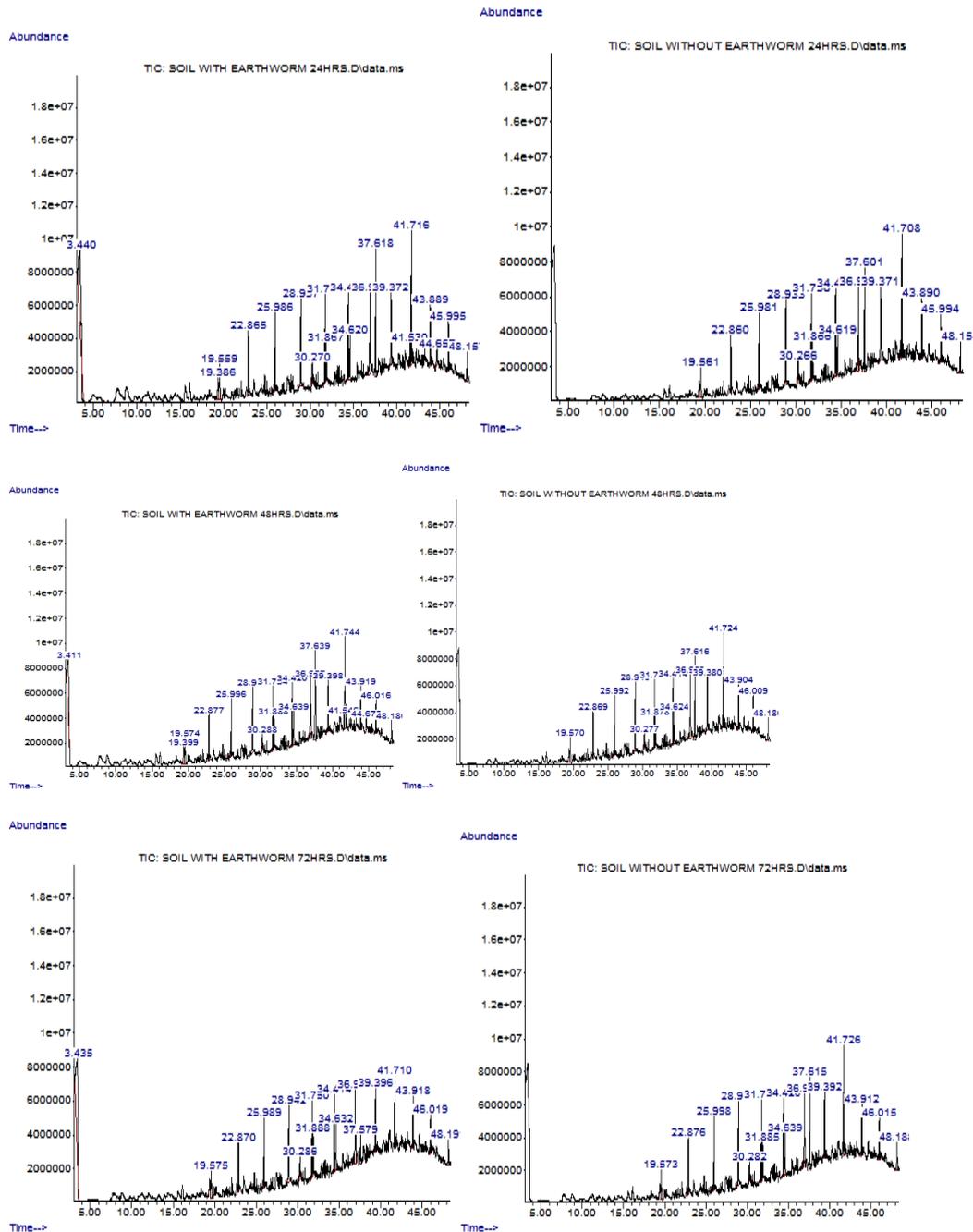
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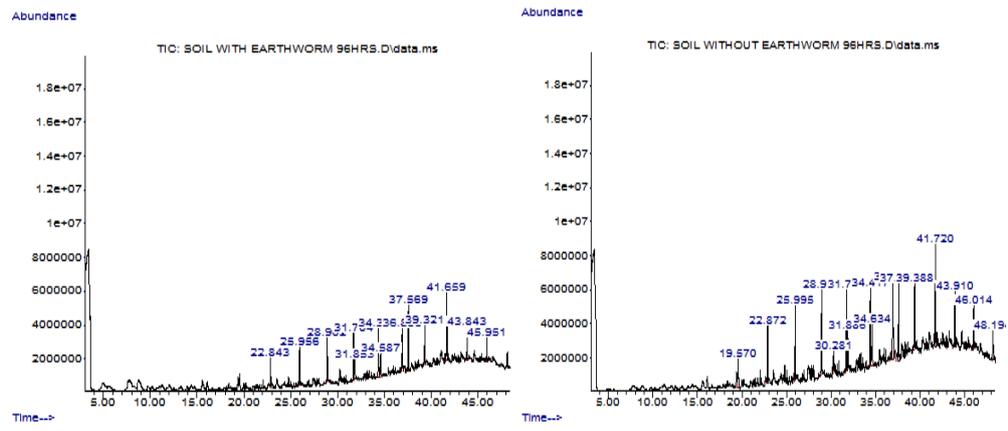
- Azaripa, H., Behdarvand, P., Dhumal, K.N. and Younesi, A. (2013) Vermiremediation of microelements and soluble salts in sewage sludge by earthworms. *International Journal of Current Research*. 5 (12): 3628 – 3632
- Azizi, A. B., Liew, K. Y. , Noor, Z. M and Abdullah, N. (2013) Vermiremediation and Mycoremediation of Polycyclic Aromatic Hydrocarbons in Soil and Sewage Sludge Mixture: A Comparative Study. *International Journal of Environmental Science and Development*. 4, (5): 565 – 568
- Barkley, J, Davidson, S., Gough, H., Nassau, E., and Azwell, T., (2011) Vermi-remediation of Crude Oil Contaminated Soils. www.cfr.washington.edu/classes/esrm.409/2011_student.../barkley.pdf
- Contreras-Ramos, S.M., Alvarez-Bernal, D. and Dendooven, L. (2008). Removal of polycyclic aromatic hydrocarbons from soil amended with biosolid or vermicompost in the presence of earthworms (*Eiseniafetida*). *Soil Biology and Biochemistry* 40: 1954-1959
- Dabke, S. V. (2013) Vermi-remediation of Heavy Metal-Contaminated Soil *Blacksmith Institute Journal of Health and Pollution* 3 (4): 4-10
- Eijasacker, H., Van Gestel, C.A.M., De Jonge, S. Muijjs, B. and Slijkeman, D. (2001). PAH-polluted dredge peat sediments and earthworm: A mutual interference. *Journal of Ecotoxicology*. 10: 35-50
- Hickman, Z.A. and Reid, B.J. (2008) Earthworm assisted bioremediation of organic contaminants. *Environment International*; 34(7):1072-1081
- Mohan K.V, Hrushikesh. N, Sreehari. K, Aravindkumar, T, Vidyavathi, N, and Pallavi. A (2011) Studies on bioremediation of Phenol by earthworm. *International Journal of Environmental Sciences* 1 (6): 1268 – 1273
- Rajiv, P., Rajeshwari, S., Yadav, R. H. and Rajendran, V. (2013) Vermiremediation: Detoxification of Parthenin toxin from Parthenium weeds. *Journal of Hazardous Materials*, 262: 489-95.
- Rodriguez-Campos, J., Dendooven, L., Alvarez-Bernal, D. and Contreras-Ramos, S.B. (2014) Potentials of earthworms to accelerate the removal of organic contaminants from soil: A Review. *Applied Soil Ecology*, 79: 10-25
- Sinha, R. K., Bharambe, G. and Ryan D. (2008) Converting wasteland into wonderland by earthworms—a low-cost nature's technology for soil remediation: a case study of

vermiremediation of PAHs contaminated soil. *The Environmentalist: the International Journal for all Environmental Professionals*, 28(4): 466-475.

Tejada, M. and Masciandaro, G. (2011). Application of organic wastes on a benzo(a)pyrene polluted soil. Response of soil biochemical properties and role of *Eiseniafetida*. *Ecotoxicology. Environment and Safety*. 74: 668-674

APPENDICES





A STOCHASTIC MODEL OF SOME ENDEMIC INFECTIONS

Nkemnole E. B.^{1*}, & Osunkeye R. O.^{2*}

*Department of Mathematics, University of Lagos, Nigeria.
enkemnole@unilag.edu.ng¹, raphealosunkey@rockemail.com²

ABSTRACT

This research investigates the endemic level and knowledge of persistence time of endemic diseases in a population by the use of Stochastic Model such as Markov process with continuous time and discrete state space which also required the Monte Carlo Simulation. It assesses some areas of active research in efficient procedures for simulation in health sector and addresses the influence of gender as regards to the average days a particular disease dies out. There is also an emphasis on the average population to be infected on a monthly basis. The data from medical records of General Hospital Gbagada, Lagos State are used for the study. The Monte Carlo simulation carried out shows the trend line and equations of the data. Empirical analysis showed a significant association between gender and persistence time of endemic diseases in a population.

Keywords: continuous time Markov chain, epidemic, stochastic epidemic models

INTRODUCTION

Disease is an abnormal condition that affects the body of an organism. It is often constructed as a medical condition associated with specific symptoms and signs. It sometimes includes disabilities, infections and typical variations of structure and function. When infection persists in the population for a long time, the disease is said to be endemic. Endemic diseases are ones that are always present in a community, usually at a low, more or less constant frequency. Malaria, arthritis, and high blood pressure are examples. Endemic diseases are in most communities around the world, all the time. Cholera is a strictly epidemic disease; it comes and goes but doesn't stay in a community for extended periods. In addition, there is a form Typhus (there are actually four forms, spread by different bugs which bite people) called "endemic typhus". Endemic typhus occurs most commonly in warm, coastal regions. An infection is said to be endemic in a population when that infection is maintained in the population without the need for external inputs. For example, chickenpox is endemic in Nigeria likewise malaria. For an infection that relies on person-to-person transmission to be endemic, each person who becomes infected with the disease must pass it on to one other person on average. Assuming a completely susceptible population, that means that the basic reproduction number (R_0) of the infection must equal 1. In the population with some immune individuals, the basic reproduction number multiplied by the proportion of susceptible individuals in the population (S) must be of each 1. This takes account probability of each individual to whom the disease may be transmitted actually being susceptible to it, effectively discounting the immune sector the population. For the disease to be in an endemic steady state:

$$R_0 \times S = 1 \quad (1) \quad \text{In}$$

this way, the infection neither dies nor does the number of infected people increases exponentially then the infection is said to be in an endemic steady state. An infection that starts as an epidemic will eventually either die out or reach the endemic steady state, depending on the number of factors, including the virulence of the disease and its mode of transmission. If a disease is in endemic steady state in a population, the relation above allows us to estimate the R_0 of a particular infection.

World Health Organization (WHO) reported that infectious disease crisis of global proportions is today threatening the ground-breaking accomplishments that have been recorded in world health thereby increasing life expectancy. Infectious diseases are now the world's biggest killer of children and young adults. They account for more than 13 million deaths a year – one in two deaths in developing countries. Over the next hour alone, 1500 people will die from an infectious disease- over half of them are children under five. The rest will mostly be working-age adults. This report argues that we have a window of opportunity to make dramatic progress against ancient diseases, and to establish an early warning system to protect us from new and unexpected diseases. The spread of infectious disease through a population can be modeled as a stochastic process.

LITERATURE REVIEW

Mathematical modelling of infectious diseases has a long history; see, in particular, Bailey (1975). Early modelling contributions for infectious disease spread were often for specific diseases. The starting point is generally taken to be a paper by Bernoulli, (1760) on the prevention of smallpox by inoculation; an account of his model-based analysis of data can be found in Daley and Gani (1999). Ross (1911) modelled the transmission of malaria. One of the first more general research was conducted by Kermack and McKendrick (1927). Later important contributions were made by Bartlett (1949) and Kendall (1956), both also considering stochastic models.

Early models were often deterministic with questions such as: Is it possible that there is a big outbreak infecting a positive fraction of the community?, How many will get infected if the epidemic takes off?, What are the effects of vaccinating a given community fraction prior to the arrival of the disease?, What is the endemic level? As problems were resolved, the simple models were generalised in several ways towards making them more realistic. Some such extensions were for example to allow for a community where there are different types of individual, allowing for non-uniform mixing between individuals (i.e. infectious individuals don't infect all individuals equally likely), for example due to social or spatial aspects, and to allow seasonal variations.

Another generalization of the initial simple deterministic epidemic model was to study stochastic epidemic models. A stochastic model is of course preferable when studying a small community. But, even with a large community, which deterministic models primarily are aimed for, some additional questions can be raised when considering stochastic epidemic models: What is the probability of a major outbreak?, and for models describing an endemic situation: How long is the disease likely to persist (with or without intervention)? Later stochastic models have also shown to be advantageous when the contact structure in the community contains small complete graphs; households and other local social networks being common examples. Needless to say, both deterministic and stochastic epidemic models have their important roles to play and deterministic and stochastic models are used for epidemiological modeling however, the focus in the present paper is on stochastic model. The stochastic model is a Markov population process with continuous time and discrete state space.

Nasell (2002) averred that stochastic models should be established and studied for several endemic infections with demography. Approximations of quasi-stationary distributions and of times to extinction are derived for stochastic versions of Susceptible and Infected (SI), Susceptible Infected Susceptible (SIS), Susceptible Infected Recovered (SIR), and Susceptible Infected Recovered Susceptible (SIRS) models. The approximations are valid for sufficiently large population sizes. Conditions for validity of the approximations are given for each of the models. These are also conditions for validity of the corresponding deterministic model. It is

noted that some deterministic models are unacceptable approximations of the stochastic models for a large range of realistic parameter values. For him, SIS model without demography is a univariate model. The stochastic version of this model is a finite-state birth-death process with an absorbing state at the origin. The goal of the mathematical analysis of this model is to find approximations of the quasi-stationary distribution and of the time to extinction. He used the Kolmogorov equation by introducing four parameters, namely the expected population size N in case where there are no infected individuals, the contact rate β , the death rate per susceptible individual μ , and an additional death rate μ_1 such that the death rate per infected individual is $\mu + \mu_1$. Among these, N is a large positive integer, β and μ are positive, and μ_1 is non-negative. In addition to the four parameters $N, \beta, \mu, \text{ and } \mu_1$ introduced, he used γ_1 to denote the recovery rate per infected individual. The SIS model takes the form of a bivariate Markov population process. The Kolmogorov forward equations for the state probabilities are:

$$P_{si}(t) = P\{S(t) = s, I(t) = i\}$$

Nasell (2002) also formulated a stochastic SIR model with demography. The model is a Markov population process with three state variables, S, I, and R, standing for the number of susceptible, infected, and recovered individuals, respectively. The recovered individuals are assumed permanently immune to additional infections. He used five basic parameters as for the SIS model namely: the expected population size N if all individuals are susceptible, and the death rate per susceptible or removed individual μ , the additional death rate per infected individual μ_1 , the contact rate β , and the recovery rate per infected individual γ_1 .

The state probabilities are defined by:

$$P_{sir}(t) = P\{S(t) = s, I(t) = i, R(t) = r\}. \quad (3)$$

2.1 Statistics as Regard Infections

Nishirura (2010) maintained that the reporting interval of infectious diseases is often determined as a time unit in the calendar regardless of the epidemiological characteristics of the disease. No guidelines have been proposed to choose the reporting interval of infectious diseases. His study aimed at translating coarsely reported epidemic data into the reproduction number and clarifying the ideal reporting interval to offer detailed insights into the time course of an epidemic. He derived a corrected expression for this quantity and proposes simple algorithms to estimate the effective reproduction number as a function of time, adjusting the reporting interval to the generation time of a disease and demonstrating a clear relationship among the generation-time distribution, reporting interval and growth rate of an epidemic.

Svensson (2007) is of the view that the statistical method to determine the reporting interval is density estimation, which may suggest a stochastic model for this project. To interpret the time course of an endemic, case notifications are used to estimate a key variable that characterizes transmissibility with time. The effective reproduction number at time t , R_t , defined as the average number of secondary cases per primary case at time t (for $t > 0$), is a useful measure to inform about the transmission potential of a disease and indications of the expected number of secondary transmissions and of control efforts required to curb the epidemic. Although the most precise reporting interval would certainly yield the most ideal interpretation of the transmission dynamics, it is often impractical to get data and analyze on an hourly or daily basis.

Eckhoff (2012) proffered that a global malaria eradication effort will require massive changes to complex web of interconnected biological systems. The optimal path to eradication is intrinsically unpredictable because of the potential for parasites and vectors to evolve, the waxing and waning of human immunity, and behavioral changes in human and vector populations. To succeed, eradication will require a strategic plan that is constantly updated with

the surveillance, monitoring, and evaluation data. Moreover, planning processes involve some sort of conceptual model, and this model will necessarily consider many potential sources of uncertainty. Rational quantitative mathematical models provide that best way to synthesize information, quantify uncertainty, and extrapolate current knowledge. Such models can provide critical quantitative insights that are not otherwise possible.

The objective of this study is to investigate the endemic level and knowledge of persistence time of endemic diseases in a population by the use of Stochastic Model such as Markov process with continuous time and discrete state space with a view to determining the proportions of population infected and equally know the duration until the disease dies out. The outline of the remainder of this article is organized as follows: Section 3 describes the data and discusses the method of analysis. Results of our analysis are presented in Section 4, while Section 5 concludes.

DATA AND METHODS

Data

The data used for this study is obtained from the medical record of the General Hospital Gbagada, Lagos State, comprising of children from age 0 to 12 years and adults from age 13 years and above. Research was carried out on the following: Diseases of children from the age 0 to 12 years which include: Neonatal jaundice (NNJ), Neonatal sepsis (NNS), Bronchopneumonia (BPN), Plasmodiasis (PD), Gastroenteritis (GN), Malaria; diseases of adults from the age of 13 years and above which include: Critical Cardiac Failure (CCF) Cardiovascular (CV), Chronic Kidney Disease (CKD), Hyperglycemia (HG), Appendicitis, Oral sepsis (OS).

Method

The study utilizes the Markov population process with continuous time and discrete state space. In a continuous time Markov chain (CTMC), time is continuous, but the state variable is discrete. Markov chain can be thought of as a directed graph of states of the system. The difference is that, rather than transitioning to a new (possibly the same) state at each time step, the system will remain in the current state for some random; exponentially distributed, amount of time and then transition to a different state. According to Allen (2010), the CTMC epidemic processes are defined on a continuous time scale, $t \in [0, \infty)$, but the states $S(t)$, $I(t)$, and $R(t)$ are discrete random variables.

Here, the stochastic process depends on the collection of discrete random variables and their associated probability functions $(t) = (p_0(t), \dots, p_N(t))^T$.

In our study, attempt was made in formulating the CTMC based on the SIR epidemic models to the Diseases. To numerically compute a sample path of a CTMC model, we used the fact that the interevent time has an exponential distribution. This follows from the Markov property.

The probability distribution function (PDF) of an exponential distribution is given by:

$$f(x) = \begin{cases} \lambda e^{-\lambda x} & x \geq 0 \\ 0 & x < 0 \end{cases} \quad (5)$$

The cumulative distribution function (CDF) of an exponential distribution is

$$F(x) = \begin{cases} 1 - e^{-\lambda x} & x \geq 0 \\ 0 & x < 0 \end{cases} \quad (6)$$

Let $U = F(x)$

Make x the subject of formula,

$$x = \frac{-1}{\lambda} \log(1 - u) \quad (7)$$

U denotes the generated random numbers.

$$\lambda = \frac{1}{\text{mean}}$$

Thus $X = \frac{-1}{\lambda} \log(RAND (0,1))$ (8)

Consequently, the Microsoft Office Excel Package with the Monte Carlo simulation add-in was used to carry out Monte Carlo simulation for the diseases-data thereby generating sample paths and the probability distribution associated with CTMC SIR epidemic models. The output gives the trend line and trend equation, that is; $= 11.439e^{-0.011x}$, histogram and cross tabulation which explains the average, minimum, maximum and standard deviation for both the duration of time the diseases die out and the population to be infected.

RESULTS

Running the simulation on Monte Carlo add-in package on Microsoft Excel with 1000 repetitions, that is, 1000 sample spaces into the future prior to the original data gotten from the medical record of the General Hospital, Gbagada; the results are presented on Figures 1-12 and Tables 1-2 shown below with its respective summary statistics for Male and Female infected adults and Male and Female infected children.

Table 1 is a presentation of the approximate average days that a disease would die out in a male and female patient respectively: Appendicitis (12, 11); CCF (15, 12); CVD (27, 17); Chronic Kidney Disease (11, 10); Hyperglycemia (12, 12); Oral sepsis (11, 9).

Table 1. Estimates of Duration of Diseases in infected Male and Female adults with corresponding infections

Statistic	APPD		CCF		CVD		CKD		HG		OS	
	M	F	M	F	M	F	M	F	M	F	M	F
Average	12.196	10.647	14.816	12.447	26.936	16.622	11.236	10.332	10.704	9.331	12.455	12.204
Std. Dev.	0.4365	1.2944	3.1748	1.4836	12.7936	0.4561	1.8731	0.4539	0.2430	5.1005	1.5597	0.4441
Maximum	13.005	12.063	45.449	24.065	114.000	19.632	25.442	14.892	12.791	18.189	26.903	12.687
Minimum	11.442	3.481	12.280	11.117	14.432	16.144	9.585	9.924	10.470	0.024	11.181	9.915

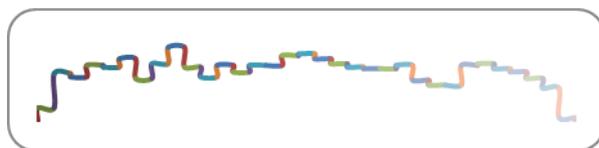


Fig 1a: Histogram for Appendicitis (Male)



Fig 1b: Histogram for Appendicitis (female)



Fig 2a: Histogram for Critical Cardiac Failure (Male)

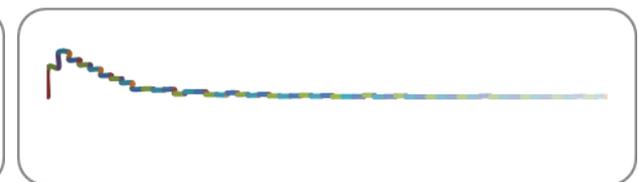


Fig 2b: Histogram for CCF (female)

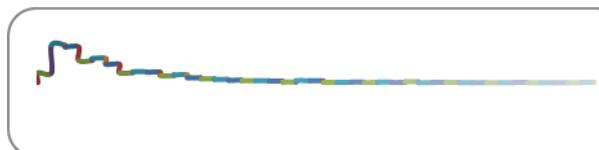


Fig 3a: Histogram for Cardiovascular disease (Male)

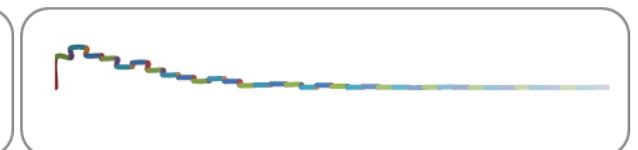
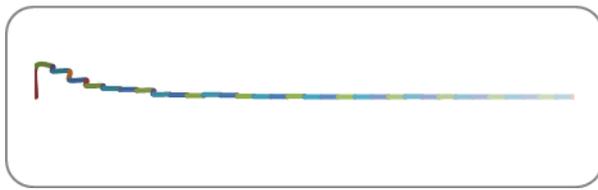


Fig 3b: Histogram for Cardiovascular Disease (Female)



4a: Histogram for Chronic Kidney Disease (Male)



Fig 4b: Histogram for Chronic Kidney Disease (Female)

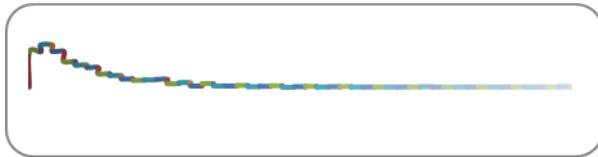


Fig 5a: Histogram for Oral Sepsis (Male)

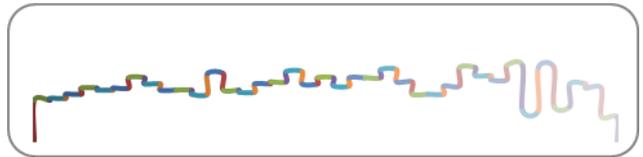


Fig 5b Histogram for Oral Sepsis (Female)

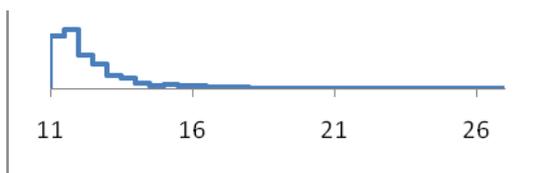


Fig 6a: Histogram for Hyperglycemia (Male)

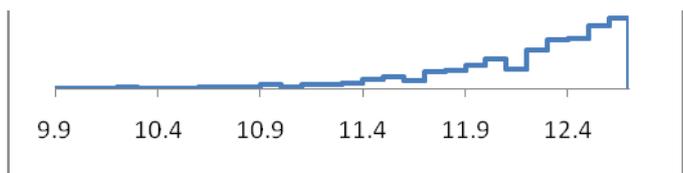


Fig 6b: Histogram for Hyperglycemia (female)

Figure 1-6: Graphical representation of Duration of Diseases in infected Male and Female adults with corresponding infections.

Table 2 is a presentation of the approximate average days that a disease would die out in a male and female children respectively: neo natal jaundice (7, 6); neo natal sepsis (5, 7); bronchopneumonia (5, 4); Plasmodiasis (3, 3); Gastroenteritis (4, 4); Malaria (2, 5).

Table2.Estimates of Duration of Diseases in infected Male and Female children with corresponding infections

Statistic	NNJ		NNS		BPN		PLASM		GN		MALARIA	
	M	F	M	F	M	F	M	F	M	F	M	F
Average	6.674	5.929	5.081	6.990	4.508	3.591	2.603	2.755	3.793	4.279	1.999	4.664
Std. Dev.	1.3846	0.5989	0.4443	0.9296	0.1473	0.4296	0.1498	0.1563	0.0916	0.2244	1.899	0.3861
Maximum	8.338	6.601	7.841	8.071	5.441	7.096	3.547	3.964	3.888	4.515	3.081	5.082
Minimum	0.755	2.975	4.656	2.499	4.363	3.221	2.460	2.610	3.361	2.836	1.822	2.321

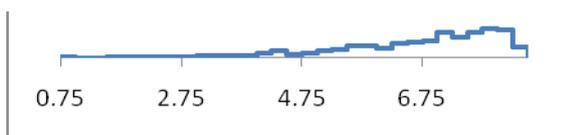


Fig 7a: Histogram for Neo Natal Jaundice (Male)

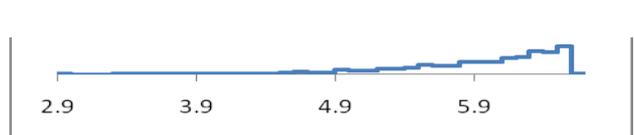


Fig 7b: Histogram for Neo Natal Jaundice (Female)

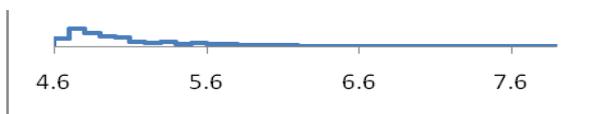


Fig 8a: Histogram for Neo Natal Sepsis (Male)



Fig 8b: Histogram for Neo Natal Sepsis (Female)



9a: Histogram for Bronchopneumonia (Male)

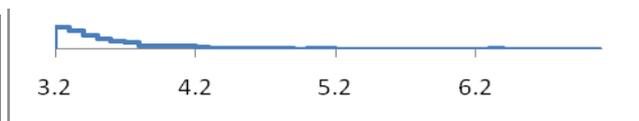


Fig 9b: Histogram for Bronchopneumonia (Female)

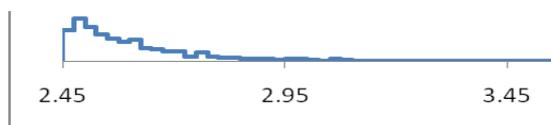


Fig 10a: Histogram for Plasmodiasis (Male)

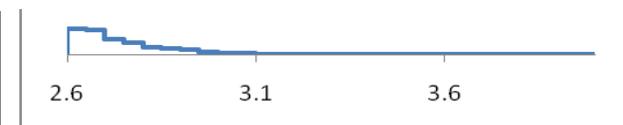


Fig 10b: Histogram for Plasmodiasis (Female)

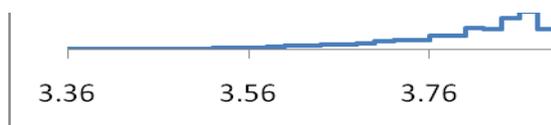


Fig 11a: Histogram for Gastroenteritis (Male)

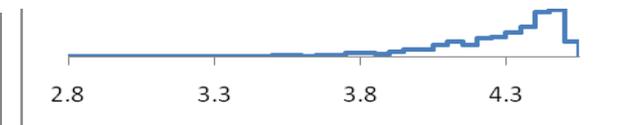


Fig 11b: Histogram for Gastroenteritis (Female)

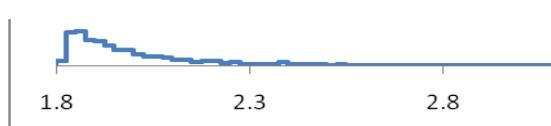


Fig 12a: Histogram for Malaria (Male)

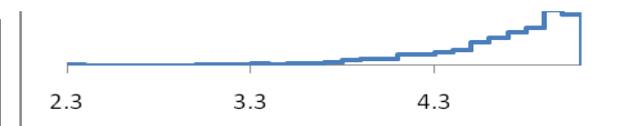


Fig 12b: Histogram for Malaria (Female)

Figure 7-12: Graphical representation of Duration of Diseases in infected Male and Female Children with corresponding infections

Forecast

The above procedure is used to forecast the average population to be infected with the diseases on a monthly basis which is categorized into the children category of ages 0 to 12years and adults from ages 13years and above. The results are presented on Tables 3-4 shown below with its respective summary statistics. The observed and predicted monthly incidence are plotted and displayed in Figures 8-16 (red line represents predicted disease while blue line represents observed disease).

Table 3 is a presentation of the forecast on the average population to be infected on a monthly basis in male and female adults respectively: Appendicitis (1, 1); Critical Cardiac Failure (2, 2); cardiovascular disease (2, 2); Chronic Kidney Disease (2, 1).

Table 3. Estimates of forecast on Male and Female adults to be infected with the diseases on a monthly basis

Statistic	APPD		CCF		CVD		CKD	
	M	F	M	F	M	F	M	F
Average	1.491	0.915	1.509	2.211	2.080	1.671	1.643	1.271
Std. Dev.	0.2238	0.2665	0.0909	0.1604	0.0063	0.0294	0.0787	0.2912
Maximum	3.306	1.410	2.438	3.301	2.087	1.876	1.724	4.523
Minimum	1.294	0.0000	1.426	2.060	2.039	1.642	1.248	1.040

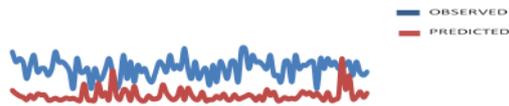


Fig 8a: Appendicitis (Male)



Fig 8b: Appendicitis (female)

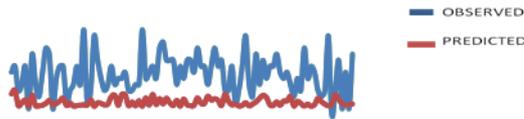


Fig 9a: Critical Cardiac Failure (Male)



Fig 9b: Critical Cardiac Failure (female)

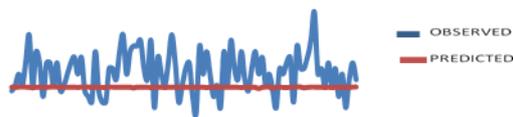


Fig 10a: Cardiovascular disease (Male)

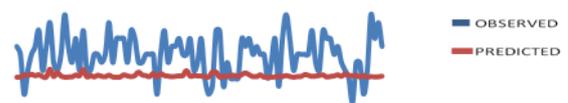


Fig 10b: Cardiovascular Disease (Female)

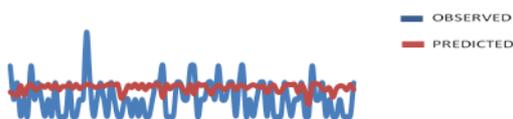


Fig 11a: Chronic Kidney Disease (Male)

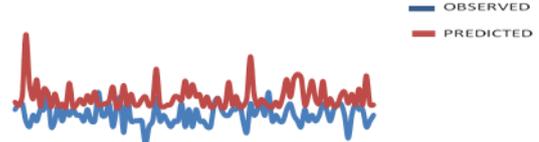


Fig 11b: Chronic Kidney Disease (Female)

Table 4 is a presentation of the forecast on average population to be infected on a monthly basis in male and female children respectively: Neo Natal Jaundice (4, 1); Neo natal sepsis (1, 3); Bronchopneumonia (7, 5); Gastroenteritis (4, 1); Malaria (8, 6).

Table 4. Estimates of forecast on Male and Female children to be infected with the diseases on a monthly basis

Statistic	NNJ		NNS		BP		GASTRO		MALARIA	
	M	F	M	F	M	F	M	F	M	F
Average	4.104	0.826	0.826	3.266	7.262	4.963	3.800	0.843	7.666	5.810
Std. Dev.	0.4440	0.5933	0.5933	0.0186	1.6350	0.2572	0.3281	0.7085	2.7100	5.4742
Maximum	4.571	4.427	4.427	3.286	9.313	5.214	6.116	9.349	37.704	67.309
Minimum	1.673	0.215	0.215	3.179	1.154	3.231	3.497	0.179	5.754	2.898

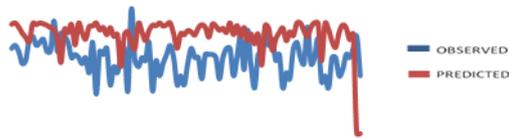


Fig 12a: Neo Natal Jaundice (Male)

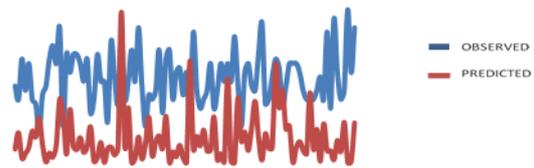


Fig 12b: Neo Natal Jaundice (Female)

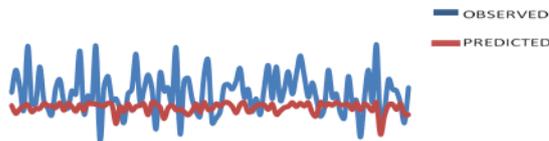


Fig 13a: Neo Natal Sepsis (Male)

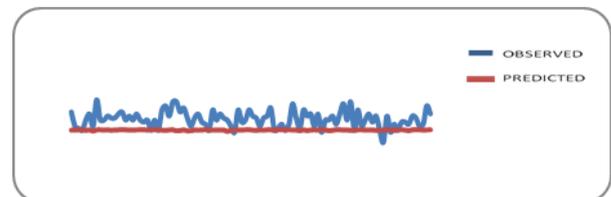


Fig 13b: Neo Natal Sepsis (Female)

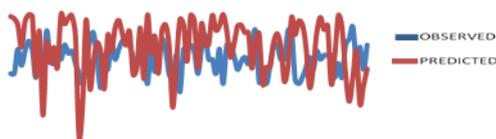


Fig 14a: Bronchopneumonia (Male)

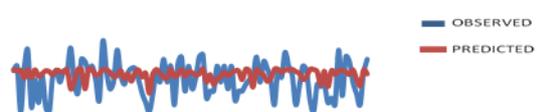


Fig 14b: Bronchopneumonia (Female)



Fig 15a: Gastroenteritis (Male)

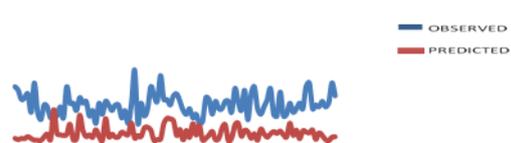


Fig 15b: Gastroenteritis (Female)



Fig 16a: Malaria (Male)

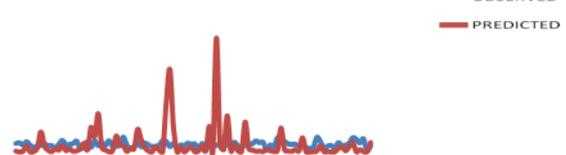


Fig 16b: Malaria (Female)

CONCLUSION

The study is centered on the investigation of endemic level and knowledge of persistence time of endemic diseases in a population by the use of Stochastic Model such as Markov process with continuous time and discrete state space with a view to determining the proportions of population infected and time until the disease dies out. The data from medical records of General Hospital Gbagada are used for the study. We have focused on presenting results for a fairly simple stochastic epidemic model; the reasons being that even in simple models results are far from trivial. The Microsoft Office Excel Package with the Monte Carlo simulation add-in was utilized to carry out Monte Carlo simulation for the diseases-data thereby generating sample paths and the probability distribution associated with the CTMC SIR epidemic model. The output is an indication that there was a significant association between gender and duration in which a

disease dies out, and also between diseases and population of male and female to be infected on a monthly basis respectively.

REFERENCES

1. Allen, L. J. S. (2010). An Introduction to Stochastic Processes with Applications to Biology, 2th Edition, Chapman and Hall.
2. Bailey, N.T.J. (1975). The Mathematical Theory of Infectious Diseases and its Applications., Griffin , London.
3. Daley, D. J., Gani, J. (1999). Epidemic Modelling An Introduction. Cambridge Studies in Mathematical Biology, Vol. 15. Cambridge Univ. Press, Cambridge.
4. Eckhoff P (2012) Malaria parasite diversity and transmission intensity affect development of parasitological immunity in a mathematical model.
<http://www.malariajournal.com/content/11/1/419>
5. Kendall, D.G. (1956) Deterministic and stochastic epidemics in closed populations.
6. Proc. Thirs Berkeley Symp. Math. Statist. & Prob., 4, 149-65.
7. Kermack, W. O. and McKendrick, A. G. (1927) Contributions to the mathematical theory of epidemics, part I. Proceedings of the Royal Society of London A,115, 700–721.
8. Nasell I. (2002). Endemicity, persistence, and quasi-stationarity. In: Castillo-Chavez, C. with Blower, S., van den Driessche, P., D. Kirschner, D., Yakubu, A. In Mathematical Approaches for Emerging and Reemerging Infectious Diseases An Introduction. Springer-Verlag, New York, pp. 199–227.

ANTIBIOTIC RESISTANCE PROFILE OF BACTERIA IN PHARMACEUTICAL WASTEWATERS FROM SOUTH WESTERN NIGERIA

Avemaria Obasi, Cyril Nwachukwu & Esther Ugoji

Department of Microbiology, University of Lagos, Lagos Nigeria
avemariaobasi@yahoo.com

ABSTRACT

Understanding the pharmaceutical wastewater resistome is essential in understanding the evolution and development of antibiotic resistance and its spread between species. Bacteria were isolated from wastewaters emanating from ten pharmaceutical industries in Lagos megacity, Nigeria. Total population densities of the bacterial isolates (cfu/ml) range between 2.7×10^4 to 2.7×10^{11} ; both Gram-positive and Gram-negative bacilli, cocci and coccobacilli were obtained with different morphological characteristics. Antibiotic susceptibility test were carried out using 13 types of antibiotics of commercially available discs (Abtex, Oxoid) according to the Kirby-Bauer method. The overall antibiotic resistance patterns of the bacterial isolates showed that 77.93% of the isolates were resistant, 13.28% had intermediate sensitivity and 8.78% were susceptible. High percentages of bacterial resistance were noticed in ampicillin (93.79%), cefuroxime and augumentine (91.72%) and the least resistance was observed in ciprofloxacin (55.17%); intermediate sensitivity was high for gentamicin (31.72%) but low for ampicillin (1.38%); highest sensitivity of the bacterial isolates were observed in ciprofloxacin (25.52%) and ceftazidime (2.76%) recorded the lowest sensitivity. The results of this study identified the resistance profiles of the bacterial isolate in pharmaceutical wastewaters in Nigeria and these elements can be used to enhance the understanding of the emergence and dissemination of novel antibiotic resistance from the natural reservoir.

Keywords: *Antibiotics, pharmaceutical wastewater, Antibiotic resistance, Kirby-Bauer*

INTRODUCTION

Most developing countries such as Nigeria are yet to routinely pass wastewater through treatment plants before delivery into the lakes and rivers (Ngwuluka *et al.*, 2011). Countries such as Italy, Germany, United States, United Kingdom, Taiwan, India have been determining and monitoring pharmaceutical waste, there is no apparent indication that Nigeria is monitoring it and there is little or no awareness that pharmaceutical waste is an emerging contaminant with growing concern (Ngwuluka *et al.*, 2011). This trend has been associated with an increase in the prevalence of single and multiple-antibiotic resistance in indicator organisms. A city like Lagos with more than 40 pharmaceutical industries may have increase in prevalence of antibiotic resistance as well as pharmaceuticals with concentrations that may be of great concern (Ngwuluka *et al.*, 2011). There has not been any information or reference to the prevalence of antibiotic resistance in wastewaters from pharmaceutical industries in Nigeria. The development of bacterial resistance, especially multidrug resistance to antimicrobial agents has resulted in increasing rates of morbidity and mortality of patients in health care institutions in Nigeria. Lateef *et al.*, (2005) reported that the emergence of bacteria resistant to most of the commonly used antibiotics/drugs is of considerable medical significance, because of the public health implications. Moreover, wastewater from animal agricultural facilities, human sewage treatment plants, hospitals, and pharmaceutical plants has been associated with increased levels of zoonotic pathogens as well as increasingly resistant and virulent organisms. Antibiotics from these settings could potentially act as a selection pressure that further influence the acquisition and spread of resistance genes

METHODS

Sampling sites and sample collection

Wastewaters from the discharge point of ten pharmaceutical industries located in the south western region of Nigeria were collected aseptically from different discharge points into sterile universal bottles on ice, these were transported to the laboratory and were analysed immediately in the microbiology research laboratory of the University of Lagos, observing standard routine microbiological analysis.

Microbiological Analysis

Water samples were serially diluted to obtain 10^{-3} , 10^{-5} , and 10^{-7} dilutions which were spread evenly on the surface of an already prepared nutrient agar plate accordingly to the spread plate method (Nwachukwu and Akpata, 2003), these were incubated at 37°C overnight. Isolation of the bacteria was done based on their morphology on plates which were then streaked on sterile nutrient agar plates already prepared to obtain pure cultures. Preliminary identification was done by their morphological characteristics, Gram stain (Nwachukwu and Akpata, 2003) and using 3% KOH method for the determination of Gram-negative bacteria (Gregersen, 1978).

Antibiotic Susceptibility Tests

The Bacterial isolates were inoculated in nutrient broth (NB) at 37°C for 24hours. A McFarland standard of 0.5 was achieved with an overnight culture in a tube and a sterile cotton wool swab dipped into the bacterial suspension was streaked over the entire sterile Mueller – Hinton agar plates, streaking was repeated two more times, rotating the plates approximately 60° each time to ensure even distribution of the inoculums. As a final step, the rim of the agar is swabbed. The inoculated plates were allowed to dry before placing the diffusion discs containing antibiotics. Susceptibility of the isolates to 13 types of antibiotics was performed using the standard Kirby-Bauer method as described by Robert *et al.*, (2009). Commercially available discs (Oxoid and Abtek, UK) containing Ampicilline (AMP10), Gentamycine (GEN10), Ciprofloxacin (CPR5), Ofloxacin (OFL5), Augmentine (AUG30), Ceftazidime (CAZ30), Cefuroxime (CRX30) and Nitrofurantoin (NIT300), Erythromycin (E15); Clindamycin (DA2); Nalidixic acid (NA30); Chloramphenicol (C30); Sulphamethoxazole/Trimethoprim (SXT25) were placed on the surface of the agar plates and incubated at 37°C for 24 h. The diameters of inhibition zones formed surrounding each isolate were measured inclusive diameter of the discs. Results were expressed as susceptible (≥21 mm); intermediate (16 to 20 mm) or resistant (≤15 mm) following a standard range by Liasi *et al.*, (15). *Escherichia coli* and *Bacillus subtilis* served as control strains for these assays.

RESULTS

Total population densities of bacterial isolates (cfu/ml) range from 2.7×10^4 to 2.7×10^{11} ; total number of bacterial isolates were 145 and their morphological characterization on plates showed that they were mostly roundish in form, transparent and opaque, milky in colour, raised or flat, entire in margin and smooth on the surface; 121 of the isolates were bacilli of tiny, short, long and slender rods, 21 were cocci of various sizes and 3 were coccobacilli. High percentages of bacterial resistance was noticed in ampicillin (93.79%), cefuroxime and augmentine (91.72%) and the least resistance was observed in ciprofloxacin (55.17%) (Figure 2); intermediate sensitivity was high for gentamicin (31.72%) but low for ampicillin (1.38%) (Figure 3); highest sensitivity of the bacterial isolates were observed in ciprofloxacin (25.52%) and ceftazidime (2.76%) (Figure 4) recorded the lowest sensitivity. Susceptibility patterns showed that the overall antibiotic resistance patterns of the bacterial isolates were 77.93% resistant, 13.28% intermediate and 8.78% susceptible (Figure 5C). Considering the different Gram reactions and the resistance

patterns; Gram-negative bacteria was of a higher resistance value (82.60%), when compared to the Gram-positive bacteria (72.73%) (Figure 5A and B).

DISCUSSION

This study found that the bacterial isolates had high antibiotic resistance which might have resulted from their ability to detoxify the antibiotic substances by altering the transport of compounds, through the bacterial cell membrane produce specific enzymes that can modify the antibiotics (Ong *et al.*, 2011). This calls for concern over the possible emergence of antibiotics resistant bacteria; these resistant strains might have resistance gene coded in the R plasmid or coded in the transposon (Herwig *et al.*, 1997). The R plasmid can transfer genetic material among different species in the conjugation and transformation processes. Thus, the bacterial isolates might have the R plasmid that carry four basic mechanisms of resistance which involve inactivation, the creation of substitute metabolic pathways, impermeability of cytoplasmic membranes and alteration in the target site. . It is very likely that resistance observed in this study is inherent and thus may be due to combined mechanisms of resistance such as impermeability and efflux (al Naiemi *et al.*, 2006; Weldhagen *et al.*, 2003) and they have been known to be opportunistic pathogens responsible for nosocomial infections, further experiments will be carried out to support this hypothesis. In this preliminary study, we have successfully established that bacterial isolates from the pharmaceutical industries showed bacteria with antibiotic resistance; these resistance patterns corresponds to that of clinically relevant species. This suggests that the evolution of intrinsic resistance in environmental and clinical bacteria developed along the same line. These strains might be infectious, as possibilities are that they could transfer their resistant gene to related species or their other counterparts. Further studies will be done to identify the species of all the isolates and the most widely used method for identification is genetic techniques such as the 16S rRNA gene analysis for phylogenetic study (Rasheed *et al.*, 2009).

CONCLUSION

In this study, we have been able to relate the ability of microorganisms to survive and develop certain antibiotic resistance capabilities due to selective pressure in the drug polluted waste water (Allen *et al.*, 2010). The antibiotic resistant bacterial isolates from these pharmaceutical wastewaters could cause increased difficulty in the treatment of human bacterial pathogens; antibiotic resistance acquisition due to selective pressure is of public health concerns as resistance genes can be disseminated in nature and transferred to pathogenic counterparts of bacterial species by genetic mobile elements (Wellington *et al.*, 2013), thus the need for effective treatment of the drug wastewaters before they are discharge into the environment.

REFERENCES

- al Naiemi, N., Dium, B. and Bart, A. (2006). A CTX-M extended –spectrum beta-lactamase in *Pseudomonas aeruginosa* and *Stenotrophomonas maltophilia*. *J. Med. Microbiol.* 55: 1607-1608.
- Allen, H.K., Donato, J., Wang, H. H., Cloud-Hansen, K.A., Davies, J. and Handelsman, J. (2010). Call of the wild: antibiotic resistance gene in natural environments. *Nature Reviews: Focus on antimicrobial resistance. J. Microbiol.* 8: 251- 259.
- Bauer, A.W., Kirby, W.M., Sherris, J.C. and Turck, M. (1966). Antibiotic susceptibility testing by a standardized single disc method. *Am. J. Clin. Pathol.* 45:493-496.
- Gregersen, T (1978). Rapid method for Distinction of Gram Negative from Gram Positive Bacteria. *European J. of Appl. Microbiol. and Biotechnol.* 5: 123- 127

- Herwig, R. P., Gray, J. P and Weston, D. P (1997). Antibacterial resistant bacteria in surface sediments near salmon net-cage farms in Puget Sound, Washington. *Aquaculture*. 149: 263-283.
- John, D.T., James, H. J., Murray, P. R., Baron, E. J., Pfaller, M. A., Tenover, F. C., Perry, J. B and Morton, D (2009). Manual of Clinical Microbiology (7th ed.), Washington D.C.: *American Society for Microbiology*. pp: 302-305.
- Lateef, A. (2004). The microbiology of pharmaceutical effluent and its public health implications. *World J. Microbiol Biotechnol*. 20:167-171.
- Lateef, A., Oloke, J. K and. Gueguimkana E. B (2005). The prevalence of bacterial resistance in clinical, food, water and some environmental samples in southwest Nigeria. *J. Environmental Monitoring and Assessment*. 100: 59–69.
- Liasi, S. A., Azmi, T. I., Hassan, M. D., Shuhaimi, M., Rosfarizan, M and Ariff A. B (2009). Antimicrobial activity and antibiotic sensitivity of three isolates of lactic acid bacteria from fermented fish product, Budu. Malaysian. *J. Microbiol*. 5: 33-37.
- Nwachukwu, S. C. U and Apata, T. V.I (2003). Principles of quantitative microbiology (First edition), University of Lagos Press, Lagos, Nigeria.
- Ong, K. S., Chin, H. S and Teo, K. C (2011). Screening of antibiotic sensitivity, antibacterial and enzymatic activities of microbes isolated from ex-tin mining lake. *African Journal of Microbiology Research*, 5(17): 2460-2466
- Rasheed, F., Khan A., Kazmi, S. U (2009). Bacteriological analysis, antimicrobial susceptibility and detection of 16S rRNA gene of *Helicobacter pylori* by PCR in drinking water samples of earthquake affected areas and other parts of Pakistan. Malaysian. *J. Microbiol*. 5: 123-127.
- Robert, A.P., Lorraine, F., Walter, M. and Ronald, M.R. (2009). Laboratory exercises in Microbiology (3rd ed.) U.S: John Wiley & Sons, Inc.
- Robert, A.P., Lorraine, F., Walter, M., Ronald, M.R (2009). Laboratory exercises in Microbiology (3rd ed.) U.S: John Wiley & Sons, Inc.
- Talaro, P. K (2009). Foundations in Microbiology. San Francisco: Pearson Benjamin Cummings
- Weldhagen, G.F., Poirel, L and Nordmann, P. (2003). Ambler class A extended-spectrum β -lactamases in *Pseudomonas aeruginosa*: novel developments and clinical impact. *Antimicrob. Agents Chemother*. 47: 2385-2392.
- Wellington, E.M.H., Boxall, A.B.A., Cross, P., Feil, E.J., Gaze, W.H., Hawkey, P.M., Johnson-Rollings, A.S., Jones, D.L, Lee, N.M., Otten, W., Thomas, C.M. and Williams A.P. (2013). The role of the natural environment in the emergence of antibiotic resistance in Gram-negative bacteria. *Lancet Infect. Dis. Rev*. 13:155-165.

APPENDIX

Table 1: Antibiotic resistance profile of Bacterial Isolates from pharmaceutical wastewaters

Susceptibility Tests Antibiotics/ Organisms	Resistant			Intermediate			Susceptible		
	Gm +ve	Gm -ve	Total Bacteria	Gm +ve	Gm -ve	Total Bacteria	Gm +ve	Gm -ve	Total Bacteria
AMP10	59	77	136	2	0	2	7	0	7
CAZ30	58	71	129	6	6	12	4	0	4
CRX30	57	76	133	6	1	7	5	0	5
GM10	34	55	89	30	16	46	4	6	10
CPR5	31	49	80	20	8	28	17	20	37
OFL5	38	47	85	17	17	34	13	13	26
AUG30	57	76	133	4	0	4	7	1	8
NIT300	44	50	94	12	14	26	12	13	25
E15	49	53	102	12	18	30	7	6	13
DA2	57	71	128	9	3	12	2	3	5
NA30	48	54	102	12	14	26	8	9	17
C30	54	61	108	9	7	16	5	9	14
SXT25	57	72	129	5	0	5	6	5	11

AMP10, ampicilline; CAZ30, ceftazidime; CRX30, cefuroxime; CN10, gentamycin; CPR5, ciprofloxacin ; OFL5, ofloxacin, AUG30, augmentine; NIT300, nitrofurantion, E15, Erythromycin; DA2, Clindamycin; NA30, Nalidizic acid; C30, Chloramphenicol; SXT25, Sulphamethozazole/Trimethoprin

Table 2: Percentage susceptibility of the bacteria to different antibiotics

Susceptibility Tests Organism/ Antibiotic	Resistant (%)			Intermediate (%)			Susceptible (%)		
	Gm +ve	Gm -ve	Total Bacteria	Gm +ve	Gm -ve	Total Bacteria	Gm +ve	Gm -ve	Total Bacteria
AMP10	86.76	100	93.79	2.94	0	1.38	10.29	0	4.83
CAZ30	85.29	92.20	88.97	8.82	7.79	8.28	5.88	0	2.76
CRX30	83.82	98.70	91.72	8.82	1.30	4.83	7.35	0	3.45
GM10	50.00	71.42	61.38	44.12	20.78	31.72	5.88	7.79	6.90
CPR5	45.59	63.64	55.17	29.41	10.39	19.31	25.00	25.97	25.52
OFL5	55.88	61.04	58.62	25.00	22.08	23.45	19.18	16.88	17.93
AUG30	83.82	98.70	91.72	5.88	0	2.76	10.29	1.30	5.52
NIT300	64.71	64.94	64.80	17.65	18.18	17.93	17.65	16.88	17.24
E15	72.06	68.83	70.34	17.65	23.38	20.69	10.29	7.79	8.97
DA2	83.82	92.20	88.28	13.23	3.90	8.28	2.94	3.90	3.45
NA30	70.59	70.13	70.34	17.65	18.18	17.93	11.76	11.69	11.72
C30	79.41	79.22	74.48	13.23	9.09	11.03	7.35	11.69	9.66
SXT25	83.82	93.31	88.97	7.35	0	3.45	8.82	6.49	7.59

AMP10, ampicilline; CAZ30, ceftazidime; CRX30, cefuroxime; CN10, gentamycin; CPR5, ciprofloxacin ; OFL5, ofloxacin, AUG30, augmentine; NIT300, nitrofurantion, E15, Erythromycin; DA2, Clindamycin; NA30, Nalidizic acid; C30, Chloramphenicol; SXT25, Sulphamethozazole/Trimethoprin



Figure 1: Susceptibility As Shown By The Zone Of Clearance On The Plates

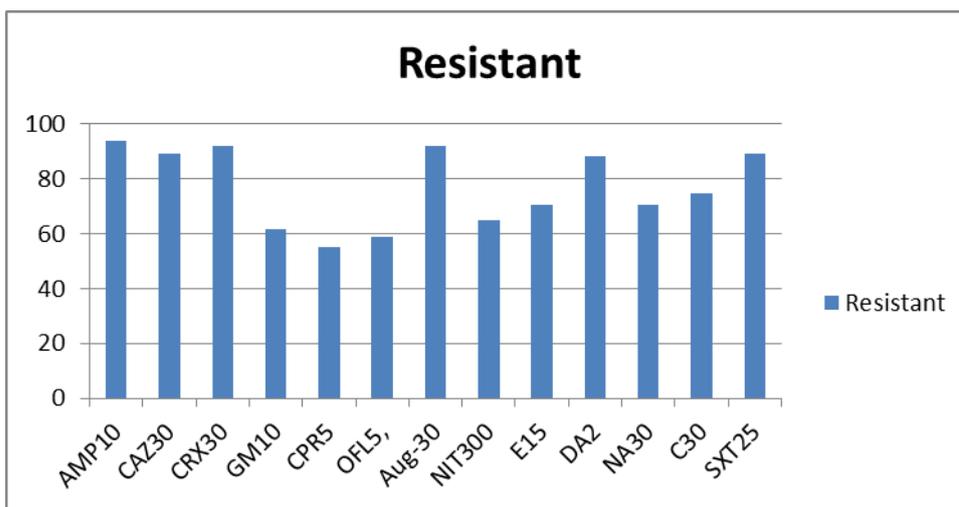


Figure 2: Bar Chart Showing The Percentage Resistance Of The Bacterial Isolates To Antibiotics

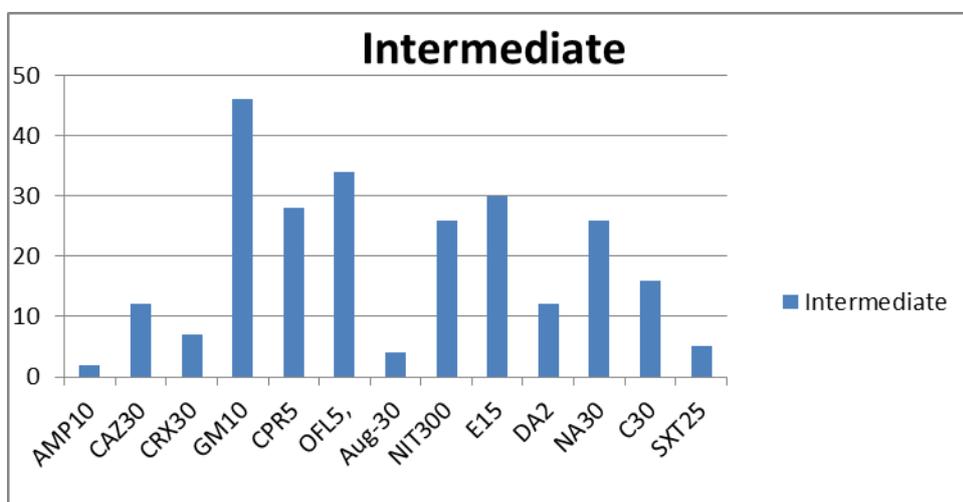


Figure 3: Bar Chart Showing The Percentage Intermediate Resistance Of The Bacterial Isolates To Antibiotics

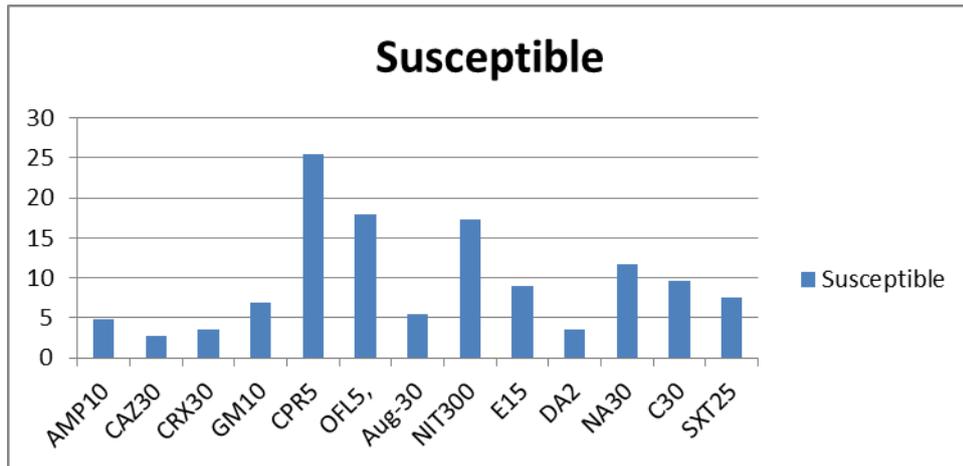


Figure 4: Bar Chart Showing The Percentage Susceptibility Of The Bacterial Isolates To Antibiotics

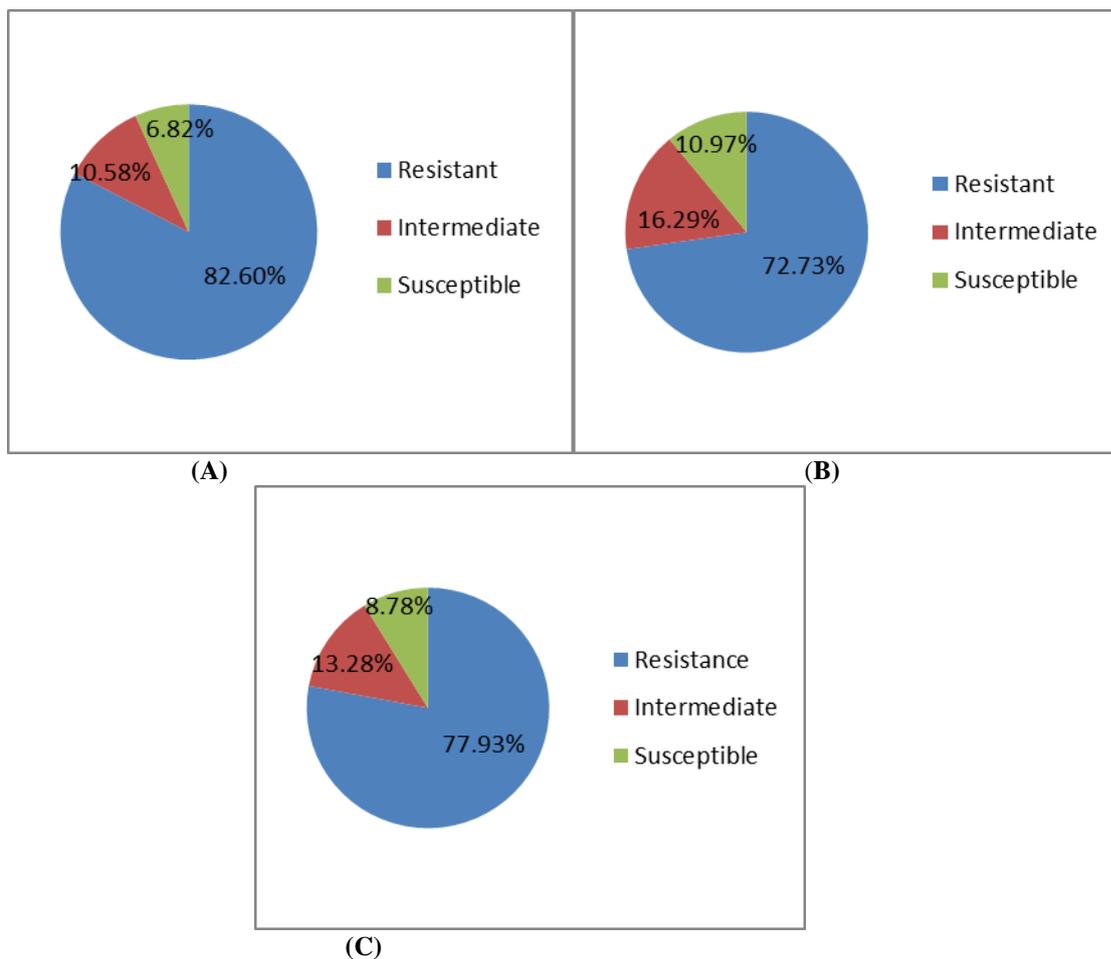


Figure 5: Pie Chart of The Susceptibility Patterns of Gram- Positive (A) Gram-Negative (B) And Overall Bacterial Isolates (C)

MAINSTREAMING ICTs IN SOCIAL SECURITY SCHEMES IN SUB-SAHARAN AFRICA

Okewu Emmanuel

Centre for Information Technology and Systems, University of Lagos, Nigeria
eokewu@unilag.edu.ng, okewue@yahoo.com

ABSTRACT

Social security has elicited research interests in recent times in different countries, including countries in Sub-Saharan Africa because of its perceived potentials for curbing social tensions and menace. However, there is need to empirically justify this claim through case study reports from several countries. Using content analysis, data on pervasive social insecurity and information on corrupt practices inherent in social security schemes were extracted from reports on existing empirical case studies. The outcome is a comprehensive compendium of social threats and subsisting safety net initiatives that suggests more case studies are required. Sub-Saharan Africa as a developing region with a lot of people in the vulnerable groups - unemployed, rural poor, women and persons with disabilities - need social security schemes to cater for these groups. Nevertheless, there is need to incorporate Information and Communications Technologies (ICTs) for purposes of accountability, transparency and equity in the distribution of social benefits. More so as there has been reports of corrupt practices in social security schemes that has prevented the target audience from getting planned benefits. This paper reports the application of ICTs in social security schemes. The research provides a basis to empirically verify the import of social protection on societal security. The result of the case study yielded a usable biometric design for Sub-Saharan Africa, and closed the gap in literature on social security initiatives in the African region.

Keywords: Information, Communication, Technologies, Poverty, Social security, Unemployment

INTRODUCTION

There is a general consensus that African countries need social security systems that would prevent people from acting desperately before they can make meaningful progress across the socio-economic spectrum. A coordinated and holistic social security system that will not only protect its citizenry from economic and social risks but also help in reducing the high rate of poverty in on the continent. Social security places responsibility on the state to protect and provide for the individual when he is unemployed, or losses his job as a result of occupational injury, accident , when he or she grows old and when a woman is on maternal leave or economically challenged, just to mention a few. The state of vulnerable groups like women, persons with disabilities, and the thousands of unemployed youths on the continent underscores the fact that all challenges that have impinged on successful implementation of social security system for several decades need to be urgently addressed. Over time, ICTs have proven to be useful in scaling upward the productive capacity of people either directly or indirectly. The economic productivity it induces brings about development and social transformation. The bottom line is that in the face of economic prosperity and social transformation, people find social ills unattractive and the continent is the better for it. Whereas directly ICTs skills, empowerment, jobs and income for the underprivileged and help secure their socio-economic future, it has also found relevance in entrenching accountability, transparency, probity and equity in initiatives that touch on the vulnerable groups.

This study examined the ongoing Boko Haram insurgency in Nigeria and acknowledged the sect has been recruiting members of the vulnerable groups for nefarious activities in Nigeria (Table 1), particularly as suicide bombers who detonate Improvised Explosive Devices (IEDs):

Table 1: Engagement of vulnerable groups in Boko Haram insurgency

SN	Vulnerable Group	Insecurity mission
1.	Persons with disability	Used as suicide bombers to detonate IEDs
2.	Unemployed young women	Used as suicide bombers to detonate IEDs
3.	Unemployed young men	Engaged as foot soldiers for gorilla welfare and as suicide bombers

A social security scheme is a strategic intervention aimed at empowering the socially vulnerable so that they will apply their minds productively for developmental purposes. According to Paime (1992), there is a correlation between security and survival. Whereas survival is an essential condition, security is viewed as safety, confidence, free from danger, fear, doubt, among others. Therefore, security is 'survival-plus' and the word 'plus' could be understood from the standpoint of being able to enjoy some freedom from life-determining threats and some life choices (Booth, 2007). Therefore, making available social safety nets is a developmental agenda that channels the energies of economically challenged people into national development.

Nwagboso (2012) examines the security challenges in Nigeria and the extent to which the insurgencies of different militia groups as well as the prevailing internal insurrections across the country have adversely affected the Nigerian economy. The Nigerian experience is a reflection of security threats across Africa as are highlighted in Table 2.

Table 2: Select security threats in Africa

SN	Security threat	Period	Country
1.	Ethnic cleansing	April - June 1994	Rwanda
2.	Civil War	1989 - 1996, 1999 - 2003	Liberia
3.	Arab Spring	2011 - 2012	Egypt
4.	Arab Spring	2011	Tunisia
5.	Arab Spring	2011 - to date	Libya
6.	Civil War	1991 - 2002	Sierra Leone
7.	Niger Delta crisis	1999-2007	Nigeria
8.	Jos crisis	2001- to date	Nigeria
9.	Civil War	2013- to date	South Sudan
10.	Militia uprising	2013 - to date	Central African Republic
11.	Boko Haram crisis	2009 – to date	Nigeria

On the other hand, Information and communication technologies (ICTs) include any communication device—encompassing radio, television, cellular phones, computer and network hardware and software, satellite systems and so on, as well as the various services and applications associated with them, such as videoconferencing and distance learning. The research study reveals that the application of ICTs in the field of social security has popularized the concept of Information and Communication Technologies for Social Security (ICT4SS) as both a developmental agenda and academic discipline.

Information and Communication Technologies for Social Security (ICT4SS) refers to the use of Information and Communication Technologies (ICTs) in enhancing the socioeconomic wellbeing of the poor, disable, unemployed and vulnerable women. The theory behind this is that

more and better information and communication usage in social safety nets furthers the development of a society. The concern is less on e-readiness and more on the impact of ICTs on development. Additionally, there is more focus on the poor as producers and innovators with ICTs (as opposed to being consumers of ICT-based information).

After a study of the role of technology as a tool for development and social transformation over decades of economic evolution, the author tabulated findings as follows:

Table 3: Economic evolution and technologies used

Economic phase	Period	Technology Used
1st phase (Industrial revolution)	1770 - 1850	Water-powered mechanization
2nd phase (Kondratiev wave)	1850 - 1900	Steam-powered technology
3rd phase	1900 - 1940	Electrification of social and productive organization
4th phase	1940 - 1970	Motorization and automated mobilization of society
5th phase	1970 - to date	Digitalization of social systems

Despite the potentials of ICT4SS for development, social transformation and improved security, developing countries far lag developed nations in computer use and internet access/usage as shown in Fig. 1. Studies have shown that, on average only 1 in 130 people in Africa has a computer while in North America and Europe 1 in every 2 people have access to the Internet 90% of students in Africa have never touched a computer.

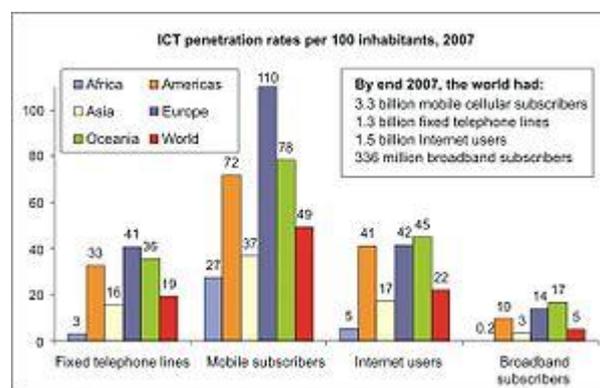


Figure 1: Graph of ICT penetration per 100 inhabitants by International Telecommunication Union (ITU)

As laudable as ICT interventions in social protection are, there is need for greater surveillance to curb unwholesome practices that may prevent the vulnerable groups from enjoying the dividends the schemes are meant to deliver. In this paper, the author proposes a biometric system for capturing and validating the particulars of would-be beneficiaries of the scheme as antidote to tackling the corrupt practices.

In next section, various direct applications of ICT are studied. Under *Related Works*, a number of case studies in this field are analyzed. The succeeding section, *Proposed ICT Solution*, presents the proposed biometric system design. In the second to last section, *Discussion*, the study analyzes the proposed system. The last section, *Conclusion and Further Work*, wraps up this research paper with details about further work on the proposed solution.

Direct ICT Interventions in Socio-Economic Empowerment of Vulnerable Groups

There are various direct applications of ICT that have empowered the less privileged across Africa (Table 4):

Table 4: Empowerment of the less privileged across Africa via ICT initiatives

SN	Country	Government Initiative
1.	Nigeria	e-wallet system for providing information about distribution of agricultural inputs to rural farmers using mobile technology. So far, 12 million farmers have benefitted from the scheme.
2.	Gambia	The telecentre application used to disseminate information on development issues such as agriculture extension, health, and education to poor communities.
3.	Mali	Wi-Fi antenna set up in Mali to relay information to the rural areas.
4.	Ghana	Satellite Internet access via VSAT under the Ecamic Project is used to make information available to the rural poor.
5.	Uganda	Charging mobile phone from car battery is to enable the less privileged to keep their mobile phones alive for information access.
6.	Burundi	Use of mobile telecommunications and radio broadcasting to fight political corruption in Burundi.
7.	Tanzania	Study shows the use of mobile phones has impacted rural living in the following ways (Bhavni et al, 2008): entrepreneurship and job search, easy access to information, correcting market inefficiencies, transport substitution, disaster relief, education and health, social capital and social cohesion.
8.	Kenya	Study identified innovation in mobile technologies for development (Masiero, 2013), in particular the success of M-PESA mobile banking which impacts on sectors like m-agriculture and m-health.
	Ethiopia	Evidence from Ethiopia indicates that farmers use mobile phones for interactions but may feel reluctant to call individuals whom they have never met personally, which restrains the usability of mobile phones in regions with limited transportation options (Matous et al, 2014).

According to the literature, the livelihoods of the following vulnerable groups have been greatly enhanced by ICTs (Deepak, 2012; Watkins, 2012; Motes, 2010; Maier, 2007):

- People with disabilities
- Rural farmers
- Women empowerment
- The unemployed

Related Work

The deliberate use of communication to facilitate development is not new. The essence of ICT-for-development (ICT4D) is to make use of this ongoing transformation by actively using the enabling technology to improve the living conditions of societies and segments of society. Social transformations over time such as industrial revolution had culminated in an interplay between enabling technology, desired guiding policies and strategies, and resultant social change (Freeman and Louca, 2002; Schumpeter, 1939; Perez, 2004). This three-dimensional interplay has been depicted by Hilbert (2012) as a cube shown in Figure 2 in tandem with the Schumpeterian school of thought. Put in another fashion, the three factors enabling socio-economic transformations are technology (infrastructure, generic services and capacities/knowledge), social services (education, health, business, government) and policies (regulation and incentives). When ICT practices are applied in a regulated and incentivized manner to scale up productivity in the social sectors, we have improved social services variants like e-government, e-business, e-health and e-education catalyze transformation, development and social security.

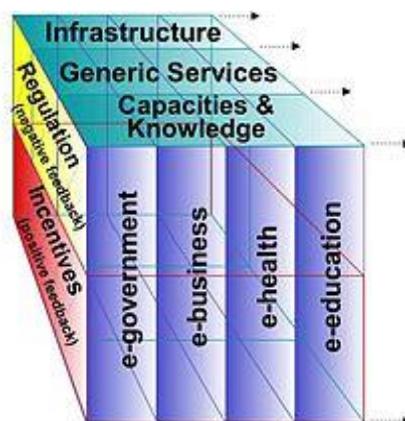


Figure: 2 ICT4D cube (Source: Hilbert, M. 2012. Towards a Conceptual Framework for ICT for Development)

Many development partners and researchers have leveraged on the ICT4D cube framework to impact positively on the livelihoods of the vulnerable groups in Africa - the poor, unemployed, women and the disabled using ICT. For that purpose they initiated various ICT policies, programmes and projects (Dymond and Oestermann, 2004; Languépin, 2010):

- International Telecommunication Union (ITU)
- World Bank
- Catholic Relief Services (CRS) ICT4D Conference
- ICT4D in Africa
- Mobile Technologies Providers

According to ITU, mobile communications and technology has emerged as the primary technology that will bridge in the least developed countries. As evidence, countries in Africa have recorded magnificent growth in using mobile phones to access the Internet. A case in point: In Nigeria, 77% of individuals aged 16 and above use their mobile phones to access the Internet as compared to a mere 13% who use computers to go online. This unfolding scenario in developing countries will bridge the digital divide between least-developed countries and developed countries (Fig. 3) although there are still hiccups in making these services affordable.

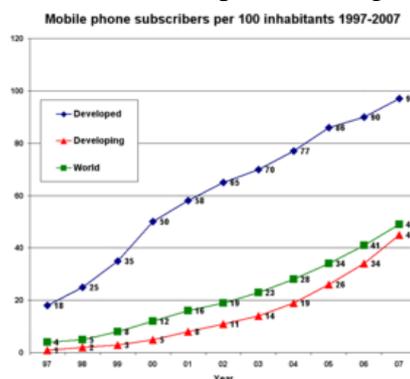


Figure: 3 Mobile phone subscribers per 100 inhabitants growth in developed and developing world between 1997 and 2007 (Source: ITU)

The use of mobile phones as key component of ICT4D initiatives has been successful as the widespread distribution of mobile telephony has made it possible for poor people to have easy access to useful and interactive information (Languépin, 2010). In India, for example, the total number of mobile phone subscriptions reached 851.70 million in June 2011, among which 289.57 million came from rural areas, with a higher percentage of increase than that in urban areas. This unprecedented growth of affordability and coverage of mobile telephony services has

underscored its importance not just as a means of two way communication but that of ease-of-access to information as well.

After careful analysis of existing case studies, the author observed with concern that none fulfilled all of the following criteria:

- a study that highlights social security initiatives by African governments as a matter of deliberate policy.
- a current study on corrupt practices inherent in social protection schemes in Africa.
- a study modelling a biometric system for curbing corrupt practices in social security initiatives.

This study thus proposed a new model that fulfilled these criteria. Whereas the underlying logic is to ensure the deliverables meant for the vulnerable groups get to them, the strategy is integration of biometric enrolment and verification system into social security schemes.

As seen from above direct applications, the integration of ICT in the drive to empower the less privileged adds significant value to socio-economic transformation and indirectly offers social protection for this segment of the society. Notwithstanding, governments across Africa still mount social security schemes as a matter of deliberate policy to impact positively on the same set of people and ICT plays vital role. When mainstreamed in social protection efforts, ICT safeguards numerous government social security schemes from abuse owing to corrupt practices. In Burundi, for example, it is popular to use mobile telecommunications and radio broadcasting to fight political corruption. This study reveals further that deliverables of social safety nets such as conditional cash transfer and free medical care for the vulnerable groups are being diverted by unscrupulous elements for personal gains. Even when benefits are delivered, they are in less than budgeted measure. Hence, there is need to integrate a biometric system and mobile devices into such schemes for validating genuine beneficiaries as well as disseminating information to them on the release and allocation of resources by government agencies. The following session outlines a blueprint for the electronic design of a social security scheme.

Proposed ICT Solution

Nigeria accounts for about 25% of Africa's population and remains the most populous black country in the world. The researcher considered that social security initiatives in Nigeria are, to a reasonable extent, quiet representative of trends on the continent. On analyzing select social security schemes in Nigeria, a table (Table 5) was developed to highlight various governments' social security schemes.

Table 5: Select social security programmes in Nigeria

S N	Code Name	Government	Type	Target	Commencement date	Status	Supervising ministry
1.	SURE-P (Subsidy Reinvestment Programme)	Federal Government	Safety-net tagged Community Service Scheme (CSS)	Women, disabled and unemployed	2012	Take-off stage – capacity building and empowerment of women, unemployed youths and disabled. Stipends and seed money offered.	Ministry of Labour and Productivity
2.	National Social Insurance Trust Fund	Federal Government	Social insurance	All categories	1961	Passive – the common man is yet to feel its impact	Fed. Min. of Labour & Productivity
3.	Social Security	Ekiti State	Social pension	The elderly – 65 years and above	October 2011	Functional – beneficiaries receive monthly stipend of 5,000 naira	State Ministry Labour, Productivity and Human Capital Development
4.	Project Comfort	Cross River	Safety Net – conditional cash transfer	Poor (vulnerable) households	2012	Functional - beneficiaries receive monthly stipend of 5,000 naira	State Ministry of Social Welfare
5.	Agba Osun	Osun State	Social pension	The elderly – 65 years and above	November 2012	Functional - beneficiaries receive monthly stipend of 5,000 naira	Office of the Governor
6.	National Health Insurance Scheme (NHIS)	Federal Government	Social protection	All ages	1989	Passive – the common man is yet to feel its impact	Fed. Min. of Health
7.	Project Hope	Cross River	Safety Net – free health care services	Women and children under 5 years	2012	Functional – 7 local governments receiving free health care	State Ministry of Social Welfare

Source: Okewu's field survey, 2014

From the above table it is observed the downtrodden are clearly targeted by the various governments for delivery of social benefits that free medical care, conditional cash transfer, among others. Hence, the author proposes a biometric system that captures beneficiaries' information and validates same at the point of disbursing the benefits with a view to curtailing the activities of fraudsters who intend to divert same to selfish purposes.

While designing the biometric verification system, the following are taken into cognizance (Ndeh-Che, 2008):

- Engagement of Systems Integrator that:
 - possess a deep understanding of, and the resources for, the analysis, design, development, deployment and maintenance of the systems and processes for the social security programme.
 - demonstrate proven track record of outstanding work in the area of biometric enrolment and verification, as well application development, deployment and integration.
- The systems integrators will:
 - integration reliable systems for identifying and registering eligible beneficiaries,
 - setup systems to support delivery of benefits, accounting for benefits, and monitoring and evaluation of the Social Benefit Scheme.
- Effort should be geared towards production of systems, processes and human resource requirements which will serve as an information platform; and as a service delivery medium for all stakeholders.

Systems integrator firms are saddled with the provision of systems integration services as needed by the government. They will assist government in the conceptualization, analysis, design, development, and deployment and maintenance of information systems that will ensure effective and secure management of the benefits scheme including, inter alia, (a) enrolment system for bona-fide beneficiaries, (b) biometric identity management and verification, (c) ID card production, and (d) system for the accounting of benefits.

On considering the above guidelines, the scope of work for the proposed biometric design will include:

1. Software and services for development and deployment of biometric enrolment system and training of technical personnel and provision of technical support during verification and enrolment effort – Personal and biometric data are captured and stored in a relational database system. Human error can be mitigated by using state-of-art forms processing systems, whilst time-tested biometric approach shall eliminate multiple enrolments of the same individual. During the exercise, beneficiaries will also have their supporting documents scanned, converted into e-forms and archived in a document management system. Support team will be on ground throughout, in order to ensure that the enrolment exercise runs smoothly. After the initial phase of the verification and enrolment exercise, continuous verification and enrolment will continue to ensure that new potential beneficiaries are properly verified and registered. Figure 4 and Figure 5 highlight enrolment infrastructure and enrolment process respectively.

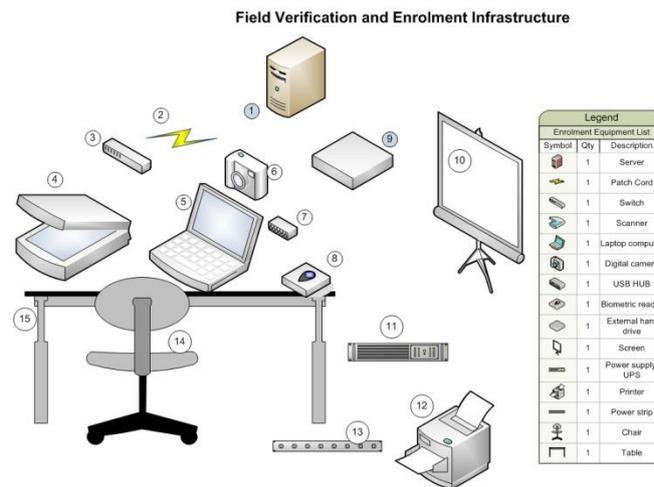


Figure 4: The enrolment infrastructure for an enrolment centre

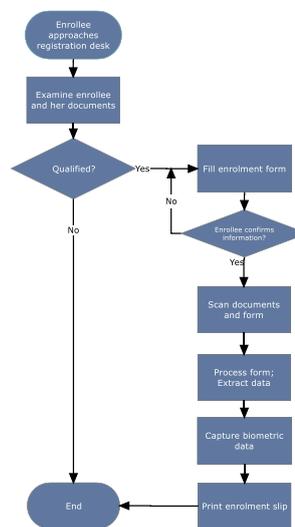


Figure 5: The enrolment process

- Systems integration for biometric enrolment database and identity management system – After field enrolment, the various biometric enrolment databases from enrolment centres, the scanned documents and the e-forms, are consolidated in a central database. To avoid duplicate enrolments across enrolment centres, an Automated Fingerprint Identification System (AFIS) should be deployed.

An identity management system can be set up, based on the consolidated database, to provide identification services. Figures 6 and 7 respectively model a consolidated view and the consolidation process.

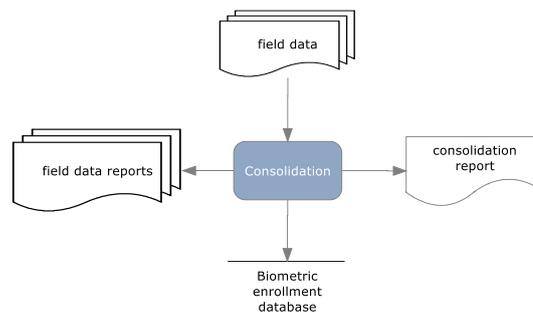


Figure 6: Consolidated view

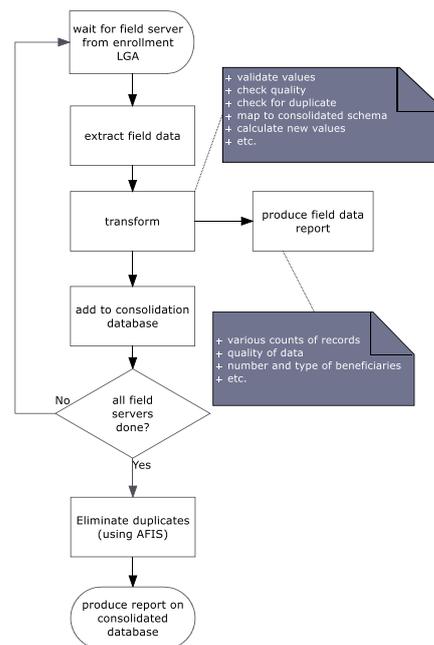


Figure 7: Consolidation process

3. Systems integration for ID card production, card acceptance devices and identity verification system – A likely outcome of the exercise is the production of authentic identity card (ID card). Beneficiaries can be provided with secure smart ID cards as proof of eligibility to receive benefits. Each card contains biometric information to verify the beneficiary on location, as well as other data as may be decided from time to time by the government. In the absence of the ID card, verification will still be possible over a remote connection to the central identity system. A production station should be set up for the design and production of the smart ID cards. The ID cards and ID card verification systems should be deployed at strategic locations (e.g. Benefits Stations) to prevent abuse of the scheme. Figure 8 shows a typical card printing infrastructure just as Figure 9 presents an ID card-enabled verification process. In the event a beneficiary has no card, he/she can still be verified remotely using finger print as captured in Figure 10.

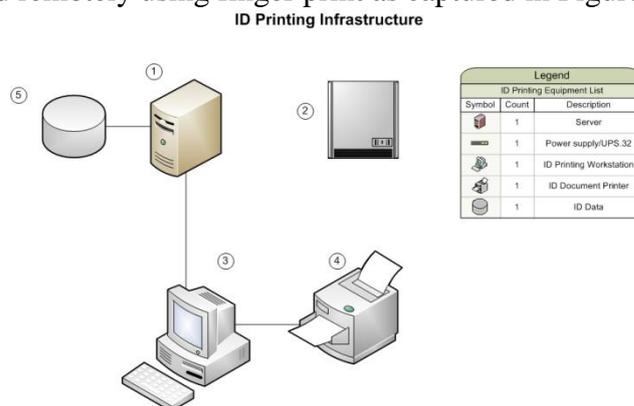


Figure 8: Card printing infrastructure

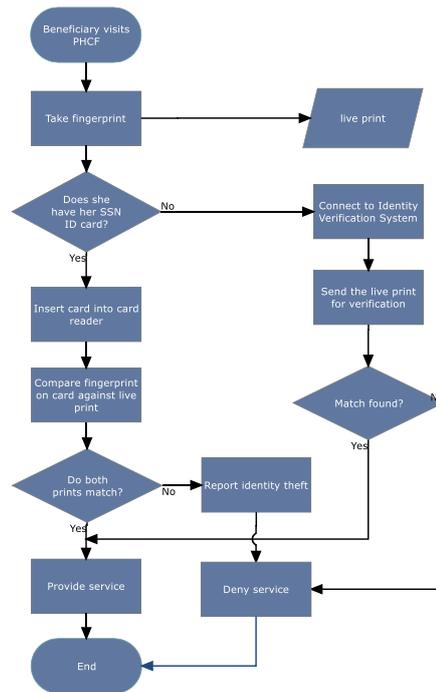


Figure 9: ID Card Verification Process

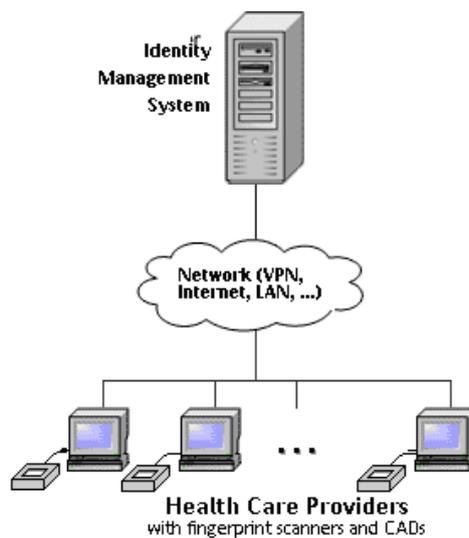


Figure 10: Identity verification process

4. Software and services for development and deployment of Benefits Accounting System – In order to ensure proper management of benefits accruing to citizens under any social security scheme, system integrators should partner with the government to develop a benefits administration system. This system will be custom-built to suit the specific requirements of the respective social safety net programme.
5. Technical and End-User Training – The need for adequate capacity building cannot be overemphasized. System Integration firms should provide comprehensive capacity building services to ensure that all human resources participating in the social protection programme are able to carry out their roles and responsibilities. Training categories could

- include i) Enrolment Officers, ii) Identity Management System Administrators, iii) Benefits Administration System End Users and iv) Benefits Administration Support Personnel.
6. Ongoing Support and Maintenance – To ensure smooth running of all systems deployed, the system integrator will provide ongoing support and maintenance services to the government.

The firm should deploy a multi-disciplinary team of professionals and support personnel, working over a stated period to complete and roll out the systems for the scheme. Emphasis should be placed on the engagement of a reputable firm to assist the government in realizing its vision of delivering social welfare packages such as free health care for, and financial assistance to the under-privileged. References of track record of successfully delivering expected project outcomes in similar engagements for other clients should be taken into cognizance. The firm should understand the challenges, possess the skill sets and emphasize client collaboration. Modalities should be put in place to guarantee fruitful working relationship between the firm and government.

The proposed solution will succeed if the following measures serve as guidelines (Ndeh-Che, 2008):

- Establishment of a uniform, clearly defined and objective criteria for determining eligibility for the scheme
- Collection of realistic baseline data on poverty for target setting
- Establishment of realistic targets and timeframes
- Establishment of a comprehensive Monitoring & Evaluation (M&E) Framework for all aspects of the scheme
- Sensitization of beneficiaries and stakeholders
- Institutionalizing transparency, accountability and good corporate governance in the scheme from the onset.
- Proper identification and registration of beneficiaries using the latest advances in identity management technologies
- Adoption of a holistic approach to achieving scheme objectives
- Reuse of data and resources from complementary initiatives such as census data and images and Roll Back Malaria initiative

DISCUSSION

This study revealed that mainstreaming ICT in rural Africa makes inroads into development and hence can curb social tensions and crisis. However, poor ICT infrastructure, cultural inhibitions, lack of proper disposal/recycling facilities, illiteracy, et al are challenges confronting ICT4SSS. Notwithstanding, vital lessons have been learnt from implementation of various ICT pilot programmes for the vulnerable groups and these have culminated in the following recommendations (Batchelor et al, 2003):

- Involve target groups in project design and monitoring.
- When choosing the technology for a poverty intervention project, pay particular attention to infrastructure requirements, local availability, training requirements, disposal and technical challenges. Simpler technology often produces better results.

- Existing technologies—particularly the telephone, radio, and television—can often convey information less expensively, in local languages, and to larger numbers of people than can newer technologies. In some cases, the former can enhance the capacity of the latter.
- ICT projects that reach out to rural areas might contribute more to the MDGs than projects based in urban areas and hence should be prioritized.
- Financial sustainability for ICT-for-development initiatives should be factored in.
- Projects that focus on ICT training should include a job placement component.

CONCLUSION

Though the social security scheme is a new concept in Africa and indeed in Nigeria, it has come to stay. Countries like Zambia, South Africa, Libya and Egypt have edged in social security programmes for citizens. There is need for the above biometric design to be developed for implementation in Nigeria. Secondly, for external and general validity of this model, it has to be tested in other African countries. As Africa joins the league of continents whose governments' execute ICT-driven socially responsible programmes for need-based citizens, it will gather lost confidence from citizens with far-flung expectations. And more importantly, idle minds will be engaged productively hence mitigating the chances of such citizens being indoctrinated and used as foot soldiers for fuelling crisis.

REFERENCES

1. Paime, M. A., (1992). *Guardians of the gulf*. New York: Free Press.
2. Booth, K., 2007. *Theory of world security*. London; Cambridge University Press.
3. Nwagboso, C., *Security Challenges and Economy of the Nigerian State (2007 – 2011)*. American International Journal of Contemporary Research Vol. 2 No. 6; June 2012
- Rothschild, E. (1995). *What is security?* New York: Columbia University Press.
4. Bhavni, Asheeta; Rowena Won-Wai Chiu, Subramaniam Janakiram, Peter Silarszky, Deepak Bhatia (June 15, 2008). *The Role of Mobile Phones in Sustainable Rural Poverty Reduction*.
5. Silvia Masiero. (2013). *Innovation and Best Practice in Mobile Technologies for Development, Economic and private sector professional evidence and applied knowledge services*
6. Petr Matous, Yasuyuki Todo, Tatsuya Ishikawa (2014) *Emergence of multiplex mobile phone communication networks across rural areas: An Ethiopian experiment*, Network Science.
7. Deepak, Bhatia. *ICTs and Disabilities*. Retrieved August 15, 2012.
8. Watkins, Amanda. *ICTs In Education For People With Disabilities*". UNESCO Institute for Information Technologies in Education. Retrieved August 15, 2012.
9. William C. Motes, *Modern Agriculture and Its Benefits – Trends, Implications and Outlook*.
10. Sylvia Maier (2007) *Empowering Women Through ICT-Based Business Initiatives: An Overview of Best Practices in E-Commerce/E-Retailing Projects*
11. C. Freeman and F. Louçã, *As Time Goes By: From the Industrial Revolutions to the Information Revolution*, Oxford University Press, USA, 2002.
12. J. Schumpeter. *Business Cycles: A Theoretical, Historical, And Statistical Analysis of the Capitalist Process*. New York; McGraw-Hill, 1939.
13. C. Perez. *Technological Revolutions, Paradigm Shifts and Socio-Institutional Change” in E. Reinert, Globalization, Economic Development and Inequality: An alternative Perspective*.

14. Hilbert, Martin (2012). *Towards a Conceptual Framework for ICT for Development: Lessons Learned from the Latin American “Cube Framework*. Information Technologies & International Development, 8 (4, Winter; Special issue: ICT4D in Latin America), 243–259 (Spanish version: 261–280).
15. Dymond, A.; Oestermann, S. (2004). *A Rural ICT Toolkit for Africa*. Information for Development Programme (infoDev) of the World Bank (PDF). World Bank, Washington D.C., USA. Retrieved 2007-04-08.
16. Languepin, Olivier (2010). *How mobile phones can help reduce poverty*.
17. *Highlights of Telecom Subscription Data as on 30th June 2011* (PDF) (Press release). Telecom Regulatory Authority of India. 8 Aug 2011. Retrieved 24 Oct 2011.
18. Ndeh-Che, F., 2008. *Positioning Cross River State Government to Deliver a World Class Social Safety Net Program*. A Technical Proposal. Abuja, Nigeria.
19. S. Batchelor, S. Evangelista, S. Hearn, M. Pierce, S. Sugden, M. Webb (November 2003). *ICT for Development Contributing to the Millennium Development Goals: Lessons Learned from Seventeen infoDev Projects*. World Bank.

SHORT TERM EFFECTS OF ENERGY DRINK ON SPERM HEAD MORPHOLOGY AND BEHAVIOUR OF ADULT MALE MICE

Olaleru, F.¹ & Odeigah P.G.C.²

¹Department of Zoology, University of Lagos

²Department of Cell Biology and Genetics, University of Lagos
folaleru@unilag.edu.ng

ABSTRACT

With the rising popularity of energy drink among Nigerian youths and males especially, there is the need to investigate the possible side effect of its major stimulant, caffeine on diverse health related issues in general and reproductive outcome in particular. To test the mutagenic and other effects of energy drink, Red Bull energy drink was offered *ad libitum* to adult male mice assay, in increasing concentration of the drink for twenty eight days. Sperm head abnormality count was conducted at 7, 14, and 28 days of exposure, while body movements studies of the mice were conducted on the last five days of energy drink exposure. The study showed that mice offered 75% concentration of Red Bull for 14-28 days had significantly ($P \leq 0.05$) negative effects on sperm head abnormalities. Mice on 75% and 100% Red Bull showed significantly different ($P \leq 0.05$) body movement when compared to Control on day 24 of exposure. This could imply that exposure to energy drink should be at low concentration and not for long period so that it does not induce negative reproductive and behavioural outcomes.

Keywords: *Mutagen, Energy Drink, Red Bull, Sperm morphology.*

INTRODUCTION

Energy drinks, non-alcoholic carbonated drinks designed to boost energy and categorized under Food and Beverage Industry are gaining wide use in Nigeria especially among youths, sportsmen and adult males. They are marketed with catchy names that convey strength, power, speed, sexuality and often with appropriate music (Akande and Banjoko, 2011).

Like all soft drinks, energy drinks contain little nutritional value and high amount of sugar. What really differentiates energy drinks from soft drinks is that they also contain significantly higher doses of caffeine. Common energy drinks contain around 160 – 300mg caffeine per 500 ml, while coffee contains 40 – 80mg/cup and tea 20-60mg/cup. Depending on the brand, energy drinks may also contain other additives such as B vitamins, taurine, ephedrine, carbonated water, guarana, glucuronolactone, maltodextrin, inositol, carnitine, creatine and ginseng.

A variety of physiological and psychological effects have been attributed to energy drinks and their ingredients. Two studies reported significant improvements in mental and cognitive performances as well as increased subjective alertness (Howard and Marczinski, 2010). In a web survey conducted by Serfert *et al* (2011), it was reported that energy drinks were consumed by 30% to 50% of adolescents and young adults. Frequently containing high and unregulated amounts of caffeine, these drinks have been reported in association with serious adverse effects, especially in children, adolescents, and young adults with seizures, diabetes, cardiac abnormalities, or mood and behavioral disorders or those who take certain medications. Of the 5448 US caffeine overdoses reported in 2007, 46% occurred in those younger than 19 years.

Nehlig and Debry (1994) reported that the mutagenic potential of coffee and caffeine has been demonstrated in lower organisms, but usually at doses several orders of magnitude greater than the estimated lethal dose for caffeine in humans. They concluded that the chances of coffee and caffeine consumption in moderate to normal amounts to induce mutagenic effects in humans are almost nonexistent. They also stated that caffeine seems to potentiate rather than to induce

chromosomal aberrations, transforms sub-lethal damage of mutagenic agents into lethal damage and that coffee and caffeine are also able to inhibit the mutagenic effects of numerous chemicals. In the Philippines, Red Bull was banned because of the suspected effects on infertility in men. In a comprehensive literature review, Pennington *et al.* (2010) stated that specific effects that have been reported by adolescents that used energy drink included jitteriness, nervousness, dizziness, the inability to focus, and insomnia. In another report from the United States, students that took energy drink on their way to school were observed to be restless and had destructive tendencies. As regards the psychological effect of energy drink, two studies reported significant improvements in mental and cognitive performances as well as increased subjective alertness (Howard and Marczinski, 2010).

Even though the caffeine in energy drink has been implicated to cause infertility in men, agitation, nervousness and anxiety in children and adolescents, the few local researches done were on their biochemical and histological effects on tissues and organs (Akanke and Banjoko, 2011) with little on mutagenesis. The objectives of this study were to look at the short term effects of “Red Bull” energy drink on sperm morphology and behaviour on adult male mice.

METHODS

Animal Husbandry

Thirty six (36), eight weeks old adult Albino male mice, (*Mus musculus*) bioassay model were purchased from a stock raised in the Zoology Laboratory, University of Lagos. They were acclimatized to their new cages for a period of four days (in the same Laboratory) during which they were fed pelletized food purchased from a reputable source and given water *ad libitum*. Mice were chosen as a model for this study because according to Pagulayan and Gutay-Baoanan (1993) their spermatogenesis is similar to that of man.

Test Substance

Red Bull^R Energy Drink, a product of Austria was purchased from retail outlets in Lagos. The ingredients stated on the product’s label were: water, sucrose, glucose, acidity regulator (sodium citrates), carbon dioxide, taurine (0.4%), glucuronolactone (0.24%), caffeine (0.03%), inositol, vitamins (niacin, pantothenic acid, B6, B12), flavourings, colours (caramel, riboflavin). Each 100 ml contained: Energy 192 kj (45 kcal), protein 0 g, carbohydrates 11.3g, fat 0 g, with vitamins as % recommended daily allowance.

Experimental animals were exposed to it through their drinking water, which was changed daily.

Treatment Arrangement

The 36 adult male mice were weighed and randomly divided into treatment groups. Each treatment group (except the Control that had four) had a total of eight mice sub-divided into four per cage. The disparity in weight of mice in each group was ± 2.0 grammes. The mice were fed with pelleted food and given *ad libitum* Red Bull energy drink mixed with water in the concentrations shown on Table 1.

Table 1: Test substance, Red Bull and water ratios, in volume/volume

Treatment	% Energy Drink	% Water	Ratio
1 (CONTROL)	0	100	0:1
2	25	75	0.25:0.75
3	50	50	1:1
4	75	25	0.75:0.25
5	100	0	1:0

On days 7, 14, and 28 epididymis samples were collected from the mice for sperm morphology count.

Sperm Morphology Count

Mice were sacrificed for epididymes collection by cervical dislocation. The sperm from excised epididymes were stained and examined under electron microscope for sperm head abnormality; these were compared with a work done in a similar environment and reported by Otubanjo and Mosuro (2001).

Body Movements

Animal behaviour was determined by counting the number of body movements per minute as described by Abalaka and Auta (2010). This was conducted during the last week of the experiment. Counted body movements were lifting of head, walking, climbing, and eating.

Data Analyses

The mean and standard deviation of the sperm head counts (normal and abnormal), blood parameters and body movement were analysed using Microsoft Excel. Means that differed with the Control were compared using Student-t two tail tests.

RESULTS

Red Bull Energy Drink Effect on Sperm Morphology of Adult Male Mice

Plate 1 showed photograph of normal, while plates 2-4 showed abnormal sperm head morphologies. Black arrow was used to show the sperm head depicted. Seven of the abnormal sperm heads as described by Otubanjo and Mosuro (2001) were observed with amorphous and pin heads being the most common.

Table 2 showed the normal and abnormal sperm head counts and their deviation from mean. On days 7 and 28, all the means of the normal sperm heads for the four treatments were significantly different ($P \leq 0.05$) from the Control. On day 14, only Treatment 5 (100% energy drink) was significantly different at $P \leq 0.05$ from the Control. The means of the abnormal sperm heads for all the Treatments were significantly different at $P \leq 0.05$ from Control on day 14, and on day 28 for Treatment 3 (50% energy drink).

Figure 1 shows the graph of normal sperm count with increasing concentration in Red Bull intake on sperm count. Figure 2 shows the graph of abnormal sperm count with increasing concentration in Red Bull intake on sperm count.

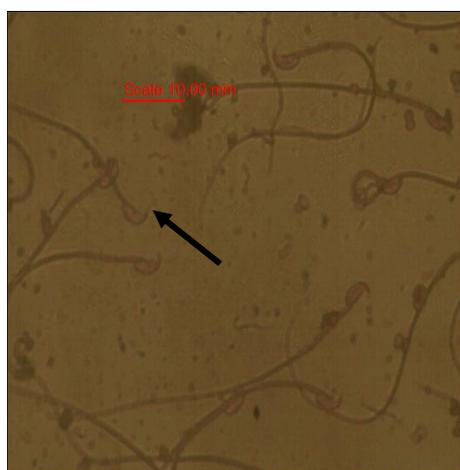


Plate 1: Normal mouse sperm head of Trt 1 on day 28 (Mag. x 200)

Note: Trt = Treatment on all the Plates

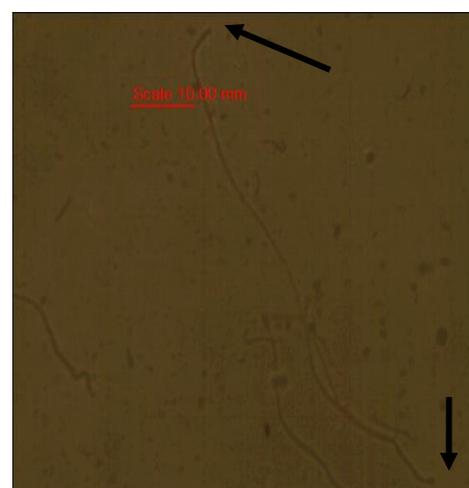


Plate 2: Pin sperm head of Trt 2 mouse on day 14 of exposure to Red Bull (Mag. x 200)



Plate 3: Pin head sperm of Trt 4 mice on day 14 of exposure to Red Bull (Mag. x200)



Plate 4: Amorphous sperm head of Trt 5 on day 14 of exposure to Red Bull (Mag. x 200)

Table 2: Concentration of, and duration of exposure to Red Bull effect on mice sperm head count

Normal Sperm head count

Period of exposure (Days)	Mean±SD value for each group based on % concentration of Red Bull drink				
	1	2	3	4	5
7	1114.25±62.8	208±61.8*	120.5±70.0*	184.25±111.5*	312±192.8*
14	1114.25±62.8	1227±461.4	1152.75±157.5	1113.25±64.6	574.5±48.8*
28	1114.25±62.8	564±313.7*	617.75±317.4*	152.75±82.9*	418±211.9*

Abnormal Sperm head count

7	20.25±17.8	20.25±12.6	8.25±8.3	17.5±15.2	42.25±32.6
14	20.25±17.8	100.5±46.9*	134.25±73.5*	115.5±57.5*	103.25±50.6*
28	20.25±17.8	35.5±11.3	115.5±24.3*	40.5±28.7	141.75±93.7

SD= Standard Deviation; * = significantly different from the Control group at $P \leq 0.05$

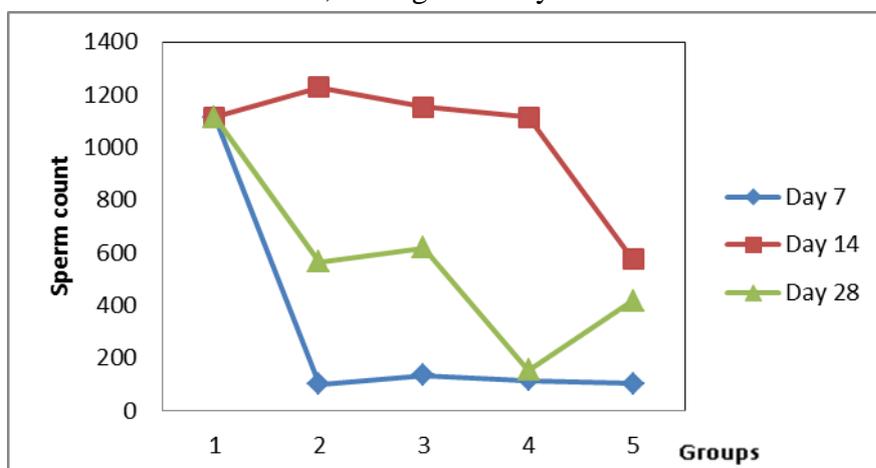


Figure 1: Variation in normal sperm count with increasing concentration in Red Bull intake

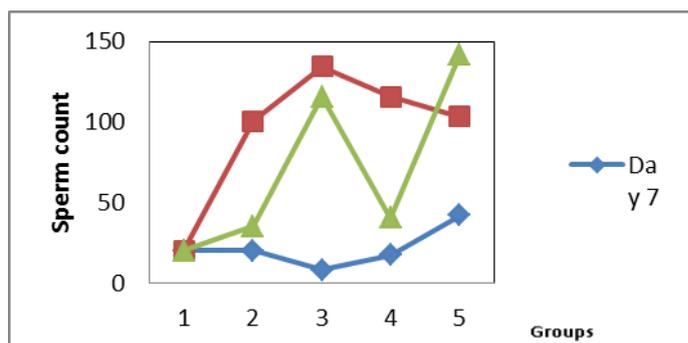


Figure 2: Variation in abnormal sperm count with increasing concentration in Red Bull intake

Red Bull Energy Drink Effect on Adult Male Mice Body Movement

Table 3 shows the means of body movements of adult mice offered different concentrations of Red Bull and compared with the Control group. Only mice on 75% and 100% Red Bull had significantly different means, at $P \leq 0.05$, from control on day 24 of the test period. On day 26, mice on 25% and 75% Red Bull showed significant difference ($P \leq 0.05$) from the Control.

Table 3: Effect of Red Bull on body movement of mice

Period of exposure/ Days	Mean±SD value for each group based on % concentration of Red Bull drink				
	1	2	3	4	5
24	36±3.1	38.2±4.5	44±12.9	52.7±5.6*	48.7±11.0*
25	45.7±6.7	40.7±11.9	52.7±12.3	52±12.5	46.3±11.6
26	47.3±5.1	38.3±4.2*	45.2±10.1	54.7±4.5*	50.2±9.0
27	47.7±4.4	48.7±7.1	42.5±8.1	54.2±8.1	50.3±7.5
28	58.7±3.1	44.7±8.7*	39.3±12.5*	52.3±8.7	47±10.3*

SD= Standard Deviation; * = Significantly different from the Control group at $P \leq 0.05$

DISCUSSION

Effects of concentration and exposure time of Red bull on mice sperm head morphology

Normal sperm head counts were highest for mice on 25% Red Bull on day 14 of exposure, while the lowest was observed for mice on 75% and on day 14. Abnormal sperm head counts were lowest on Control followed by 25% and 75% on day 28. This could imply that high concentration and prolonged use of Red Bull caused a reduction in normal while increasing the incidence of abnormal sperm heads. Amorphous and pin heads were the major forms of abnormalities in sperm morphology encountered during the study. These did not have acrosome needed for penetration of ovum during fertilization.

Other substances have been reported to cause abnormal sperm heads. Odeigah (1997) recorded increasing percentage of abnormal sperm heads with increasing concentration of formaldehyde treated rats. Pagulayan and Gutay-Baoanan (1993) reported the incidence of variant abnormal shapes of acrosome that was dose dependant with almost 4 fold increment when Malathion was used on mice. They alluded that changes in head shape may be correlated to changes in the motility and penetrating capacity of the sperm, with balloon types as the most critical, because of the absence of hook which is vital for the entry of sperm to egg.

The higher values of sperm head abnormalities of mice exposed to varying concentrations and exposure time of Red Bull indicates that the substance might have caused damage to the pre-meiotic stage of spermatogenesis which is the period when deoxy ribonucleic acid (DNA) synthesis occur Odeigah (1997).

Effect Red Bull Energy Drink on Body Movement of Adult Male Mice

Only mice on 75% and 100% Red Bull had significantly different means from control on day 24 of the test period. On day 26, mice on 25% and 75% Red Bull showed significant difference from the control. This implied that activity rate of adult male mice reached peak on 75% Red Bull. Forbes *et al.* (2007) reported that during repeated cycling tests in young healthy adults an energy drink significantly increased upper body muscle endurance. In laboratory studies, caffeine at a dose of about 6 mg/kg body weight (e.g., 490 mg for a 180-lb person) has often proved effective at enhancing exercise performance lasting from 1-120 min (Graham, 2001).

CONCLUSION

Normal sperm count decreased with increasing concentration of Red Bull intake while abnormal sperm heads increased with increasing concentration of Red Bull intake. There is an inherent challenge in extrapolating this result from mice studies to humans. However, the result did indicate the potential health risks associated with regular and prolonged use of Red Bull energy drink on spermatogenesis. More information is needed on behavior, and the effect of energy drinks on oogenesis in female mice.

Despite the warning on the label: “Not recommended for children and persons sensitive to caffeine”, there is no monitoring and control over this group accessing it. Public regulatory and health agencies should be proactive in taking measures that would inform the vulnerable group, young people and non- alcohol users know the attendant side effects of energy drink. As damage to deoxy ribonucleic acid (DNA) is the fundamental mechanism of induced mutation, mutagenicity testing of common energy drinks in the Nigerian market is necessary.

REFERENCES

- Abalaka, S.E. and Auta, J. (2010). Toxic effects of aqueous extract of *Parkia biglobosa* on *Clarias gariepinus* adults. *World Journal of Biological Research*. **3** (1): 9-17.
- Akande, I.S. and Banjoko, O.A. (2011). Assessment of Biochemical Effect of “Power Horse” Energy Drink on hepatic, renal and histological functions in Sprague Dawley rats. *Annual Review and Research in Biology* **1** (3): 45-56.
- Forbes, S.C., Candow, D.G., Little, J.P., Magnus, C., Chilibeck, P.D. (2007). Effect of Red Bull energy drink on repeated Wingate cycle performance and bench-press muscle endurance. *International journal of sport nutrition and exercise metabolism* **17** (5): 433-444.
- Graham, T.E. (2001). Caffeine and exercise: metabolism, endurance, and performance. *Sports Medicine*. 31:785-807.
- Howard, M. A.; Marczinski, C. A. (2010). Acute effects of a glucose energy drink on behavioural control. *Experimental and Clinical Psychopharmacology* **18** (6): 553-561.
- Nehlig, A. and Debry G. (1994). Potential genotoxic, mutagenic and antimutagenic effects of coffee: a review. *Mutation Research*, 317 (2): 145-162.
- Odeigah, P.G.C. (1997). Sperm head abnormalities and dominant lethal effects of formaldehyde in Albino rats. *Mutation Research*, **389**, 141-148.
- Otubanjo, O.A. and Mosuro, A.A. (2001). An *in vivo* evaluation of induction of abnormal sperm morphology by some anthelmintic drugs in mice. *Mutation Research*, **497**, 131-138.
- Pagulayan, I. F., Gutay-Baoanan, Z. P. (1993). Effect of Malathion on sperm morphology of mice. *Science Diliman*, **5** (1): 19-40.
- Pennington, N., Johnson, M., Delaney, E. and Blankenship, M.B. (2010). Energy Drinks: A New Health Hazard for Adolescents, *Paediatrics: The Journal of School Nursing* **26** (5): 352-359.
- Seifert, S.M., Schaechter, J.L., Hershorin, E.R. and Lipshultz, S.E. (2011). Health effects of energy drinks on children, adolescents, and young adults. *Pediatrics*. **127** (3): 511-528.

REMEDIATION OF PHOSPHATE FROM LAUNDRY WASTEWATER

Olayinka K. O., Adegoke M. I. & Oladosu N. O.

ABSTRACT

Phosphate is usually the limiting nutrient for algal growth in inland water bodies. Phosphorus-containing effluent must be treated before its discharge to inland and estuarine water bodies via the drainage to prevent eutrophication. This study focused on the removal of phosphate from laundry effluents using chemical precipitation. Lime ($\text{Ca}(\text{OH})_2$), alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were the coagulants used to precipitate phosphate from effluents collected from two laundry outfits within Lagos State. Phosphate was determined by the molybdenum blue method using Genesys 10-S UV-VIS Spectrophotometer. The effects of effluent matrix, coagulant dosage and pH on the precipitation efficiency were studied. The pH ranges used were 5.0-7.0, 5.5-7.5 and 9.0-11.0 for ferric chloride, alum and lime respectively. For ferric chloride, the best removal efficiency achieved was 73 % at pH 5.0. An optimum dosage of 120-240 mg/L was observed for this coagulant. The highest removal efficiency by alum was 64 % achieved at pH 6.5 and dosage of 160-240 mg/L. About 70 % of phosphate was removed from the effluent by lime at pH 9.0 and optimum dosage of 450-600 mg/L. Phosphate removal increased with increasing dose of every coagulant until the optimum dose was reached and it descended afterwards. The highest phosphate removal attained with a particular coagulant varied from one effluent to another owing to the presence of interferent species. It was also observed that phosphate removal depended on coagulant dosage and pH. Ferric chloride demonstrated greater phosphate removal.

Keywords: Phosphate, Precipitation, Matrix, Dosage, pH

INTRODUCTION

Phosphorus is an essential macro-nutrient for the growth of plants and microorganisms. The load of phosphorus discharged to receiving waters comes from various sources including agricultural and urban runoff, domestic and industrial wastewater, and atmospheric deposition (Plaza et al., 1997). Phosphates in the form of sodium tri-polyphosphate (STPP) are used in making dishwashing detergents because they easily break down grease and remove stains. The benefit of its optimal ability to remove stains very well is offset by the fact that detergents enter the wastewater system and pose eutrophication problems. This means that activities such as taking showers, washing dishes and laundry, will lead to additional phosphorus in the sewers and the wastewater systems which then must be removed before it enters the receiving waters (Oram, 2005).

In wastewater, phosphorus exists as one of several possible phosphate compounds which includes inorganic phosphate (i.e. orthophosphate, polyphosphates) and organic phosphate (Crites and Tchobanoglous, 1998). Inorganic phosphate is contributed by detergents and household cleaning products such as soaps while organic phosphate is contributed by human excreta (feces) and food residues (Gold and Sims, 2001). As phosphorus is released into the ecosystem, its bioavailable component is readily taken up by plants. This is used for plants' growth; animals can then obtain the phosphates by feeding on plants and other animals that have ingested the phosphates. The materials are broken down and can be used as energy. As the plants and animals approach the end of their life cycle they die and microorganisms slowly release the nutrients stored in the organisms back into the ecosystem through decomposition (Herried, 2007).

The discharge of large quantities of this nutrient into receiving water bodies raises the growth of algae and results in eutrophication of lakes and streams (Banu, et al., 2008). This can in turn disturb the balance of organisms present in water and affect water quality, mainly through the depletion of dissolved oxygen as the algae decay. Reduced oxygen level can have harmful effects on fish and other aquatic life, causing reduction in biodiversity. It may cause an offensive odour and brings about colour changes in water bodies. It also renders water bodies useless for drinking, fishing, recreation, irrigation or industrial purposes (Carpenter et al., 1998).

Various technologies which were used for phosphate removal from wastewater are divided into physical, chemical and biological methods (Peleka and Delianny, 2009; Vasudevan et al., 2009). The chemistry of phosphate precipitation is dependent on many factors such as pH, coagulant dose, alkalinity, speed of mixing, and side reactions of the metal ions with ligands in the wastewater. Side reactions between the metals and alkalinity to form insoluble hydroxides are also important (James et al., 2003). The most often employed multivalent metal ions are the compounds of calcium, aluminum, and iron (Tchobanoglous et al., 2003). According to researches, phosphate removal efficiency was greater using ferric chloride, compared to alum.

Sarparastzadeh et al., (2007) suggested that ferric chloride has the greater tendency to react with phosphate even at lower dosage. There was a limitation of alum where the greatest phosphorus removal efficiency could only be achieved at 200 mg L⁻¹ dosage. Hence, it was an advantage of using ferric chloride in the removal of phosphate by chemical precipitation process. It was reported that 80-90% phosphate removal efficiency was observed when ferric chloride was dosed between 140 mg L⁻¹ and 200 mg L⁻¹. Only a small amount of ferric chloride was able to give rise to high phosphorus removal efficiency, which was helpful in reducing the operation cost.

Smith et al. (2008) reported that the highest phosphorus removal efficiency occurred between pH 5.5 and 7.0 for ferric chloride. Because ferric chloride is acidic and, is capable of lowering pH, adjustments to the pH might be needed to achieve high removal efficiencies when the alkalinity is insufficient to buffer the wastewater adequately. Hector (2004) reported that when the lowest dosages of alum and hydrated lime were compared, alum performed better in reducing total phosphorus and dissolved reactive phosphorus. With an alum dosage of 108 mg Al L⁻¹, the levels of total phosphorus and dissolved reactive phosphorus were reduced by 88.2% and 65.4% respectively. For the same parameters, the lowest dosage of hydrated lime (676 mg Ca L⁻¹) reduced the levels by 37.3% and 51.7% respectively.

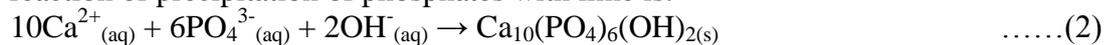
The following equation represents a simplified reaction of phosphate precipitation by aluminum ion (Lind, 1988):



Al ion also generates Al_x(OH)_y(PO₄)_z with phosphate. The dosage rate required is a function of the phosphorous removal required. The efficiency of coagulation falls as the concentration of phosphorous decreases. In practice, an 80-90% removal rate is achieved at coagulant dosage rates between 50 and 200 mg/l. Dosages are generally established on the basis of bench-scale tests (Lenntech, 2009). The optimum solubility for alum was previously reported to occur at a pH range of 5.5 to 6.5. Recent studies showed that the range of pH for alum is between 3.5 and 7.5 with the highest efficiency between pH 4 and 6 (Szabo et al, 2008).

When lime was added to wastewater to precipitate phosphate, as the pH increased above 10, calcium ions reacted with phosphate to precipitate hydroxylapatite [Ca₅(OH)(PO₄)₃]. It was found that an increase in lime concentration increased the percentage removal of phosphorous and reduces the residual concentration at higher pH values. This is ascribed to the fact that the higher the concentration of lime the higher the ability of calcium ions to form a complex with phosphate

and precipitate it out of solution at a pH range 8.5-10.0 (Plants et al., 2002). A simplified reaction of precipitation of phosphates with lime is:



Phosphate precipitation by Ca ion generates more phosphorus compounds including CaHPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ as shown below (Szabo et al., 2008):



Similarly, ferric ion precipitates phosphate as shown in the following simplified equation:



Other reactions of iron (iii) with alkaline substances in the wastewater precipitate $\text{Fe}_x(\text{OH})_y(\text{PO}_4)_z$ and $\text{Fe}(\text{OH})_3$.

This work investigated the removal of phosphate from laundry effluents using chemical precipitation. The effects of interference in the effluent matrix, coagulant dosage and pH of the effluent on the precipitation efficiency were also studied.

METHODS

Sampling and Sample Preservation

Plastic bottles used in sampling were washed with 5 % HCl and rinsed with redistilled water. All analytical reagents were purchased from BDH Chemicals UK, Surechem Products UK and Sigma-Aldrich Germany. High purity redistilled water was used for preparation of reagents and analysis. Two laundry effluent samples were collected in plastic bottles pre-rinsed with the same effluent from two laundry outfits in Lagos State. Samples were immediately transferred to the laboratory and frozen in Haier Thermocool freezer (HTF-219H) in order to suppress biochemical degradation and analysis was completed on all samples within 48 h.

Analysis of untreated effluent

The effluents were allowed to reach room temperature and a 25-mL aliquot of each effluent was filtered with filter paper (Whatmann) into a 50-mL beaker and was analyzed for phosphate by the molybdenum blue method according to Standard Methods (APHA, 2005) using UV-Visible spectrometer (Thermo Spectronic, Genesys 10-S) as the detector and this formed the initial phosphate concentration.

1) Treatment of effluent with ferric chloride hexahydrate

1.a.) Effect of pH variation on percentage phosphate removal

In ferric chloride treatment, five 25-mL aliquots of the effluent were placed in 100-mL conical flasks and their pH values were adjusted to 5.0, 5.5, 6.0, 6.5, and 7.0 by adding drop wise 1M HCl from a burette and checking the pH with a Mettler Toledo pH meter (AG 8603). They were each dosed with 0.002 g of ferric chloride hexahydrate. Immediately after adding the coagulant, samples were shaken rapidly for 40 s on a reciprocating shaker. This was followed by filtration with filter paper (Whatmann). Analysis of the filtrate was performed immediately to determine the concentration of phosphate that was not removed (i.e., residual phosphate) in the coagulation treatment using the molybdenum blue method. The difference in concentration of phosphate between the untreated and the treated was evaluated to calculate the percentage phosphate removal.

1.b.) Effect of increasing coagulant dosage on percentage phosphate removal

Five more sets of the effluent were similarly processed as in (1.a.) above but with a series of increasing doses of 0.003 g, 0.004 g, 0.005 g, 0.006 g and 0.007 g of ferric chloride hexahydrate to obtain residual phosphate level.

1.c.) Effect of effluent matrix on percentage phosphate removal

The entire procedures (1.a.) and (1.b.) above were repeated for the second effluent sample using ferric chloride hexahydrate.

2) Treatment of effluent with hydrated aluminum sulphate (alum)**2.a.) Effect of pH variation on percentage phosphate removal**

In alum treatment, five 25-mL aliquots of the effluent were placed in 100-mL conical flasks and their pH values were adjusted to 5.5, 6.0, 6.5, 7.0 and 7.5 by adding drop wise 1M HCl. They were each dosed with 0.002 g of alum and processed as in (1.a.) above to obtain residual phosphate.

2.b.) Effect of increasing coagulant dosage on percentage phosphate removal

Five more sets of the effluent were similarly processed as in (1.a.) above but with a series of increasing doses of 0.004 g, 0.005 g, 0.006 g and 0.007 g of alum to obtain residual phosphate level.

2.c.) Effect of effluent matrix on percentage phosphate removal

The entire procedures (2.a.) and (2.b.) above were repeated for the second effluent sample using alum.

3) Treatment of effluent with calcium hydroxide (lime)**3.a.) Effect of pH variation on percentage phosphate removal**

Five 25-mL aliquots of the effluent were placed in 100-mL conical flasks and their pH values were adjusted to 9.0, 9.5, 10.0, 10.5, and 11.0 by adding drop wise 1 M NaOH solution. They were each dosed with 0.010 g of alum and processed as in (1.a.) above to obtain residual phosphate.

3.b.) Effect of increasing coagulant dosage on percentage phosphate removal

Five more sets of the effluent were similarly processed as in (1.a.) above but with a series of increasing doses of 0.0113 g, 0.0125 g, 0.0138 g, 0.0150 g and 0.0163 g of lime to obtain residual phosphate level.

3.c.) Effect of effluent matrix on percentage phosphate removal

The entire procedures (3.a.) and (3.b.) above were repeated for the second effluent sample using lime.

RESULTS AND DISCUSSION

The results of the remediation studies are represented in the bar charts below. 70 % of phosphate was removed from the effluent by lime at pH 9.0 and about 67 % was removed at pH 9.5 in sample A (Fig. 4.1). These best results were achieved at optimum dosage of 450-600 mg/L. Removal efficiency by lime decreased with increasing pH from 9.0 to 11 in sample A (Fig. 4.1) whereas it increased with increasing pH in sample B (Fig. 4.2). These dissimilar trends were due to the presence of interfering substances in the samples. Another effect of the interference is the lower removal efficiency obtained in sample B (maximum removal = 51 %, Fig. 4.2) in contrast to that of sample A (maximum removal = 70 %, Fig. 4.1).

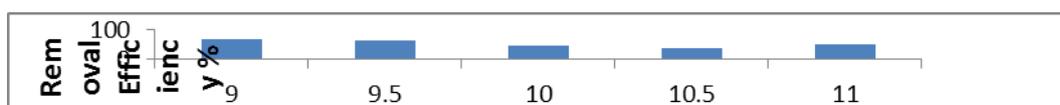


Figure 4.1: The dependence of phosphate removal on pH and sample matrix using lime.

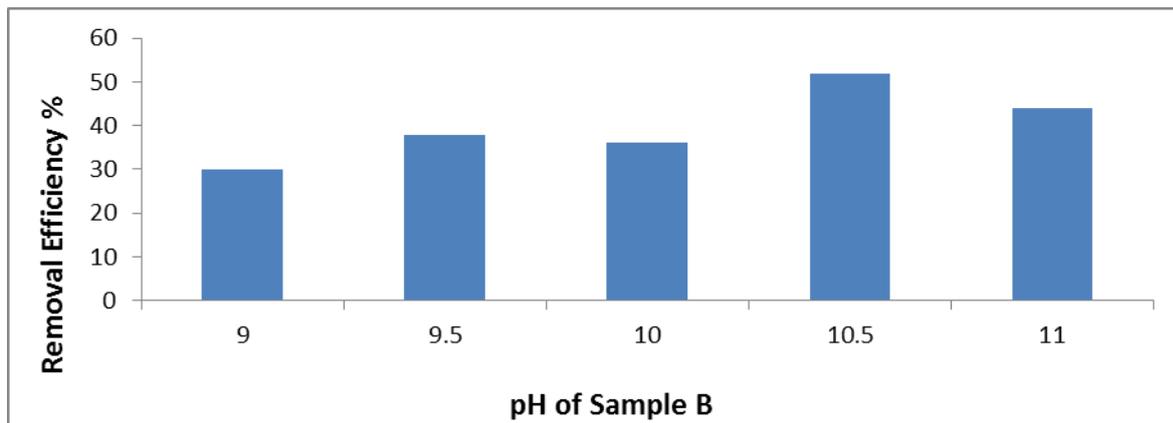


Figure 4.2: The dependence of phosphate removal on pH and sample matrix using lime.

The highest removal efficiency by alum was 64 % achieved at pH 6.5 (Fig. 4.3) and dosage of 160-240 mg/L in sample A. Similarly in sample B, the highest removal (45 %) was achieved at pH 6.5 (Fig. 4.4). The observed optimum pH of 6.5 was similar to the findings of Georgantas and Grigoropoulou (2006). The removal efficiency by alum was lower in sample B than A and this was the pattern in the case of lime treatment. This further confirmed that interference in sample B was stronger than in sample A.

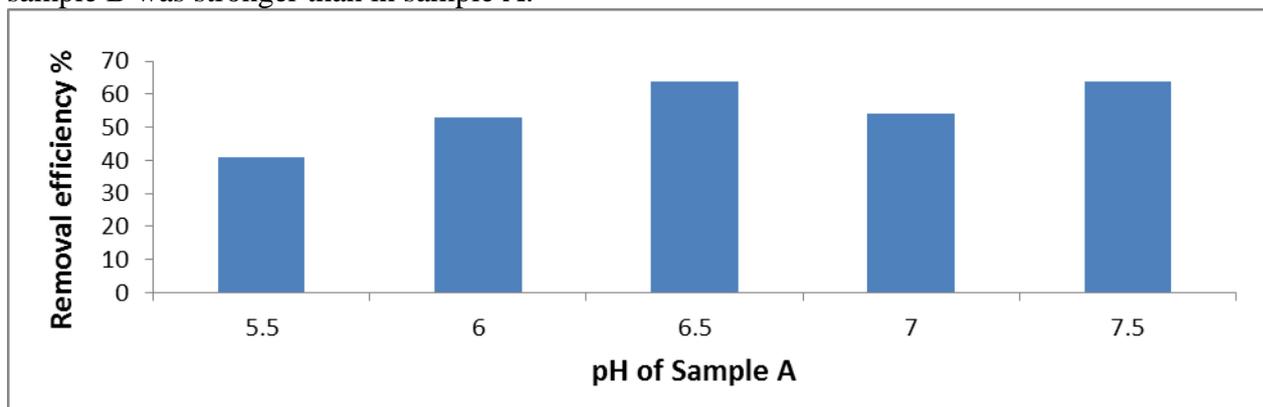


Figure 4.3: The dependence of phosphate removal on pH and sample matrix using alum.

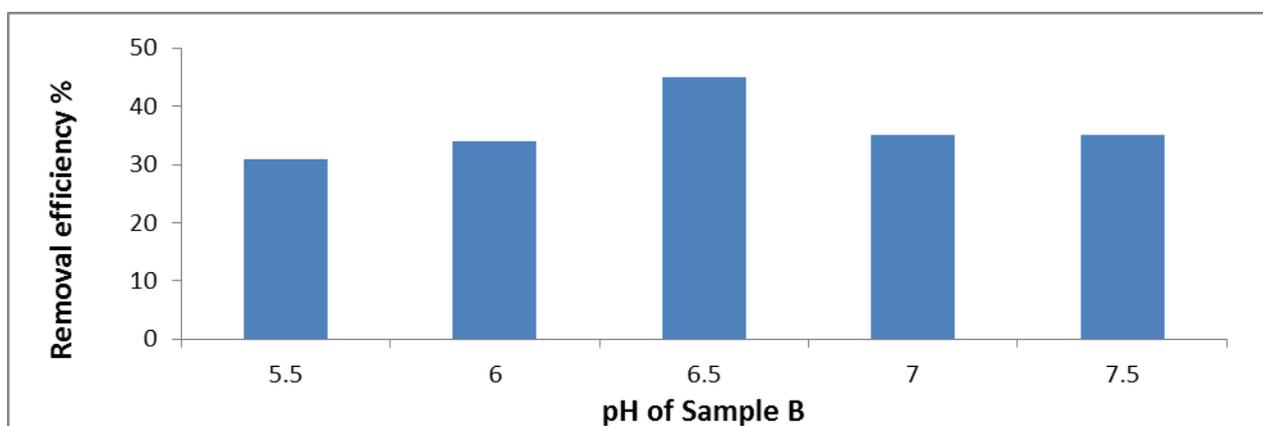


Figure 4.4: The dependence of phosphate removal on pH and sample matrix using alum.

For ferric chloride, the best removal efficiency achieved was 73 % at pH 5.0 in sample A (Fig. 4.5). At pH 7.0, a good removal efficiency of about 70 % was also obtained in sample A (Fig. 4.5). An optimum dosage of 120-240 mg/L was observed for this coagulant. In sample B, ferric chloride removed about 62 % of phosphate at pH 7.0 (Fig. 4.6) which was similar to the pH value obtained in sample A. This agreed with Smith et al. (2007) who reported that the highest phosphorus removal efficiency occurred between pH 5.5 and 7.0 for ferric chloride. However, the variation of pH generally resulted in different patterns (Figures 4.5 to 4.6) in removal efficiency from sample A to B due to interference.

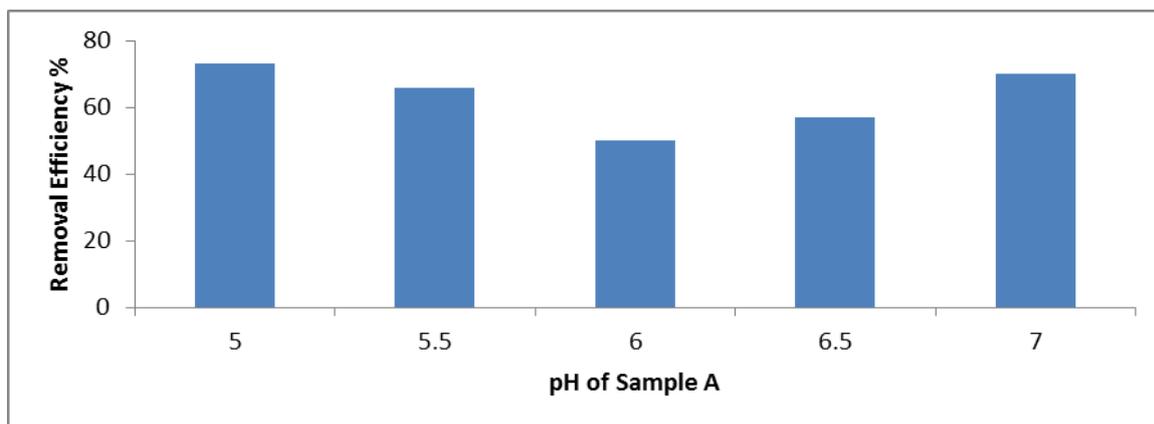


Figure 4.5: The dependence of phosphate removal on pH and sample matrix using ferric chloride.

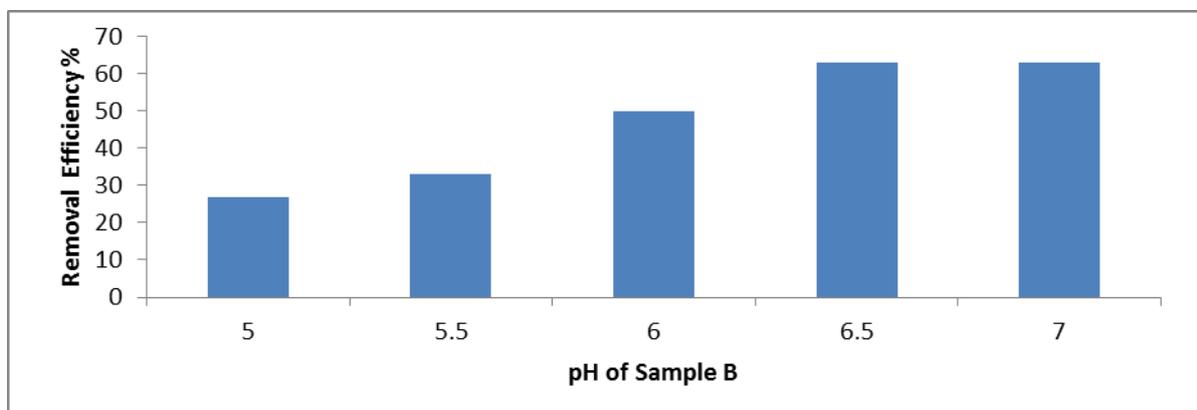


Figure 4.6: The dependence of phosphate removal on pH and sample matrix using ferric chloride.

The removal efficiency increased with increasing dose of the coagulants until the optimum dose was reached and it decreased afterwards. This trend was reported by Plant et al. (2002) that an increase in lime concentration increases the percentage removal of phosphorus and reduces the residual concentration at higher pH values.

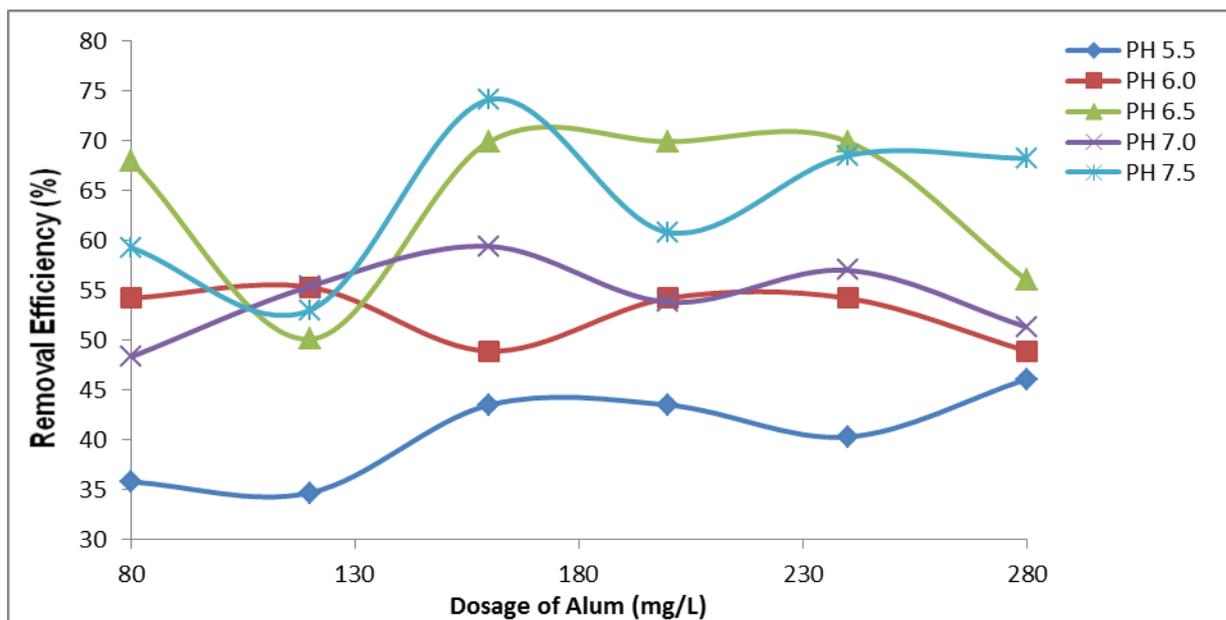


Figure 4.7: The effects of alum dosage on phosphate removal in sample A.

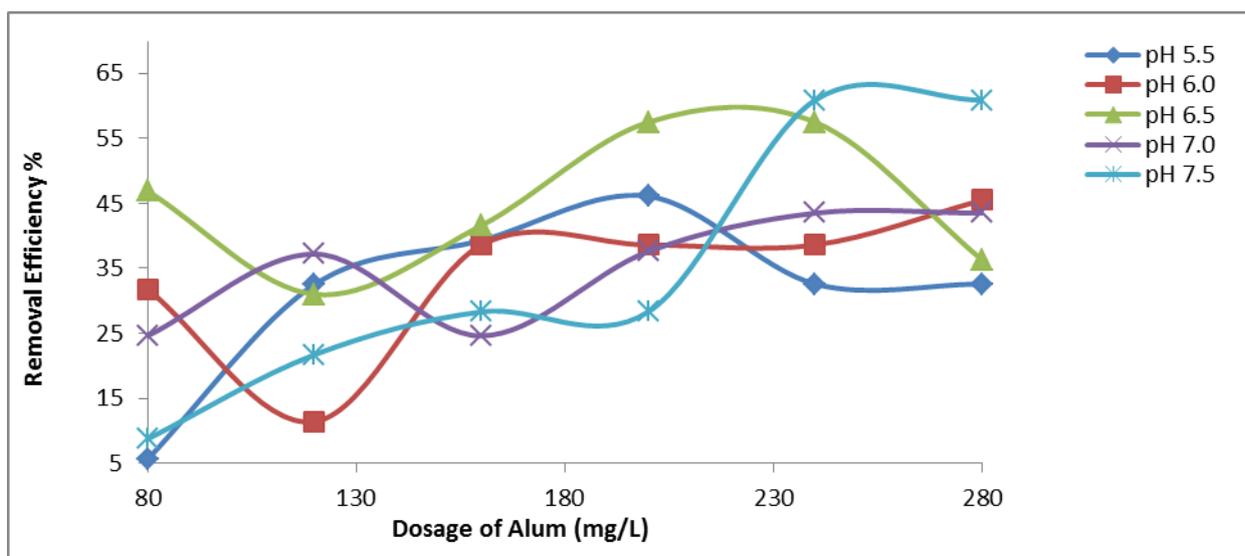


Figure 4.8: The effects of alum dosage on phosphate removal in sample B.

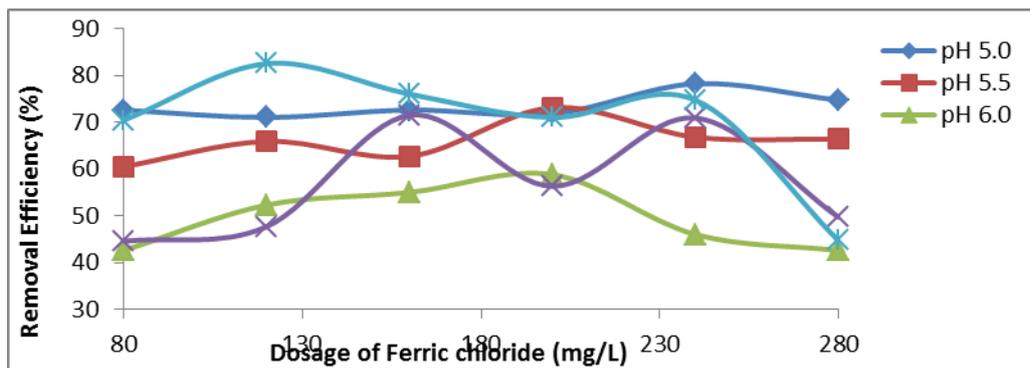


Figure 4.9: The effects of ferric chloride dosage on phosphate removal in sample A.

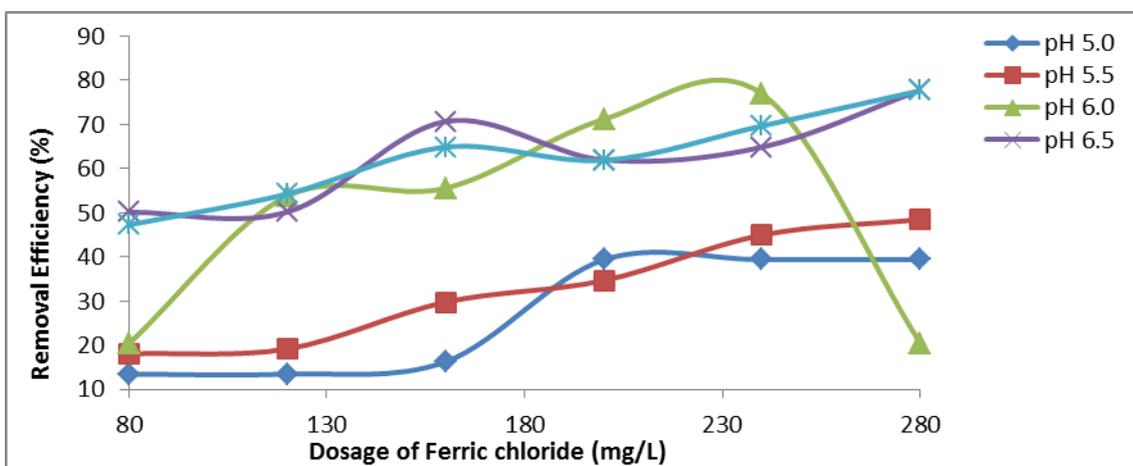


Figure 4.10: The effects of ferric chloride dosage on phosphate removal in sample B.

CONCLUSION

The phosphate removal by lime, alum and ferric chloride was found to be highly pH dependent and susceptible to interference. The removal efficiency also increased with increasing dose until the optimum dose was reached and it decreased afterwards. The use of ferric chloride for phosphate removal demonstrated the best results compared to both lime and alum. Thus the use of these coagulants could be used to address the problem of eutrophication in water bodies through removal of phosphate from effluents before being discharged.

REFERENCES

- (APHA) American Public Health Association. (2005) Standard Methods for the Examination of Water and Wastewater, 21st Ed.
- Ahmed A. L., Sumathi S., Hameed B. H., (2006) Coagulation of Residue Oil and Suspended Solids in Palm Oil Mill Effluent by Chitosan, Alum and PAC, Chem. Eng. J., 118: 99-105.
- Banu, R.J., Do, K. U. and Yeom, I.T., (2008) Phosphorus Removal in Low Alkalinity Secondary Effluent Using Alum, International Journal for Environmental Science Technology, 5(1):93-98.
- Carpenter S.R., Caraco N.F., Smith V.H., (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen, Ecological Applications, 8: 559-568.
- Crites, R., and Tchobanoglous G.(1998) Small and Decentralized Wastewater Management Systems, WCB and McGraw-Hill publications, New York, USA, pp. 93-124.

- Georgantas D.A., Grigoropoulou H.P., (2006) Phosphorus and organic matter removal from synthetic waster using alum and aluminum hydroxide, *Global NEST J.*, 8(2): 121-130.
- Gold, A.J., and Sims, J.T., (2001) Research Needs in Decentralized Wastewater Treatment and Management: A Risk-based Approach to Nutrient Contamination. In *National Research Needs Conference Proceedings: Risk-Based Decision Making for Onsite Wastewater Treatment*, EPRI, US-EPA, pp. 1147-1157.
- Herried B., (2007) Too Much Phosphorus is not a Good Thing, Tri-Lakes Management Offices: pp. 1-2.
- Hector L.J., (2004) Nutrients and solids removal by lime and alum treatment of flushed dairy manure, A thesis presented to the University of Florida, pp. 34-36.
- Irdemez S., Yalc S., (2006) Optimization of phosphate removal from wastewater by electro coagulation with aluminum plate electrodes, *Sep. Purif. Technol.*, 32: 394-401.
- James M., Ebeling Sibrell, P. L., Ogden S. R., Steven S. T., (2003) Evaluation of Chemical Coagulation-Flocculation Aids for the removal of Suspended Solids and Phosphorus from Intensive Recirculating Aquaculture Effluent Discharge, *Aquacult. Eng.*, 29: 23-42.
- Lenntech, (2009) Phosphorous Removal from Wastewater, Water Treatment and Purification, Retrieved on 28/04/2014 from http://www.lenntech.com/phosphorous_removal.htm.
- Lind C. B., (2003) Precipitation of phosphorus in wastewater, lakes, and animal wastes: In Total Maximum Daily Load (TMDL) Environmental Regulations II, A. Saleh St. Joseph, Mich.: ASAE., ed. pp.107-117.
- Oram, Brian, (2005) Total Phosphorus Water Quality Information and Impact Information, Drinking Water Testing Environmental Testing Lab Wilkes University, N.p., Retrieved on 28/04/2014 from <<http://www.waterresearch.net/phosphate.htm>>.
- Pinotti A., Zartizky N., (2001) Effect of aluminum sulfate and cationic poly-electrolytes on the destabilization of emulsified wastes, *Waste Manage.* 21(6): 535-542.
- Plant L.J., House W.A., (2002) Precipitation of calcite in the presence of inorganic phosphate, *Coll. surf.*, 203: 143-153.
- Peleka E.N., Deliyanni E.A., (2009) Adsorptive removal of phosphate from aqueous solutions, *Desalination*, 245(1-3): 357-371.
- Plaza, E., Levin, E., and Hultman, B., (1997) Phosphorus Removal from Wastewater- A Literature Review, Division of Water Resources Engineering, Department of civil and Environmental Engineering, Royal Institute of Technology, Stockholm, pp. 3-25.
- Sarparastzadeh H., Saeedi M., Naeimpoor F., Aminzadeh B., (2007) Pretreatment of Municipal Wastewater by Enhanced Chemical Coagulation, *International Journal of Environmental Research*, 1(2): 104-113.
- Smith J.A., Carliell-Marquet C.M., (2008) The digestibility of iron-dosed activated sludge, *Bioresource Technology*, 99(18): 8585-8592.
- Szabó A., Takács I., Murthy S., Daigger G.T., Licskó I., Smith.S., (2008) Significance of Design and Operational Variables in Chemical Phosphorus Removal, *Water Environment Research*, 80 (5):407-416.
- Tchobanoglous G., Burton F. L., Stensel H. D., (2003) *Wastewater Engineering: Treatment, Disposal, and Reuse*. Meltcalf & Eddy, New York: McGrawHill, Inc., 4th edition, p.1819.
- Vasudevan S., Lakshmi J., Jayaraj J., Sozhan G., (2009) Remediation of phosphate contaminated water by electro-coagulation with aluminium, aluminium alloy and mild steel anodes, *J. Hazard. Mater.*, 164(2-3): 1480-1486.

MICROWAVE ASSISTED SYNTHESIS OF LUMINESCENT DOPED AND UNDOPED GRAPHENE QUANTUM DOTS

Fagbenro-Owoseni, K., Olasupo, I. A., Soyomi, S. O., Mbaso, H. U., & Adams, L. A.

Department of Chemistry, Faculty of Science, University of Lagos,
ladams@unilag.edu.ng

ABSTRACT

Neat luminescent graphene quantum dots (GQDs) and S, N: co-doped GQDs were successfully prepared by bottom-up approach via microwave-assisted carbonization of citric acid. L-cysteine and triethylamine were utilised as dopant precursor. The luminescent graphene quantum dots were refluxed in different solvents to give water soluble conjugates of ethylene glycol (EG), dimethylsulphoxide (DMSO), dimethyl formamide (DMF) and tributylphosphine (TBP). The GQDs were examined under normal and 365nm UV light before characterization using UV-VIS spectrophotometer, FTIR and band gap calculation. The GQDs showed blue, green or yellow luminescence. FTIR indicated characteristic bands at about 1154 cm^{-1} for (P-O), 1012 cm^{-1} (S=O), 1727 cm^{-1} (C=O), 3345 cm^{-1} (OH). The UV-VIS showed maxima in the range of 240 – 350 nm and calculated band gaps between 2.96 – 4.82 eV characteristic of semi-conductors. The results indicate that the GQDs can be exploited as candidate luminescent materials for bioimaging applications.

Keywords: *Graphene quantum dots, Carbonisation, Luminescent, Microwave-assisted, Citric acid*

INTRODUCTION

Graphene, a 2-dimensional sheet of carbon atoms arranged in a honeycomb pattern has intrigued the world's science community with its extraordinary properties [1–3]. However, properties like luminescence, band gap, magnetism, etc. are absent in pure graphene which imposes limitations in its optical and electronic applications. In order to impact such properties into graphene composite materials and nano sized graphene derivatives have become desirable.

Quantum confinement of excitons of a material plays an important role in its properties. Reducing the size of a material brings quantum effects into play thereby inducing several interesting properties. GQDs are graphene sheets smaller than about 10 nm [4], which presents unique optical and electronic properties due to their quantum confinement and edge effects. GQDs do exhibit very exciting properties which are found neither in graphene sheets nor in graphitic materials.

GQDs are proposed to be applicable in many fields, such as photovoltaic devices [5], cellular imaging [6], and drug delivery [6,7]. Several methods involving “top-down” and “bottom-up” using different sources of carbon have been developed for their synthesis. Liu et al., [8] have used hexa-peri-hexabenzocoronene as a substitute for the carbon source. They produced artificial graphite by pyrolyzing the precursor at very high temperatures (600, 900 and 1200 °C) followed by oxidation and exfoliation by Hummers in producing multicolor quantum dots (QDs) with uniform morphology. Shen et al., [9] used graphite oxide (GO) as a starting material to yield luminescent QDs. Pan et al., [10] used a mixture of concentrated H_2SO_4 and HNO_3 to oxidize graphene sheets followed by hydrothermal deoxidization to obtain a strong green fluorescence QDs.

In this study, we report a simple one-step bottom-up method to selectively prepare doped and undoped GQDs by tuning carbonization degree of a common organic precursor, citric acid (CA).

METHODS

Materials

Chemicals used include: Citric acid, L-cysteine, polyvinyl alcohol, ethylene glycol (EG), dimethylsulphoxide (DMSO), dimethyl formamide (DMF) and tributylphosphine (TBP), triethylamine, distilled water and deionized water.

Preparation of GQDs Through Microwave –assisted Carbonization of Citric Acid

Graphene quantum dots (GQDs) were prepared by direct microwave assisted carbonization of citric acid (CA) in a fume cupboard. Citric acid (2g) was weighed into a beaker and heated in a microwave. After 1min 30sec, the citric acid liquefied. Subsequently with continuous heating, the colour of the liquid changed from colourless to pale yellow to orange and finally to brown in about 6mins which signifies the formation of GQDs. The effect of time on the luminescence property of the GQDs was also studied by varying the time used for the carbonization.

Preparation of S, N:GQDs Through Microwave–assisted Carbonization of Citric Acid

S, N co-doped GQD was prepared using citric acid and L-cysteine (2-Amino-3-mercaptopropanoic acid) as dopant precursor. Briefly, citric acid was mixed with L-cysteine in the ratios 2:1 and 1:1. The resulting mixture microwaved at variable wattage and time simultaneously, changed from fluffy yellow solid to brown solid implying the formation of N, S-GQDs. Similarly, tri-ethylamine was used as a dopant.

Preparation of Water Soluble Conjugates' Graphene Quantum Dots

Water soluble conjugates' Graphene quantum dots (GQDs) were prepared by refluxing the as prepared undoped GQDs in different solvents such as ethylene glycol (EG), dimethylsulphoxide (DMSO), dimethyl formamide (DMF) and tributylphosphine (TBP). Briefly, the as-prepared undoped GQDs mixed with 5ml ethylene glycol (EG) were transferred into a 50ml quick fit flask. This resulting mixture was refluxed for 6hrs with stirring at 200°C to obtain EG-GQDs. Similar procedure was used to obtain DMF-GQDs, DMSO-GQDs, and TBP-GQDs at temperatures above or close to the boiling point of the desired solvent.

Characterization

The prepared doped and undoped Graphene quantum dots and its conjugates' were characterized with ultraviolet-visible absorption spectra in the range 200 – 900nm by scanning in T80⁺ UV-Vis spectrophotometer while the Infrared spectra were recorded by using BRUKER vector 22 spectrophotometer over the range of approximately 4000-500 cm⁻¹. Optical band gap were calculated from the data obtained from UV-Vis absorption spectra using the equation below:

$$\text{Band Gap Energy (E)} = h \times c / \lambda$$

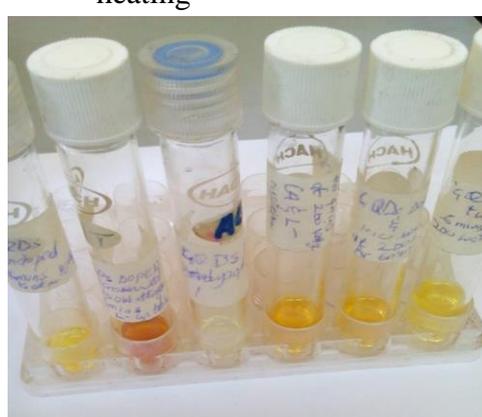
Where *E* is the band gap energy, *h* is the Planck's constant, *c* is the speed of light and *λ* is the wavelength.

The luminescence property was determined by illumination with a UV light source (365nm) in a dark room. Doped and undoped GQDs were diluted with 1ml deionized water prior to irradiation while the GQDs conjugates' were irradiated without further dilution.

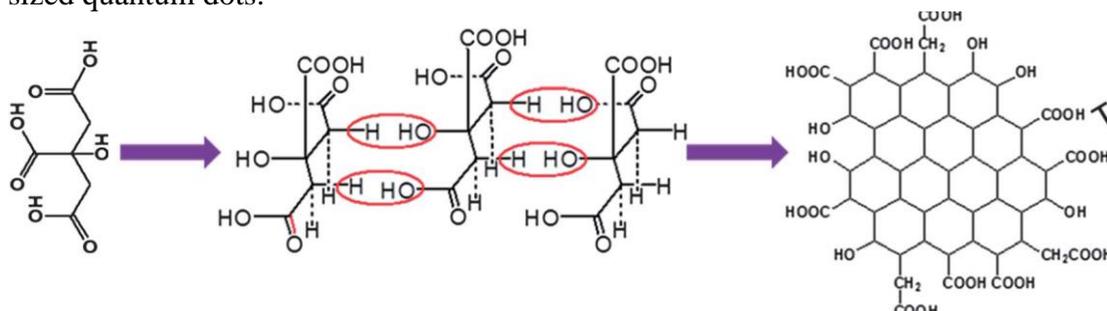
RESULTS AND DISCUSSIONS

Graphene Quantum Dots (GQDs)

Graphene quantum dots were synthesized through microwave assisted carbonization of citric acid (CA) (Fig 3.1a) by heating in the microwave which gave initially a colourless liquid (Fig 3.1b). Thereafter, on further carbonization it became pale yellow, orange and finally changed to brown liquid (Fig3.1c and d).

**Fig.3.1a:** Citric acid crystals before heating**Fig.3.2b:** Citric acid crystals liquefied after heating**Fig.3.1.c:** Synthesized GQDs**Fig. 3.1.d:** Synthesized GQDs diluted with deionized Water, varied time and heating temperature

A scheme of the carbonization process of citric acid is presented in Fig.3.2. The microwave heating method enhanced a fast and homogenous carbonization process resulting in uniform sized quantum dots.

**Fig. 3.2:** Schematic for the carbonization of citric acid.

S, N doped Graphene Quantum Dots (S, N: GQDs)

Doping with heteroatoms such as S and N provides an attractive means of effectively tuning the intrinsic properties of GQDs. Co-doping with nitrogen and sulphur was affected by adding either L-cysteine or triethylamine (N) to the precursor prior to carbonization. Fluffy GQDs were produced from the carbonization of the two reactants (Fig.3.3a and b).



Fig.3.3a: Citric acid crystals before heating **Fig. 3.3b:** After microwave heating of S,N: Co-Doped.

Water Soluble Conjugates' Graphene Quantum Dots

The GQDs conjugates were obtained by refluxing with the various solvents at their boiling points to afford EG-GQDs, DMF-GQDs, DMSO-GQDs, and TBP-GQDs respectively (Fig 3.4a-d).

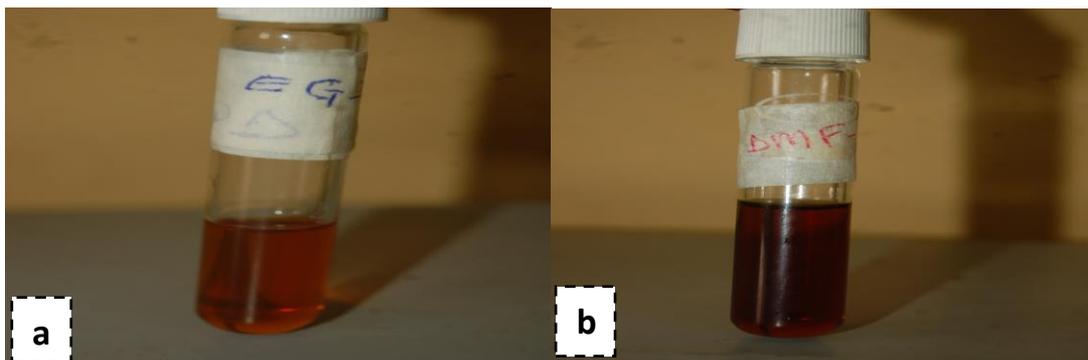


Fig 3.4: (a) Sample of EG-GQDs (b) Sample of DMF-GQDs under normal light.

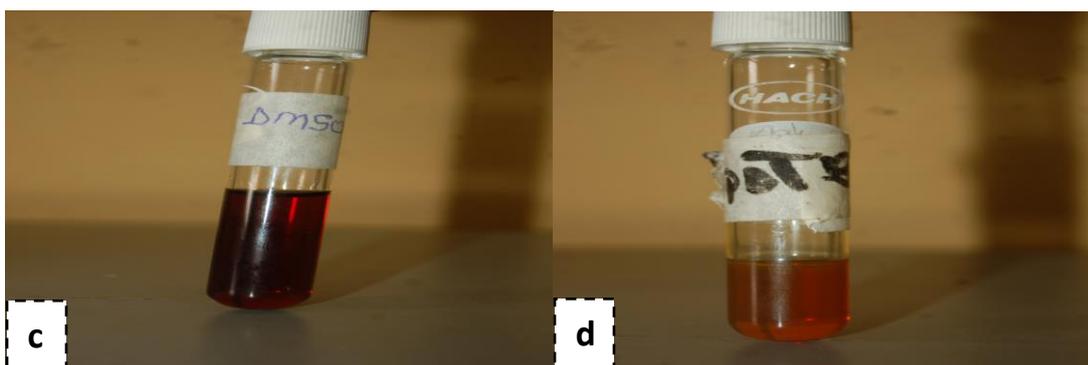


Fig 3.4: (c) DMSO-GQDs and (d) TBP-GQDs under normal light.

Optical Study of GQDs samples

Doped and undoped samples of GQDs samples were irradiation by 365nm UV. It was observed that undoped GQDs produced green luminescence (Fig. 3.5a) while doped GQDs produced blue luminescence (Fig. 3.5b) probably due to the presence of the two electron withdrawing groups (N and S) in L-Cysteine (Fig 3.5). Nonetheless the mechanism of light tuning is still not clear.

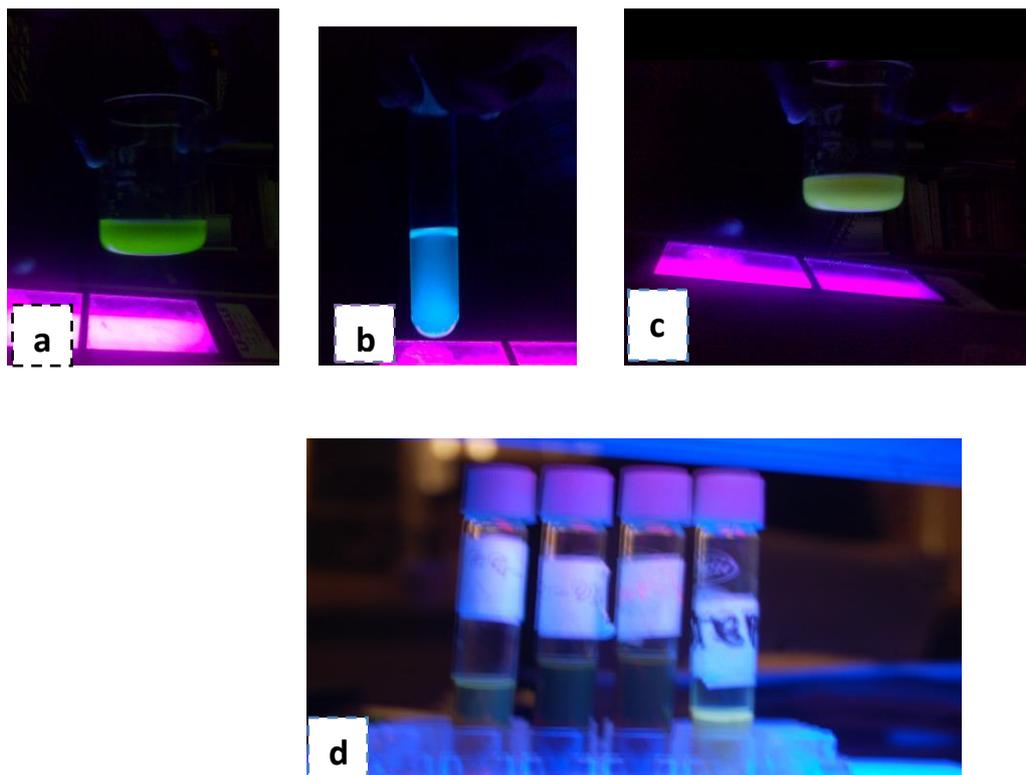


Fig.3.5: Fluorescent *GQDs* under *UV* lamp. (a) Undoped *GQDs* green, (b) *S,N*: Co-doped *GQDs*, blue, (c) Triethylamine doped *GQDs*, yellow (d) *GQDS* Conjugates' sample solutions excited with 365nm *UV* beam dull green /blue.

Dopping with triethyl amine gave yellow luminescence (Fig. 3.5c). Excitation of *GQDs* conjugates' with 365nm *UV* beam produced dull blue luminescence for *EG-GQDs* and *DMSO-GQDs*, and similarly dull green luminescence for *DMF-GQDs* and *TBP-GQDs* respectively (Fig 3.5d).

The effect of carbonization time and composition on the luminescence property of undoped and doped *GQDs* were investigated. The summary of findings is presented in the Table 3.1

Table.3.1: Graphene Quantum Dots (GQDs) Photoluminescence

S/N	Composition	Mass/Ratio	Time (Minute)	Temp (Watt)	Result
1	Citric Acid (CA) microwave assisted carbonization	2g	12	350	Non-luminescence
2	Citric Acid (CA) microwave assisted carbonization	2g	10	350	Non-luminescence
3	Citric Acid (CA) microwave assisted carbonization	2g	6	350	Green luminescence
4	Citric Acid (CA)+L-Cysteine	2g [1:1]	8	350	Blue luminescence
5	Citric Acid (CA)+ L-Cysteine	3g [2:1]	6	200	Blue luminescence
6	Citric Acid (CA)+L-Cysteine	2g [1:2]	4	200	Bright blue luminescence
7	Citric Acid (CA)+ Triethylamine	2g [1:2]	6	350	Yellow

Similarly, the summary of the effect of solvents on photoluminescence of GQDs is presented in Table 3.2

Table 3.2: Water Soluble Conjugates' GQDs Photoluminescence

S/N	Sample	Composition	Result
1.	EG-GQDs	GQDS + Ethylene glycol(EG)	Blue luminescence
2.	DMF-GQDs	GQDS + Dimethyl formamide(DMF)	Green luminescence
3.	TBP-GQDs	GQDs + Tributylphosphine(TBP)	Green luminescence
4.	DMSO-GQDs	GQDs + Dimethylsulfoxide (DMSO)	Blue luminescence
5.	All Solvent used	Solvents alone	Non-luminescence

UV-Vis Absorption Spectra of GQDs Samples.

UV-Vis spectra obtained at a scan range of 200nm- 900nm of undoped and doped GQDs shown in Fig 3.6 shows an absorption band at 248 nm, which was blue-shifted with respect to that of N-free GQDs of similar size. The absorption spectrum of EG-GQDs, DMSO-GQDs and TBP-GQDs shows characteristics absorption bands at 275nm, 300nm and 325nm respectively (Fig 3.6)

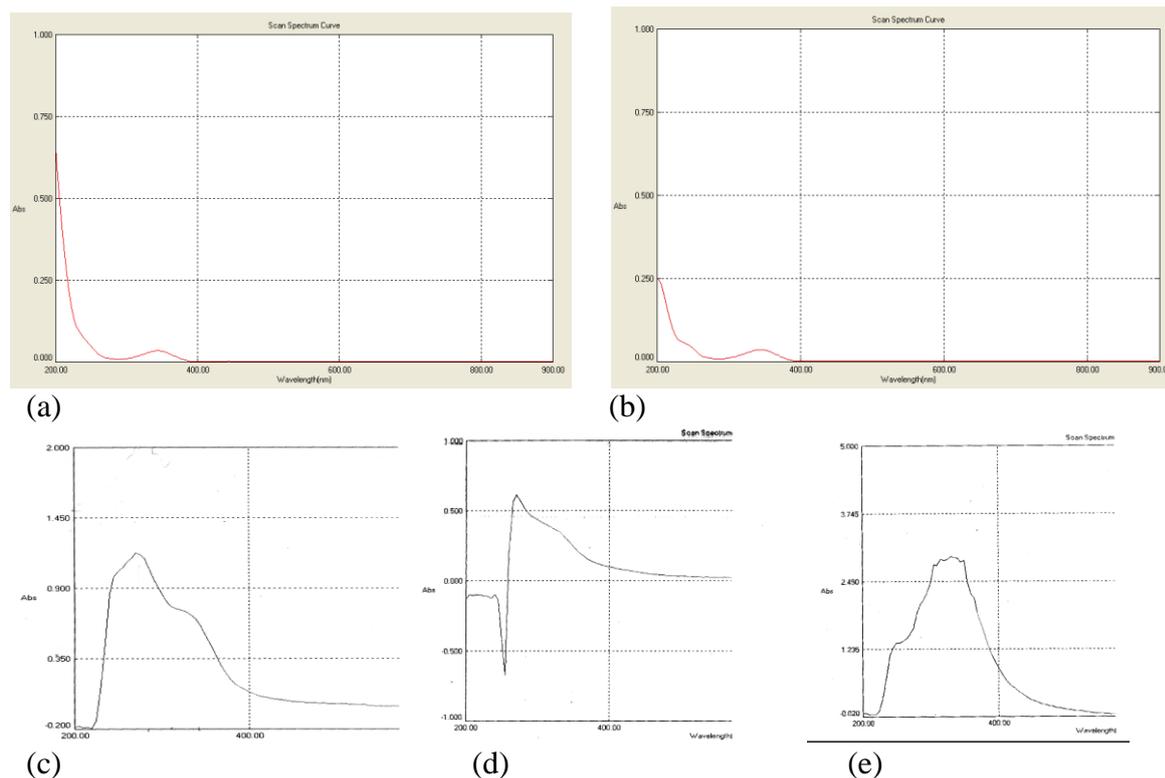


Fig.3.6: Spectrum of (A) undoped GQDs (B) doped GQDs microwaved at 350 watt for 6mins. UV-Vis Absorption Spectrum of (C) EG-GQDs (D)DMSO-GQDs (E)TBP-GQDs.

Table 3.3: Calculated Band Gap Energies from UV spectra

Sample	Wavelength(λ) nm	Band Gap energies(E)eV
Undoped GQDs	262	4.74
S,N-Co doped GQDs	258	4.82
EG-GQDs	275	3.11
DMSO-GQDs	300	3.11
TBP-GQDs	325	2.76

Infrared Spectra

Fig 3.7 shows the FTIR spectra of doped and undoped GQDs dots.

broad absorption bands 3000cm^{-1} - 3500cm^{-1} are attributed to stretching vibrations of O-H and N-H which further reveal that there are lots of amino and hydroxyl groups on the surface of GQDs having hydrophilic properties. However, the sharp absorption band at 1718cm^{-1} as well as that at 1636cm^{-1} are attributed to the vibrational absorption band of C=O in COOH and CONH respectively.

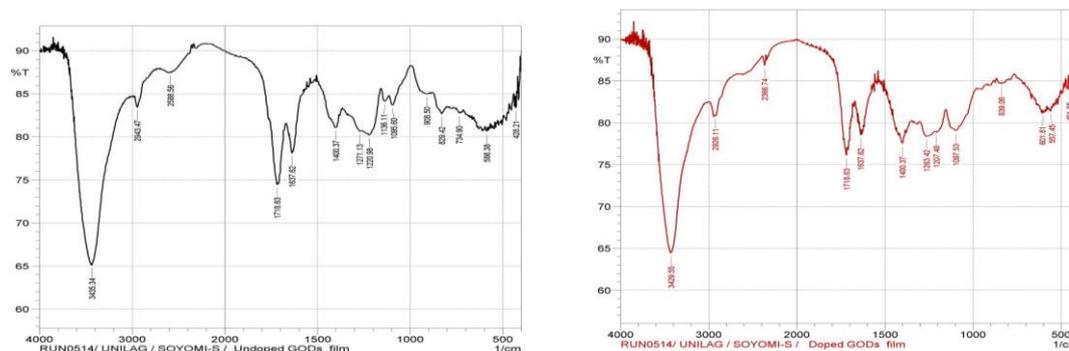


Fig.3.7: (a) FTIR spectrum of undoped GQDs (b) FTIR Spectrum of GQDs doped with L-cysteine

CONCLUSION

Graphene quantum dots with tunable properties were synthesized by carbonization through an easy bottom-up approach in which citric acid was used as an organic precursor. Nitrogen and sulphur as dopants were using L-cysteine as well as triethylamine. The GQDs synthesized herein showed photoluminescence properties which were blue, green and yellow colours. The luminescence properties were retained for few weeks.

The QDs obtained in this study are soluble in aqueous medium and are potential material for use as probes for bioimaging and biosensing applications.

REFERENCE

- [1] Geim AK. Graphene: status and prospects. *Science* (2009) 324,1530–4.
- [2] Rao CNR, Sood AK, Subrahmanyam AKS, Govindaraj A. Graphene: the new two-dimensional nanomaterial. *Angew Chem Int Ed* (2009) 48, 7752–77.
- [3] Geim AK, Novoselov KS. The rise of graphene. *Nat Mater* (2010), 34, 345-352.
- [4] Li XL, Wang XR, Zhang L, Lee SW, Dai HJ. Chemically derived, ultra smooth graphene nanoribbon semiconductors. *Science* (2008) 319(5867):1229–1232.
- [5] Yan X, Cui X, Li B, Li L. Large, solution-processable graphene quantum dots as light absorbers for photovoltaics. *Nano Lett* (2010) 10(5), 1869–1873.
- [6] Sun X, Liu Z, Welsher K, Robinson JT, Goodwin A, Zaric S, Nano-graphene oxide for cellular imaging and drug delivery. *Nano Res* (2008), 1(3), 203-212.
- [7] Liu Z, Robinson JT, Sun X, Dai H. PEGylated nanographene oxide for delivery of water-insoluble cancer drugs. *J Am. Chem. Soc.* (2008) 130(33), 10876–10883.
- [8] Liu R, Wu D, Feng X, Mullen K. *Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology. J Am Chem Soc*, (2011). 133 (39), 15221–15233.
- [9] Shen JH, Zhu YH, Chen C, Yang XL, Li CZ. *Facile preparation and upconversion luminescence of graphene quantum dots. Chem Commun*, (2011), 47(9):2580–2.
- [10] Pan DY, Zhang JC, Li Z, Wu MH. *Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots. Adv Mater*, (2010). 22(6):734–8.

CHEMICAL COMPOSITION OF SOAPS AND DETERGENTS IN SOME MARKETS IN LAGOS

***Olayinka, K.O; Adetunde, O.T and Abatan, F. E**

Department of Chemistry, University of Lagos Akoka, Yaba, Lagos, Nigeria

* kolayinka@unilag.edu.ng, keolayi20002000@yahoo.com

ABSTRACT

This study assessed the compliance of some soaps and liquid detergents in Lagos, Nigeria to the Nigerian Industrial Standard (NIS) specification of 2006 (2010 for medicated soaps). Fifteen different soaps from four classes of soap (toilet (A, B, C, D E), laundry (F, G, H, I) medicated (J, K, L) black soaps (M, N, O)) and two liquid detergents (P, Q) were purchased from local markets in Lagos, Nigeria. Total fatty matter (TFM), pH value, free caustic alkali, chloride content, matter insoluble in ethanol, total caustic alkali, matter insoluble in water, inorganic salt content, moisture and volatile content were determined as specified in the test methods for Soaps of SON (NIS 187: 1984). Apart from Samples D, G and J which had TFM values of 65.14%, 53.34% and 24.50% respectively, TFM of other soaps complied with the NIS specification of a minimum of 70% (toilet and medicated soaps), 62% (laundry soaps) and 50% (black soaps). The moisture content and volatile content of the liquid detergents complied with the NIS specification 80%. The pH was also within the limit of 7 to 10 but did not comply 5% for inorganic matter and 0.1% for insoluble matter in water. Only five of fifteen different soap brands had all their parameters complying with NIS specifications. No liquid detergent met full compliance with NIS specifications. This study reveals the need for regular quality check and enforcement by regulatory agents to ensure the quality of soaps to the minimum required standard.

Keywords: Analysis, Specification, Compliance, Parameters, Soap, Detergent.

INTRODUCTION

Soap is a product from the reaction of a fatty acid with a metallic base (saponification) (Srivastava 2002) while detergents are surfactants or a mixture of surfactants with cleansing properties in dilute solution. Soaps can be classified based on the use (e.g toilet, laundry, medicated soaps) texture, appearance (e.g black soap, transparent soaps) (Aiello, 2007). There are also hard and soft soaps. Hardness of soap is often achieved through the addition of hardening agents, so natural soaps tend to be softer. Detergents are usually synthetic in nature. They evolved after World War II to deal with dual problems of poor cleaning performance of soaps under certain conditions and competition for fat by both the food and soap industry (Knud-Hansen, 1994). A typical detergent contains surfactant(s), builder, and other miscellaneous ingredients including brighteners, perfumes, and enzymes (Pradhan and Pokhre, 2013). Detergents are sodium salts of long chain hydrophobic alkyl sulphates or alkyl benzene sulphonates. They are prepared from petrochemicals obtained from refining crude oil, which react with sulphonic acid through a process known as sulphonation and do not produce insoluble precipitates in hard water like soaps. They are effective in soft, hard or salt water (Thorpe, 2012). The chemical characteristic of soaps and detergents depend on several factors: total fatty matter (TFM), matter insoluble in water, Chloride content, free caustic alkali, total free caustic alkali, matter insoluble in ethanol, moisture content, pH, inorganic matter and impact resistance (Mak-Mensah and Firempong, 2011). These impact on the quality of the soaps. Soaps sold in the Nigerian market are of different types and qualities. SON, responsible for ensuring products are safe for use by consumers in Nigeria has drawn up standard for soaps and detergents in NIS. The

aim of this study is to assess the compliance of different soaps and liquid detergents in Nigeria (Lagos markets) with the current NIS specification of SON.

METHODS

Sampling and Preparation of Soap for Analysis

Fifteen different soaps from four classes of soap (toilet (A, B, C, D E), laundry (F, G, H, I, J) medicated (K, L, M) black soaps (N, O)) and two liquid detergents (P, Q) were purchased from local markets in Lagos, Nigeria. Table 1 shows the list of soaps. The soaps were chopped into pieces after removing their wrappers.

Analysis of Soap

The analysis of the TFM, moisture content, pH value, free caustic alkali, chloride content, matter insoluble in ethanol, total caustic alkali and matter insoluble in water for all the samples were by the test methods for Soaps of SON (NIS 187: 1984). TFM was determined gravimetrically by dissolving the soap, solidifying the fat using bee wax and reweighing the resultant solid. The percentage moisture of soap was determined gravimetrically as described in Anzene and Aremu (2007). Matter insoluble in water was also determined gravimetrically. pH of soap was determined with a pH meter after dissolving the soap in hot distilled water. Chloride content, matter in soluble in ethanol, free caustic alkali and total caustic alkali were determined as in described in Mak-Mensah and Firempong (2011). Inorganic salt content, moisture and volatile matter were also determined (only for liquid detergent) gravimetrically.

RESULT

The result of the analysis of the soaps and detergent determined are as shown in Tables 2 and 3. TFM, moisture content, pH value, free caustic alkali, chloride content, matter insoluble in ethanol, total caustic alkali and matter insoluble in water for toilet soaps were between the range of 65.14 - 94.62%, 3.31- 10.48%, 9.1 - 9.5, 0.03 - 0.03%, 0.10-0.30%, 5.80-16.90%, 0.05-0.08% and 0.35-9.45% respectively. The values for laundry soaps were between the range of 24.50 - 78.44%, 6.45-29.03%, 9.5 - 11.2, 0.03% - 0.08%, 0.07-0.49%, 17.6 - 25.2%, 0.04 - 0.12%, 7.85% - 57.25%, 7.85-7.25% respectively. For medicated soap samples the results were between the range of 80.48 - 92.23%, 4.49 -7.50%, 9.5 - 9.9, 0.03 - 0.03%, 0.02 - 0.49%, 6.85 - 8.30%, 0.09 - 0.14% respectively. The result of TFM, moisture content, pH value, free caustic alkali, chloride content, matter insoluble in ethanol, total caustic alkali and matter insoluble in water for two black soaps (N and O) were determined 56.13 and 68.79%, 11.49% and 18.45, 9.2 and 10.2, 0.05 and 0.05%, 0.06 and 0.07%, 8 and 8.9%, 0.76 and 0.79%, 2% and 6.5% respectively. For the liquid detergents (P and Q), inorganic salt content, matter insoluble in water, pH, moisture and volatile matter were measured and results were 5.17% and 5.74 %, 0.33% and 0.51 %, 7.65 and 7.90, 69.14% and 77.59 % respectively.

DISCUSSION

TFM

The regulatory standard for toilet, laundry, medicated and black soaps are stipulated by SON in NIS 004: 2006, NIS005:2006, NIS 515:2010 and NIS 490:2006 respectively. TFM of soap is a measure of its suitability for bathing and washing of materials (Ogunsuyi and Akinawo, 2012). Dry skins need soaps that are high in TFM because the fatty matter rehydrates the skin making it smooth and acts as a lubricant for them all day long (Vivian et al, 2014). Low TFM values are due to the presence of unreacted alkali in the soap (Warra and Komo, 2014) and this decreases the soap quality. The standard of TFM specified according to NIS 004: 2006, NIS005:2006, NIS 515:2010 for toilet, laundry and medicated soaps respectively is 70% while (NIS 490: 2006) value for black soap is 50%. From the result, sample E (Imperial Leather) had the highest TFM

of all the toilet soaps. A, B, C and E complied with the standard only sample D (premier soap) fell below (65.14%) the 70% TFM specification for toilet soaps. TFM of the toilet soaps in this study were higher than the TFM of Neem toilet soap from Ghana (63.75%) (Mak-Mensah and Firemping 2012). Of the five different laundry soaps, three (F, I, and H) soaps complied with the specified standard for TFM. The other two laundry soaps (G and J) had lower values (53.34% and 24.50%). The TFM values for medicated soaps and black soaps in this study were all higher than their respective NIS standard of 70% and 50%. TFM values for black soaps in this study (56.13% and 68.85 for N and O) were similar to the findings of Ogunsuyi *and* Akinawo (2012) (55.45%) and (Beetseh and Anza, 2013) (62%).

Moisture Content

Moisture content of soap is used to assess the shelf life of a product. On storage, hydrolysis of water un-saponified fat to give free fatty acid and glycerol occurs when there is high moisture content (Vivian et al, 2014). High moisture content increases the solubility of the soap and leads to waste. As the moisture content reduces, the foaming strength increases. Generally moisture content is usually higher immediately after soap production but reduces as the soap ages (Eke *et al*, 2004). Though water is an essential soap ingredient it is not expected to exceed 10% for black soap (NIS490:2006). There is no stated limit for moisture content for medicated, laundry and toilet soap however the Encyclopedia of Industrial Chemical Analysis suggested the limit should be between 10% and 15% for all soaps (Kirk, 1963). The moisture content for all the toilet soaps analyzed were below 10% while for laundry soaps, two samples F and J (Canoe and Ibukun) had moisture content above 15%. In a study of Laundry soaps in Nasarawa, Nigeria a moisture content of 14 - 18% was observed by Anzene and Aremu (2007). This is similar to 6.45 -29.03% obtained in this study for laundry soaps. All the medicated soap samples had less than 10% moisture content which is lower than the 10% to 15% suggested as limit by the Encyclopedia of Industrial Chemical Analysis. Sample N (Zee) and O (Dudu Osun) which are black soaps had moisture content of 18.45% and 11.49% and were therefore higher than the 10% moisture content and did not comply with the NIS Limit. However the moisture content (29.05%) obtained by Ogunsuyi *and* Akinawo (2012) for black soap was higher than in this study.

pH

pH is a measure of the degree of acidity or alkalinity of a substance or medium. The pH of a normal skin is 4.5 to 6 while pHs of soaps are usually in the alkaline region (7-10) since alkalis are used to saponify fat or oil in the production of soap. As the pH of soaps increases, there is a tendency to affect the fat content of the skin. Increase in pH cause skin irritations, micro flora of the skin is affected and this can lead to acne and alteration of the skin surface. The closer the pH of soap is to that of the skin, the milder its drying effect on the skin (Ansari, 2011). Apart from black soap with a limit of 7-10, there is no specified pH limit for toilet soap, laundry and medicated soap. From Table 2, the pH values for toilet soaps (9.1 - 9.5) were generally lower than values for laundry (9.5-11.2) and medicated (9.5-9.6). The two black soaps had pH values of 10.2 and 9.2 for N and O (Zee and Dudu Osun). Applying the 7-10 range limits to all the soap types sampled, only three soaps exceeded the limit. Two laundry soap samples (I (Zip) and J(Ibukun)) and N(Zee) a black soap with pH values above 10. Soaps with high pH are usually harsh to the skin. Sample J (Ibukun) had the highest pH (11.2). A pH value of 10.4 for Neem toilet soap was obtained by Mak-Mensah and Firemping 2012) this was also high.

Free Caustic Alkali and Total Free Caustic Alkali

Free caustic alkali is determines the abrasiveness of any soap. It is defined as the free NaOH or free alkali used in making the soap while total free alkali refer to the free alkali from which the

soap was made and any other alkaline substance present in soap such as sodium silicate and sodium carbonate. From NIS, the free caustic alkali should not exceed 0.05% for any soap. All the soap samples had values lower than the 0.05% specification. Excess alkali is harsh to sensitive skin.

The total free caustic alkali specified by SON for toilet and laundry soaps is 0.1% while medicated is 0.2% and 1% for black soap. Total free caustic alkali for toilet soap samples (0.05-0.08%) complied with the standard. Laundry soaps had total free alkali in range of 0.04% - 0.12%. Two soaps G (Bubble) with total free alkali of 0.11% and J (Ibukun) with a total free caustic alkali value of 0.12% did not comply with the specification. All the medicated soap analyzed total free alkali less than the specified 0.2% hence complied with the standard. Total free caustic alkali obtained for the two black soaps were 0.76% and 0.79% (N and O). The black soaps complied with the specification. Generally, Bubble and Ibukun soaps had higher total free alkali than the other soaps. The total free alkali obtained by Mak-Mensah *et al* (2011) for neem soap (0.24%). Vivian *et al* (2014) had their total free alkali for commercial soaps between ranges of 0.00% to 0.99%.

Matter Insoluble In Water And Matter Insoluble In Ethanol

High amount of matter insoluble in water and/or ethanol implies lower purity of the soap (Ogunsuyi and Akinawo, 2012). Samples A, C, and E (Eva, Lux and Imperial leather) complied with the maximum of 5% matter insoluble in water specified by SON for toilet, laundry and medicated soaps. However, B and D (Premier and Joy) did not comply. All the laundry soaps analyzed had higher matter insoluble in water than 5% specified. The percentage matter insoluble in water for black soap stated by NIS of SON is 15% and the two black soaps in this study complied (Zee and Dudu Osun). Hence both N and O (Zee (2.0%) and Dudu Osun (6.45%)) complied with the specification. The high amount of matter insoluble in water of Bubble soap might be attributed to the level of impurity of the alkali used for producing the soap.

The soap matter insoluble in ethanol should not exceed 10% as specified by SON for all soaps except black soaps for which a value of 0.2% was fixed. Three of the toilet soap samples (B (Joy), C (Lux) and E (Imperial leather)) complied with specification while samples A (Eva) and D (Premier) did not. None of the laundry soap complied with the specification for soap matter insoluble in ethanol while the medicated soaps all complied. Soap matter insoluble in ethanol obtained for black soaps did not comply with the standard of 0.2% set for black soaps.

Chloride Content

According to the NIS set by SON for different soap types, chloride content should not exceed 0.75% except for black which should not exceed 2%. All the soap (toilet, laundry, medicated and black) samples complied with their respective chloride standards. The chloride content was similar to chloride (0.30 - 0.59%) obtained by Moulay *et al* (2011). Residue of sodium chloride from salting out of soap (Ogunsuyi and Akinawo, 2012) is not desired because it reduces the solubility of soap in water (Leonce, 2012) though sodium chloride contain trace minerals such as Magnesium, Calcium, Bromine and potassium that help the body to nourish and heal itself.

Liquid Detergents

Specification for household liquid detergents is contained in NIS 519:2006 of SON. Only two different brands of liquid detergents were sampled. The Moisture and volatile matter specified for liquid detergent is a maximum of 80%. Both liquid detergents complied with the specification for moisture and volatile content in the NIS 519:2006 of SON for household liquid detergents. The NIS of SON also stated a value of 5% as the maximum allowed inorganic salt content. Both samples P and Q (liquid detergents) had values higher than the stated standard value. High inorganic salt content indicates more builders in the samples than required. The

specified amount of matter insoluble in water is 0.1%. Both samples P and Q (Morning Fresh and Mama lemon) exceeded the standard value of 0.1% for matter insoluble in water thus, did not comply with the specification required. The specified pH range according to NIS of SON is between 6 and 10. pH obtained for sample P and Q were 7.65 and 7.90 respectively. Both complied with the standard. Impact resistance carried out revealed both sample containers were able to withstand the experimental conditions and both were without leakage hence complied. Both samples complied with the specification for appearance of liquid detergent which specified the sample must be homogenous and free from any sediment or foreign matter.

CONCLUSION

The result obtained had shown that soaps like C (Lux), E (Imperial Leather), K (Tetmolsol), L(Safeguard), M (Dettol) had full compliance with standard. Other soap samples had deviation of one or more parameter from the specified standard. From the findings of this study, SON should carry out continuous monitoring of the products in the market to ensure continuous compliance with standard. The Nigerian public should be encouraged to purchase only products with the inscription “NIS” on them.

REFERENCES

- Aiello, A.E. (2007). Consumer Antibacterial Soaps: Effective or Just Risky? *Clinical Infectious Diseases* 45:S137–47.
- Anzene S.J. and Aremu M.O (2007). Quality and antiseptic properties of indogenous black soap produced in Nasarawa State, Nigeria. *Journal of Engineering and applied sciences*, 2(8)1297-1300.
- Ansari, S. A. (2011). Chapter 5 Resident Microflora and Antimicrobial Peptides of Skin *In: Nava Dayan, Philip W. Wertz (eds) Immune system of skin and oral mucosa: properties and impact in pharmaceuticals, cosmetics, and personal care products*. John Wiley & Sons, United Kingdom. Pages 384
- Beetsch,C.I and Anza, M.K. (2013). Chemical characterization of local black soap made by Using cassava peels ashes(alkali bases) and palm oil in the North zone of Nigeria. *Civil and Environmental research*, 3: 4
- Eke,U.B., Dosumu,O.O., Oladipo, E. and Agunbiade, F.O. (2004).Analysis of locally produced soap using sheabutter oil (SBO) blended with palm kernel oil (PKO). *Nigerian Journal of Science*, 38:19-24.
- Knud-Hansen, Chris (1994). *Historical perspective of the phosphate Detergent conflict: conflict research consortium* 94-54.
- Leonce, Dusengemungu (2012) Synthesis and properties of soap. *University Of Dar Es Salaam* 1-20.
- Mak-Mensah, E.E. and Firempong, C.K (2012) Chemical characteristics of toilet soap prepared from neem (*Azadirachta indica* A. Juss) seed oil. *Assian Journal of plant Science and Research*, 1:1-7.
- Moulay, Saad., Ahmed, Chalane and Zahia, Ouad-Feul (2011). Palm stearin in the soap-making process. *Natura Montenegrina, Podgorica*, 10:333-346.
- NIS 490:2006,(2006). Nigeria Industrial Standard (NIS) for Black Soap. *Standard Organization of Nigeria Lagos Operational Office*. 490, 1-13.
- NIS 515:2010, (2010). Nigeria Industrial Standard (NIS) for Medicated Soap. *Standard Organization of Nigeria Lagos Operational Office*. 515:1-11.
- NIS 004:2006, (2006). Nigeria Industrial Standard (NIS) for toilet soap. *Standard Organization of Nigeria Lagos Operational Office*. 004:1-26.
- NIS005:2006, (2006). Nigeria Industrial Standard (NIS) for hard laundry soap. *Standard Organization of Nigeria Lagos Operational Office*.005: 1-11.

- NIS 519:2006. (2006) Nigerian Industrial Standard for Liquid Detergent for household hand dishwashing. *Standard Organization of Nigeria Lagos Operational Office*. 519:1-11.
- Ogunsuyi, H.O and Akinawo, C.A (2012). Quality Assessment of soaps produced from Palm bunch ash_derived alkali and coconut. Department of Chemistry, *J.Appl. Sci. Environ. Manage*,16:363-366.
- Pradhan, S and Pokhre, M. R. (2013). Spectrophotometric determination of phosphate in sugarcane juice, fertilizer, detergent and water samples by molybdenum blue method. *Scientific World* 11(11) 58-62.
- Srivastava, A. K., (2002). Organic Chemistry Made Simple *New Age International* pg 488
- Thorpe, Edgar (2012). The Pearson CSAT manual, *Pearson Education* India, 26 pages
- Vivian, O.P., Nathan, O., Osano, A., Mesopirr, L. and Omwoyo, W.N. (2014) Assessment of the Physicochemical Properties of Selected Commercial Soaps Manufactured and Sold in Kenya. *Open Journal of Applied Sciences*, 4:33-440. <http://dx.doi.org/10.4236/ojapps.2014.48040>
- Warra, A. A and Komo, J. I (2014). Fat Quality and Cold Saponification of Shea Nut (*Vitellaria paradoxa*) Fat Extract. *Journal of Scientific Research & Reports*. 3(5): 660-667, 2014; Article no. JSRR.2014.002

Table 1: List of Soaps sampled

Soap Class	Soap name	Alphabet
Toilet	Eva	A
	Joy	B
	Lux	C
	Premier	D
	Imperial leather	E
Laundry	Canoe	F
	Bubble	G
	B29	H
	Zip	I
	Ibukun	J
Medicated	Dettol	K
	Safeguard	L
	Tetmosol	M
Black Soap	Zee	N
	Dudu osun	O
Liquid detergent	Morning fresh	P
	Mama lemon	Q

Table 2: Summary of result for liquid detergents

ID	Samples	TFM (%)	Moisture (%)	pH	Free Caustic (%)	Total Free Caustic Alkali (%)	Matter Insoluble In Water (%)	Matter Insoluble In Ethanol (%)	Chloride (%)
TOILET SOAPS									
A	Eva	80.40 ± 0.42	3.70±0.42	9.5	0.03±0	0.06±0	0.40	16.90±1.84	0.10±0.01
B	Joy	83.15±1.24	10.48±0.40	9.3	0.03±0	0.06±0	9.45±0.07	8.40±2.82	0.30
C	Lux	70.71±0.69	7.97±0.16	9.1	0.03±0	0.07±0.01	0.35±0.07	8.60±0.02	0.10±0.01
D	Premier	65.14±1.07	7.70±0.30	9.2	0.03±0	0.08±0	5.65±0.07	13.6±0.57	0.29±0.01
E	Imperial	94.62±0.56	3.31±0.21	9.1	0.03±0	0.05±0.01	2.30±0.42	5.80±0.28	0.20
	Std Values	70.00			0.05	0.1	5.00	10.00	0.75
LAUNDRY SOAP									
F	Canoe	76.43±4.72	15.35±0.40	9.6	0.03±0	0.04±0.01	13.1	22.5±0.42	0.42±0.01
G	Bubble	53.34±2.77	8.77±0.21	9.6	0.05±0	0.11±0	57.25±0.71	21.5±0.42	0.19±0.01
H	B29	78.44± 2.77	6.45±0.07	9.5	0.03±0	0.06±0	7.85±0.21	17.60±0.28	0.49±0.01
I	Zip	74.63±4.06	12.70±0.08	10.3	0.03±0	0.09±0	12.6	22.50±0.70	0.15±0.01
J	Ibukun	24.50±1.48	29.03±0.54	11.2	0.08±0	0.12±0	10.65±0.07	25.20±0.23	0.07
	Std Values	70.00			0.05	0.1	5.00	10.00	0.75
MEDICATED BAR									
K	Tetmosol	80.48±1.45	7.50±0.57	9.6	0.03±0	0.12±0	0.45±0.07	7.20±1.41	0.09
L	Safeguard	92.23±1.33	6.52±0.20	9.9	0.03±0	0.14±0	3.75±0.22	6.85±0.21	0.49±0.01
M	Dettol	82.51± 0.42	4.49±0.50	9.5	0.03±0	0.09±0	0.65±0.07	8.30 ±1.27	0.20
	Std Values	70.00			0.05	0.2	5.00	10.00	0.75
BLACK SOAP									
N	Zee	56.13 ± 0.73	18.45±0.30	10.2	0.05±0	0.79±0	2.0±0.14	8.00±0.85	0.07
O	Dudu Osun	68.85±7.95	11.49±0.69	9.2	0.05±0	0.76±0	6.45±0.21	8.90±1.56	0.06±0.01

Table 3: Summary of result for liquid detergents

S/NO	Samples	Mean (%) Moisture and volatile matter	Mean (%) Inorganic salt	Mean (%) matter insoluble in water	pH	Appearance
P	Morning fresh	69.12±0.03	5.74±0.68	0.51±0.01	7.65	Homogenous
Q	Mama lemon	77.59±0.30	5.17±0.19	0.33±0.42	7.90	Homogenous
	Standard values	80.00	5.00	0.10	6-10	Homogenous

DETERMINATION OF CAFFEINE IN TEA LEAVES AND SOME BEVERAGES USING HPLC AND DERIVATIVE SPECTROSCOPIC METHODS

Temilola Oluseyi, Kehinde Olayinka & Babatunde Akinbile

Analytical / Environmental Chemistry Research Group, University of Lagos, Akoka, Lagos
toluseyi@unilag.edu.ng

ABSTRACT

Caffeine is a naturally occurring substance found in leaves, seeds or fruits and drinks. In this research, characterization of pure caffeine and method for determining caffeine levels in selected twelve samples comprising of beverage samples, cocoa seeds, kola nut and caffeine containing drinks and sweets is reported using ultraviolet / visible spectrophotometry and results compared with the reversed phase HPLC method. Solubilization of pure caffeine was done in three solvents (dichloromethane, ethylacetate and water). Isolation of caffeine from samples was carried out by liquid-liquid extraction using dichloromethane as an extracting solvent. The caffeine extracts were analyzed using PG T80 UV/Visible spectrophotometer and 1200 Agilent HPLC series with UV detection. The highest caffeine content was found in the coffee (8.9%) and Planet energy drink (9.28%) while the lowest was observed in minicoffee kopiko sweet (0.49%) and cocoa beans(0.88%). The results also indicated that caffeine can be extracted more at the boiling temperature (100⁰C) (as found in Top tea, Nescafe coffe and Napacafe coffee with values: 11.72%, 13.25% and 14.03%) than at 30⁰C with 6.76%, 7.80% and 8.90% respectively). Generally, higher concentrations of caffeine were obtained with the UV/Vis spectrophotometric method (i.e: 6.76, 3.26 and 3.90 µg/g) compared to HPLC method (2.76, 1.00 and 1.49µg/g). This shows that caffeine has high affinity for dichloromethane and thus a better solubilization solvent than ordinary water mixed with acetonitrile.

Keywords: *Caffeine, Extraction, Derivative spectrophotometry, HPLC, UV/Vis spectrophotometry*

INTRODUCTION

Caffeine is a naturally occurring substance found in leaves, seeds or fruits of over 63 plant species in the world (Wanyika et al., 2010). It is a pharmacologically active substance and depending on the dose, can be mild central nervous system stimulant, improve cardiac performance, increase blood circulation, and exhibit vasodialatory and diuretic effects. It does not accumulate in the body over the course of time and is normally excreted within several hours of consumption (Barone and Roberts, 1996).

Caffeine is widely consumed, and the most commonly known sources of caffeine are coffee, cocoa beans, kolanut, and tea leaves. Coffee beans contain between 0.8 and 2.8% caffeine depending on its species and origin and it contributes to 10 to 30% of the bitter taste of coffee brews (Eggers and Pietsch, 2001). The amount of caffeine in coffee beverage varies depending upon the serving size, the type of product, and brewing method (Alves et al., 2007). Caffeine which is found in tea and coffee imparts bitterness and also acts as a flavour constituent (Leo, 1992). It is a mild nervous stimulant towards drowsiness and fatigue. In this respect, it is used by athletes to enhance performance since it mobilizes fats from stores a process that normally does not become maximal until intense activity is underway (Eva, 1988).

Caffeine is used as a drug on the basis of its effect on respiratory, cardiovascular and the central nervous system. It is included with aspirin in some preparations for treatment of headaches as it decreases cerebral eye blood flow. In either beverage or in nonprescription tablet form, it may be used to relieve fatigue since it increases the amount of urine flow. It is reported that there are

about 2000 non-prescription and about 1000 prescription drugs containing caffeine (Jeanne, 1987).

Along with nicotine and alcohol, caffeine is one of the three most widely used mood affecting drugs in the world (Farah *et al.*, 2006). In addition, caffeine has a slightly bitter flavour, hence decaffeination of tea, coffee and other beverages will leave the flavour slightly changed, even though no other components might be lost in the process, it should also be noted that decaffeinated coffee and tea are not caffeine free (Guzin, 2002).

Due to the widespread consumption of caffeine both in drug and as a food in beverages, hence it is important to collect precise information on their content in foods. Several analytical methods have been proposed for determination of caffeine in various matrices (environmental, biological, plants, food, etc.) covering a broad spectrum of instrumental techniques. Most research activities have been focused on chromatographic methods; however, spectrophotometric determination is preferred because of its rapidity, high accuracy and reproducibility (Komes *et al.*, 2009).

Moreover, UV-visible spectrophotometer is cheap and it is found in many laboratories. But caffeine content in tea leaves cannot be determined directly using UV visible spectrometer, due to the matrix effect of UV absorbing substances (Guzin, 2002). In this study, a direct and simple UV-spectrophotometric method for the determination of caffeine in some beverages and cola soft drinks using separation techniques and colour development was developed using derivative spectroscopy. To further establish the result, an easily adaptable HPLC method for both qualitative and quantitative determination of caffeine was investigated. Kolanut samples, commercial coffee and teas as well other solid samples were chosen such as cocoa, Kopiko sweet and Extra joss energy powder drink due to their high caffeine. Twelve samples were analysed with the validated UV/Vis spectrophotometry and their results compared with those obtained by the HPLC method.

METHODS

Twelve samples containing caffeine were obtained locally. They include: two brands commercial tea leaves – Lipton yellow label tea and Top tea, two brands of instant coffee – Napa café and Nescafe beverage, Cocoa bean seeds (*Theobroma cocoa*), two Kola nut species - *Cola nitida* and *Cola acuminata*, a brand of coffee sweet (Kopiko), two soft drink beverages – Coca cola and Pepsi cola, and two brands of energy drinks - Planet energy drink and Extra Joss Active Energy drink powder.

Chromatographic analysis was performed using Agilent 1200 HPLC system using C₈ reversed phase column (Supelcosil 250 x 4.6 i.d mm). The chemicals and reagents used in the study were of high quality of at least analytical grade. The caffeine standard was purchased from Sigma – Aldrich (UK).

Sample preparation and analytical determination

Tea and coffee sample preparation.

50 mg each of tea and instant coffee was weighed and 50ml of distilled water heated to about 30 °C was added and mixture stirred for 30 minutes. The mixture was filtered through a glass filter and cooled to room temperature. 15ml of dichloromethane was poured into the infusion and stirred. The aqueous phase and organic phase were then separated by separatory funnel. The procedure was repeated three more times to ensure efficient removal of the total caffeine in the samples. The total caffeine content in the beverage samples were later determined by UV spectrometry. Another set of samples were extracted using distilled water at 100^oC.

Kolanuts and cocoa samples preparation.

The fresh samples were dried in an oven at about 105 °C for about 2 hours until constant weight was achieved. The dried samples were ground to powder using mortar. 50.00mg of each of the

samples were accurately weighed in a 100ml beaker. 50ml of distilled water heated to about 30 °C was added and stirred continuously for about 30 minutes. The mixture was filtered through a glass filter. 15ml of dichloromethane was added to the filtrate and further stirred for 10minutes using magnetic stirrer. The aqueous phase and the dichloromethane (organic) phase were separated by separatory funnel. The procedures were repeated three more times to ensure quantitative and efficient removal of the total caffeine. The solvent layers were later combined and the total content of caffeine was determined by UV spectroscopy. The extracts of other solid samples i.e. Mini coffee kopiko sweet, Extra Joss energy drink powder were prepared using the same procedure.

Soft and energy drink samples preparation.

The drinks (Cocacola, Pepsicola, and Planet energy drink) were stored at room temperature until the time of their analysis. Each of the beverages was poured into a 250ml beaker and degassed by stirring on a hot plate with magnetic stirrer. The homogenized solution was then filtered. 50ml each of the filtrate were measured into a beaker and 15ml of dichloromethane was added. The mixture was gently swirled on the hotplate for about five minutes. The resultant mixture was separated with separatory funnel and the organic layer decanted into an Erlenmeyer flask. 15ml of DCM was added and subsequent extraction was repeated three more times. Finally, the total caffeine content was determined with a double beam spectrophotometer.

Determination of caffeine in coffee, tea and beverages by HPLC

Preparation of standard solutions.

1000ppm of caffeine stock solution was prepared by weighing 50.00mg of pure caffeine and quantitatively transferring it into 50ml volumetric flask and making it to the mark with the mobile phase (Acetonitrile). Working standards of 0.625, 1.25, 2.5, 5.0, 10.0, 25.0 and 50.0ppm were prepared by serial dilution of the stock solution with the mobile phase.

Tea and coffee samples preparation

50.00mg of tea and coffee samples were weighed and put in 100ml beakers respectively. 50ml of boiling distilled water was added and allowed to stand for five minutes with stirring. The solution was cooled and filtered into a conical flask. 5ml of the filtrate were pipetted into a clean 50ml volumetric flask and made to the mark with the mobile phase.

Other solid samples including mini coffee kopiko sweet, cocoa beans, kolanut, extra joss energy drink powder were also prepared using the procedures above (having ground their solid samples to powder). 20µL of each diluted sample was injected into the HPLC column. The relative peak areas were determined and concentration of caffeine in the samples was calculated from the calibration curve.

Preparation of recovery samples

Three samples were selected: Nescafe coffee, *cola acuminata*, and pepsi cola and were spiked with 25ppm caffeine standards in the ratio 1:1 dilution factor for recovery studies.

RESULTS AND DISCUSSION

Spectra result of pure caffeine in water

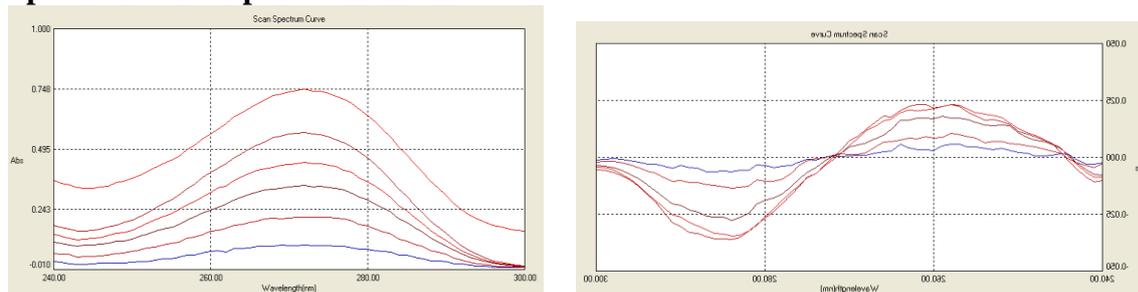


Figure 1: Absorption spectrum of caffeine standards in water. Figure 2: First derivative overlay spectrum of caffeine standards in water

From the spectra it can be observed that caffeine absorbs in the spectra range of 245 – 300nm with λ_{max} of 272nm. The spectrum in Figure 1 was derivatised to get first order derivative spectra and the zero crossing point was found to be 272nm.

Spectra result of pure caffeine in ethyl acetate.

The absorbance versus wavelength of caffeine standard solutions in ethylacetate was measured and the result is shown in Figure 3.

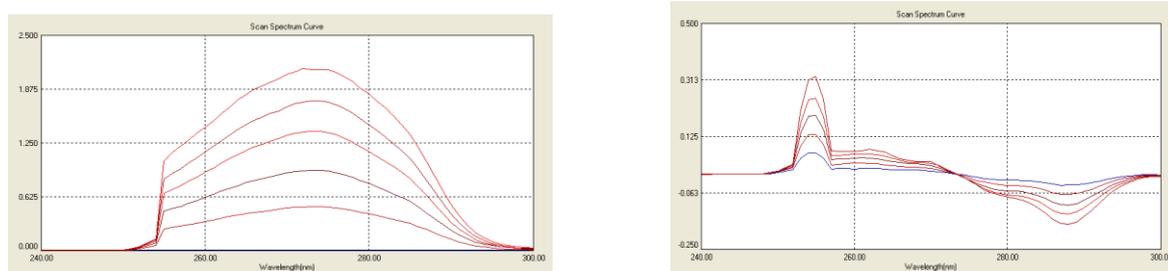


Figure 3: Absorption spectrum of caffeine standard in ethylacetate. Figure 4: First derivative overlay spectrum (D1) of caffeine standards in ethylacetate

From the spectra, it can be observed that caffeine absorbs in the spectra range between 257 to 300nm in ethylacetate at λ_{max} of 273nm. The spectra of the working standards (10 -50ppm) were overlaid and thus enables sharp identification of the λ_{max} . The spectrum obtained in Figure 4 was further derivatised to obtain first and second order derivative spectra as shown in Figure 4 the zero crossing point was found to be at 273 confirming that (λ_{max}) at the zero order spectra.

Spectra result of pure caffeine in dichloromethane

The absorption spectrum of pure caffeine in dichloromethane was measured in the spectra range of 200 – 300nm. From the spectra, it can be observed that caffeine absorbs in the spectra range of 245 – 300nm with λ_{max} of 274nm as shown in Figure 5.

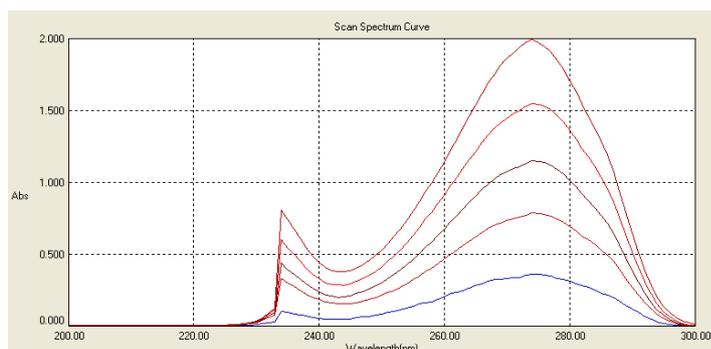


Figure 5: Absorption spectrum of pure caffeine in dichloromethane.

Derivatising the spectra further produces first and second order spectra. The zero crossing point was found also to be at 274nm and this confirms the λ_{max} value of the zero order.

Validation of the methods.

Validation of the method for UV analysis

The calibration graph correlating to the absorbance and the concentration of pure caffeine in water, ethylacetate and dichloromethane were plotted. The linear regression coefficient for water and ethylacetate were 0.9998 and 0.9994 respectively. A good linear relationship was observed for a wide concentration range. This shows that absorbance is directly proportional to the concentration.

Method validation for HPLC analysis

Linearity

Seven different concentrations of caffeine from 0.625ppm to 50ppm were analyzed according to experimental conditions. Then the calibration curve was established according to the obtained response (peak area) and the concentrations of caffeine in standard solutions. The results show a good linear relationship.

Recovery

For recovery study, one sample of known caffeine concentration from three different types of beverages was spiked with 25ppm of caffeine standard in the ratio 1:1(v/v) and recovery was calculated. As shown in Table1, the value of the obtained results were found not to be significantly different from the value of the added caffeine concentration as the recovery ranges from 99-112% with Nescafe having the highest recovery.

Table 1: Result of Recovery study from spiked beverage samples

Sample	Caffeine in sample (ppm)	Spiked Amount (ppm)	Theoretical value (ppm)	Experimental value (ppm)	Percentage Recovery (%)
Pepsi Cola	5.257	12.5	17.757	17.593	99
Kola nut	0.7440	12.5	13.244	14.333	108
Nescafe	2.950	12.5	15.45	17.299	112

Determination of caffeine contents in beverage samples

Caffeine content in tea leaves cannot be determined directly using UV-Visible spectrometer, due to the matrix effect of UV absorbing substances. Therefore, it is necessary to develop a method to overcome this difficulty. The method developed in this research work is to first dissolve caffeine in water and then extract it, using dichloromethane as mentioned in the procedure part. To determine caffeine from tea leaves, the extractions were repeated four times until the content of caffeine was found negligible.

Table 2 presents the experimental result for the determination of caffeine at two different temperatures, (30 °C and 100 °C). At 30 °C, the percentage of caffeine in Napa café coffee sample with 8.90% was the greatest of all the solid samples (tea, Extra joss energy powder, kola nuts, cocoa beans, and mini coffee kopiko sweet.) while mini coffee kopiko sweet sample had the least caffeine content (0.50%). This was followed closely by Lipton yellow tea which had caffeine content of 7.65% compared to the top tea with 6.70%. The two species of kolanuts have different amount of caffeine even though they are both of the same family. *Cola acuminata* (3.90%) had higher content of caffeine than *cola nitida* with 2.60% w/w.

In the liquid beverage samples planet energy drink had the highest caffeine content (9.28%) while Coca-Cola beverage had the least (7.20%).

From the beverage samples tested at the boiling temperature (100°C) similar to those at 30°C higher caffeine content were obtained. Top tea has the least caffeine content of the four tea and coffee samples while Napa café coffee has the greatest caffeine content. Comparing the content of caffeine at 30°C and boiling temperature, the percentage of caffeine at boiling temperature is greater. Caffeine content in tea leaves reported in this experimental work is in the range of values reported (1-8%) by Abdu et al. (2006).

Table 2: Levels of caffeine concentrations in beverage samples at two different temperatures (30 °C and 100 °C) using UV and HPLC methods

S/N	Sample	30 °C	100 °C	Caffeine % (w/w)
		Caffeine % (w/w)	Caffeine % (w/w)	
1	Top Tea	6.76	11.72	2.73
2	Lipton Yellow Tea	7.64	12.36	3.08
3	Nescafe coffee	7.80	13.25	5.91
4	Napa café coffee	8.90	14.03	6.07
5	Extra joss powder	3.26	-	1.00
6	Kopiko sweet	0.49	-	0.21
7	Cocoa beans	0.88	-	0.24
8	<i>Cola nitida</i>	2.60	-	0.20
9	<i>Cola acuminata</i>	3.90	-	1.49
10	Planet Energy Drink	9.28	-	24.74
11	Pepsi cola	7.55	-	10.51
12	Coca-Cola	7.20	-	10.08

The HPLC method values obtained were of similar trend and progression rate. The highest caffeine concentration in beverage samples was also obtained in Napa café coffee (6.0%) in the solid sample as well as planet energy drink with 24.94% in the liquid sample. Likewise, the least concentration was obtained in the kopiko sweet and *cola nitida* with 0.21 and 0.20% w/w respectively. Using HPLC method, Abdul *et al.*, (2006) reported that the caffeine content for black tea was 3.34% and green tea was 2.44%. This was similar to the result obtained in this research work with the tea samples having concentrations of 2.73 and 3.08%.

All over the world, the caffeine contents in soft drinks varies according to the type of the brand, yet its average content in soft drinks is approximately 18mg per six ounces (i.e 100ppm). In fact, the US Food and Drug administration (FDA) limits the maximum caffeine amount in carbonated beverages to 6mg/oz (200ppm) (Violeta et al., 2010). From this experimental study, the caffeine

content level in the analyzed carbonated beverage samples (Pepsi with 105ppm and coca-cola with 100ppm) were within the range for food industry guidelines.

CONCLUSION

The validated UV-Spectrophotometric method for the quantification of caffeine in beverages was found to be simple precise sensitive and accurate. To make the result more reliable, the experiment were repeated three times and the average values were taken. The spectrophotometric method proved to be the best alternative for the determination of caffeine content, exhibiting the most similar results to the HPLC instrumentation.

The order of caffeine concentration in the beverage samples were: Napa café coffee > Nescafe coffee> Lipton yellow> Extra joss energy drink powder > kolanut > cocoa beans > kopiko sweet >planet energy drink > Pepsi cola > Coca-Cola.

The results at two different temperatures reveal that, caffeine is better extracted at boiling temperature (100⁰C) as in Top tea, Lipton yellow, Nescafe and Napa café with greater values of 11.72, 12.36, 13.25 and 14.03% respectively than at 30⁰C with lower progression values of 6.76, 7.64, 7.80 and 8.90% and more extraction time will still favour more yield.

The amounts of caffeine obtained by UV/Vis spectrophotometric method were higher than those obtained by HPLC method. The caffeine content of the tea, coffee and other beverages was not found to be alarming since it correlated well with the documented values.

Since caffeine is a pharmacologically active substance that stimulates the central nervous system. Excessive amount should be avoided since caffeine consumed in large amounts have adverse health effects. Especially, people suffering from high blood pressure, pregnant women and those with coronary heart disease should avoid such beverages as caffeine disrupts normal health rhythm.

REFERENCES

- Abdul Mumin, Kazi Farida Akhter, Zainal Abedin, and Zakir Hossain, (2006). Determination and characterization of caffeine in tea, coffee and soft drinks by solid phase extraction and high performance liquid chromatography (SPE-HPLC). *Malaysian J. Chem.*, 8: 45-51.
- Alves R. C, Soares C, Casal S, Fernandes J. O and Oliveira M. B.(2007). Factors influencing the norharman and Harman contents in espresso coffee. In *Journal of Agricultural and Food Chemistry*, vol. 55, p. 1832-1838.
- Barone J J and Roberts H R (1996). Caffeine consumption. In *Food Chem Toxicol*, vol. 34, p. 119-129.
- Eggers R and Pietsch A. (2001). *Coffee Recent Development*. Iowa State University Press, Iowa, p. 33-46.
- Eva MH (1988). Nutrition. West publishing company, 4(7): 351.
- Farah A, Monteiro M C, Calado V, Franca A S and Trugo L C. (2006). Correlation between cup quality and chemical attributes of Brazilian coffee. *Food Chemistry* 98:373-80.
- Guzin Alpdogan, Kadir Karabina and Sidika Sungur, (2002). Derivative spectrophotometric determination of caffeine in some beverages. *Turk. J. Chem.*, 26: 295-302.
- Jeanne C S. (1987). Introductory clinical pharmacology. *J. B. Uppimcott Company*, 3(19): 122-125.
- Komes D, Horzic D, Belscak A, Kovacevic GK and Boljak A (2009). Determination of caffeine contents in tea and mate tea by using different methods. *Czech J. Food Sci.*, 27: 69.
- Leo ML (1992). Food analysis by HPLC. Marcel Decker Inc., 17: 656-659.
- Wanyika H. N., E. G. Gatebe, L. M. Gitu, E. K. Ngumba and C. W. Maritim (2010). Determination of caffeine content of tea and instant coffee brands found in the Kenyan market. *African Journal of Food Science*

PHYSICO-CHEMICAL AND MICROBIAL CHARACTERIZATION OF ABATTOIR WASTEWATER: IMPACT OF ABATTOIR ON THE ENVIRONMENT

*Oluseyi, T.O., Folarin, B.T & Adaramaja, M.M

Department of Chemistry, University of Lagos, Akoka, Lagos, Nigeria
toluseyi@unilag.edu.ng

ABSTRACT

Slaughtering of animals to supply meat for human consumption in abattoirs is a common practice in Nigeria. Abattoirs however put local built environment and health of nearby residents at great risk as a result of pollution from their improper management. This study therefore investigates the impact of abattoir wastewater on the quality of surrounding underground waters and the health of residents in their vicinity using Agege and Surulere abattoirs as a case study. Physico-chemical and microbiological analyses were carried out on abattoir wastewater and surrounding underground using standard analytical methods. The study went further to investigate the effect of abattoir operations on residents in the abattoir vicinity using questionnaire to determine the quality of the local built environment and health of residents. The ranges of the physico-chemical parameters studied were as follows: pH 3.8 - 4.6, Temperature 28.9°C – 29.9°C, Dissolved oxygen 6.50mg/l – 11.43mg/l, BOD 85.20mg/l – 618.82mg/l, Total Solids 1326.53mg/l – 2225.46mg/l, Total dissolved solids 226.05mg/l – 618.82mg/l, Total suspended solids 1030.04mg/l – 1606.58mg/l and Turbidity of 12.1 – 87.4 NTU in Agege abattoir. While in Surulere abattoir, physico-chemical parameters ranges were; pH 3.7 - 4.9, Temperature 28.9°C – 29.9°C, Dissolved oxygen 7.02mg/l – 12.32mg/l, BOD 87.21mg/l – 110.40mg/l, Total Solids 1221.10mg/l – 2322.50mg/l, Total dissolved solids 380.19mg/l – 1025.39mg/l, Total suspended solids 1020.01mg/l – 1707.88mg/l and Turbidity of 12.0 – 70.5. The values for most of the parameters were very high and were above the WHO and FMENV standards. The total viable bacterial count ranged from 1.80×10^5 – 3.10×10^5 cfu/ml for Agege and 1.80×10^5 – 3.10×10^5 cfu/ml for Surulere abattoir. Total fungi count ranged from 2.0×10^3 – 3.10×10^3 cfu/ml and 1.80×10^3 – 3.10×10^3 cfu/ml for Agege and Surulere abattoir respectively. The bacteria genera isolated were: *E.coli*, *Bacillus spp*, *Klebsilla spp*, *Staphylococcus aureus*, *Clostridium spp.*, and *Pseudomonas spp*. The fungi genera isolated include *Aspergillusniger*, *Fusarium spp.*, *Mucor spp.*, *Saccharomyces spp.* and *Penicillium spp*. The result showed that the air quality around the abattoir was grossly polluted. Excessive coughing, diarrhoea and eye itching were reported among the residents. Also, recreational activities around the abattoir was absent because of the odour emanating from the abattoir wastes. The findings in this study underscored the need to treat abattoir wastewater rather than discharging it into the environment and the abattoir should be built away from residential areas.

Keywords: abattoir, bacterial count, fungi, physico-chemical parameters, wastewater

INTRODUCTION

Slaughter house usually called ‘abattoir’ is a place specially created and approved by regulatory authorities for hygienic slaughtering, processing and effective preservation and storage of meat products for the consumption by man (Alonge, 2001). The nearness of abattoirs to consumers in neighbourhoods could have certain advantages, but the impact of the activities in the locally built environment and health of residents is of great concern and carries enormous risks (Bello and Oyedemi, 2009). Series of activities in abattoirs result in the production of large quantities of wastes. These wastes could be solid (condensed meat, undigested feeds, bones, horns and hair); liquid (blood, gut contents and urine) and fat and oil (Sangodoyin, 1992).

In Nigeria and many developing countries, proper sanitary practices are almost lacking in our abattoirs, such that untreated wastes together with wastewater generated during abattoir processes are discharged indiscriminately into the nearest surface water (Adeyemo et al., 2002 and Adeyemo, 2002). This wastewater percolates through the soil to underground water, thereby polluting not only the receiving surface water but also the soil and underground water (Adelegan, 2002; Adesemoye et al., 2006). Studies have shown that the indiscriminate disposal of abattoir wastes could result to pollution of surface and underground waters, air and land. Blood impact high organic pollution to receiving water and consequently depletes the dissolved oxygen of water bodies. The result of a study carried out by Chukwu et al. (2006) showed that BOD, COD and DO values of water samples collected from Tayi stream, a receiving stream of a major abattoir in Niger State, Nigeria were above the FEPA and WHO limits for waste water. Chukwu and co-researchers concluded that these values could cause the destruction of primary producers and in turn lead to diminishing consumer population in water. Rabah et al. (2010) reported a high mean count of $3.7 \pm 0.01 \times 10^6$ cfu/g and $1.4 \pm 0.4 \times 10^4$ cfu/g for bacteria and fungi respectively, during a study on soil contaminated with abattoir effluent. The presence and abundance of various species of *Bacillus* was observed and attributed to the fact that these organisms are indigenous to soil environment and are known to persist in such environment (Atlas and Bartha, 2007).

Magida and Guip examined the impact of abattoir wastes on water quality around an abattoir site in Gwagwalada-Abuja, Nigeria. Heavy metal content as well as physical and chemical properties of water samples collected from four points along a stream were studied. It was discovered that most of the analysed properties were still below the national and international accepted limits. However, continuous discharge of abattoir waste into the stream may in no distant time, pose a threat to human health. The paper concluded by recommending that mechanism should be put in place for the treatment of these abattoir wastes before they are disposed (Magida and Guip, 2012). Akinro et al. (2010) investigated the physico-chemical and microbial properties of the effluents discharged from Araromi abattoir in Akure, South West Nigeria. The results indicated that all the water samples tested were polluted biologically beyond permissible limits. The various wastewater samples were contaminated with *E. Coli* and other enteric bacteria. Abattoir effluent reaching stream may contribute significant levels of nitrogen, phosphorous and other nutrients, there by resulting in eutrophication of water bodies and consequently reducing water physical, chemical and biological qualities.

Abattoir operations generate huge amount of organic wastes with relatively high levels of suspended solids, liquid and fat. The solid waste includes condemned meat, undigested food in the gut, bones, horns, hairs and aborted fetuses. The liquid waste is usually composed of dissolved solids, blood, gut contents, urine and water. All these wastes are disposed into nearby surface waters and greatly affect the quality of these waters. The objectives of this study are to carry out quantitative analysis of water samples and some liquid waste (blood, faeces, urine and intestinal contents) from Agege and Surulere abattoirs; study the effects of the wastes on the receiving stream and underground water (well); determine the health implication on dwellers in the residential neighbourhood as a result of the abattoir activities.

METHODS

Sample area and collection of samples

Abattoir effluents were collected from two abattoirs in Oko-oba (Agege Local Government Area) and Itire (Surulere Local Government Area), Lagos State, South western Nigeria. Liquid wastes such as blood, urine, intestinal content and wash water from the abattoir processes are channeled into the canal constructed inside the abattoir, which leads into a stream near the

abattoir in both areas under study. Wastewater samples were collected from both abattoirs at upstream: 60 m before the point where the abattoir effluents meet receiving stream; midstream: at the point where the abattoir effluents meet receiving stream; and downstream: 60 m away point where the abattoir effluents meet receiving stream. At sampling point, previously cleaned sample containers were rinsed with sampled water thrice and then filled to the brim. The samples were labeled and transported to the laboratory, stored in the refrigerator at about 4^oC prior to analysis. Liquid wastes (blood, faeces, urine and intestinal contents) were also sampled for microbial analysis. Samples were collected from the month of February to April 2011.

Method for determination of Physical and Chemical Properties of water samples

Temperature was determined at point of collection of samples with a thermometer. pH was determined using Mettler Toledo pH meter. Dissolved oxygen (DO) and biochemical oxygen demand (BOD) were determined using dissolved oxygen meter, model A and standard method 5210B respectively. Total suspended solids (TSS) and total dissolved solids (TDS) were determined gravimetrically (APHA, 2005). Turbidity of water samples was determined by Nephelometric method using Lamoble 2020 portable turbidity meter.

Method for determination of microbial characteristics of water samples

Potato dextrose agar and nutrient agar were the media used in this study. Both media were sterilized according to manufacturer's instruction. Total fungi count was estimated after serial dilution of the samples were prepared from 10⁻² to 10⁻⁶, after which the prepared samples were aseptically inoculated on the PDA plates using spread plate technique, then incubated at 30^oC for 72h. The PDA plates had been supplemented with 100ug/ml Streptomycin to inhibit the growth of bacteria prior to usage (Adesomoye and Adedire, 2005). After incubation, fungal population was then estimated by counting the numbers of organisms on the plates with distinct growth. To isolate and identify fungi colonies, macroscopic examination and morphological characteristics were employed respectively.

Total bacteria were estimated using a method similar to Boulter et al., (2002). Serial dilution of samples were prepared from 10⁻⁴ to 10⁻⁹. Sterile nutrient agar plates were inoculated aseptically with prepared samples and incubated at 30^oC for 24h. After incubation, total viable bacteria count was estimated and recorded as colony forming units per ml by counting the numbers of distinct colonies on the plates. Pure isolated cultures were identified using biochemical tests.

Methodology for questionnaire

A total of fifty questionnaires each were administered to residents living within the residential neighbourhood of the studied abattoirs. This was necessary in order to generate needed answers as to the effects of the abattoir on residents and the environments. Simple statistical methods were used in analysis. Altogether the 100 questionnaires were returned thus achieving a response rate of 100 %.

RESULTS AND DISCUSSION

Physico-chemical properties of water samples

The physico-chemical properties of water samples of Agege and Surulere abattoirs collected from upstream, midstream and downstream are presented in Table 1.

Table 1: Result of physico-chemical analyses of abattoir waste waters from nearby surface water

Parameters	Agege Abattoir			Surulere Abattoir		
	US	MS	DS	US	MS	DS
Turbidity (NTU)	87.4	50.5	12.1	70.5	49.2	12.0
Temperature (°C)	28.9	28.9	29.9	27.5	28.0	28.0
pH	4.0	3.8	4.6	4.2	3.7	4.9

DO (mg/l)	11.34	6.5	9.42	12.32	7.02	10.41
BOD (mg/l)	89.41	120.36	85.2	89.21	110.4	87.21
TS (mg/l)	1326.53	2225.4	1418.21	1221.1	2322.5	1400.2
TDS (mg/l)	226.05	618.82	388.17	195.71	614.62	380.19
TSS (mg/l)	1100.48	1606.58	1030.04	1025.39	1707.88	1020.01

Key: US = upstream, MS = midstream, DS = downstream

Generally, the values of most of the parameters studied were highest at the point where the effluents meet the stream (midstream). Turbidity values ranged from 12.1-87.4NTU for Agege abattoir and 12.0- 70.5NTU for Surulere abattoir. All water samples were above WHO limit of 5 NTU. Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (such as whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches (WHO, 2003).

Hot water is usually used in large quantity for processing animals in abattoirs. It was however observed that the hot processed water from both abattoirs has lost appreciable degree of hotness before reaching the point of disposal. Observed temperature range of 28.9-29.9 °C and 27.5-28 °C for Agege and Surulere abattoirs respectively were in compliance with the Federal Ministry of Environment (FMEnv) permissible limit for the discharge of waste water.

The pH values of the water samples from both abattoirs were below FMEnv and WHO limits as the water samples were acidic with pH values ranging from 3.8 – 4.6 for Agege abattoir and 3.7 – 4.9 for Surulere abattoir. These acidic values could affect aquatic life because most metabolic processes are dependent on pH. Although, dissolved oxygen (DO) values conformed to FMEnv and WHO standards, it was however observed that a value of 6.5mg/l for midstream sample from Agege abattoir was not satisfactory when compared with values of 7.2 to 9.9mg/l needed for the successful spawning of fish. This value might in no time exceed the FMEnv limit if proper treatment practices are not imbibed. Biochemical oxygen demand (BOD) levels ranged from 85.20-120.36mg/l for Agege abattoir and 87.21-110.41mg/l for Surulere abattoir. These values are higher than the FMEnv and WHO limits for the discharge of wastewater into surface water. The high BOD values observed was not surprising because effluents from abattoirs are usually very rich in organic matters. High organic loads in the wastewater means high amount of oxygen will be required by aerobic bacteria to decompose the organic matter resulting to high BOD.

The high inorganic and organic content of abattoirs was manifested in the extremely high total suspended solids (TSS) values obtained in this study. TSS values ranged from 1030 – 1606 mg/l and 1020 – 1707 mg/l for Agege and Surulere abattoirs respectively. Adesemoye et al., (2006) also reported a high TSS value of 1750 – 1800 mg/l for wastewater in two abattoirs in Agege and Ojo Local Government Areas in Lagos State. All the water samples had levels higher than WHO standard for total dissolved solid (TDS) and total suspended solid (TSS) except downstream sample from Surulere abattoir whose TDS value of 195.7mg/l was lower but very close to 200mg/l set as limit by WHO. The value of total solid (TS) at midstream from Surulere abattoir was higher than that of Agege abattoir, though both values were above the permissible limit of 2000mg/l set by FMEnv. It was expected that Agege abattoir should have higher TS because, in addition to being in existence for about 10 years before Surulere abattoir, larger number of cow, approximately 1000 cows are killed per day compared to Surulere where only about 10 cows are killed. This lower value might be attributed to the availability of facilities to separate solid waste from liquid waste before discharge into surface water.

Microbial isolates and colony counts of water samples from Agege and Surulere abattoirs

Microbial analysis of water samples in the vicinity of abattoirs is an essential tool in order to determine the presence of microorganisms that may likely constitute a health hazard. Microorganisms commonly used as indicators of water quality include: coliforms, *Faecal streptococci*, *Clostridium perfringens*, and *Pseudomonas aeruginosa* (Adeyemo et al, 2002). All the water samples were polluted by faecal organisms such as *E. coli* and *Faecal streptococci* with values that are above the WHO recommended limit.

Table 2: Microbial isolates and colony counts of water samples from Agege and Surulere abattoirs

Abattoirs	Water Samples	Total bacteria count	Bacteria isolated	Total fungi count	Fungi isolated
Agege	UP	3.10×10^5	<i>Baccillus spp.</i> , <i>Micrococcus spp.</i>	2.0×10^3	<i>Aspergillus niger</i> , <i>Fusarium spp.</i> , <i>Mucor spp.</i>
	MS	2.40×10^5	<i>Baccillus spp.</i> , <i>Staphylococcus aureus</i>	8.0×10^3	<i>Aspergillus niger</i> , <i>Fusarium spp.</i> , <i>Penicillium spp.</i>
	DS	1.80×10^5	<i>Baccillus spp.</i> , <i>Pseudomonas spp.</i>	3.0×10^3	<i>Fusarium spp.</i>
Surulere	UP	1.40×10^5	<i>Baccillus spp.</i> , <i>Pseudomonas spp.</i>	5.0×10^3	<i>Mucor spp.</i> , <i>Saccharomyces spp.</i>
	MS	1.30×10^5	<i>Baccillus spp.</i> , <i>Micrococcus spp.</i>	1.0×10^3	<i>Fusarium spp.</i>
	DS	2.10×10^5	<i>Baccillus spp.</i> , <i>Clostridium spp.</i>	5.0×10^3	<i>Saccharomyces spp.</i> , <i>Penicillium spp.</i>

Mean microbial count of water sample isolates from Agege and Surulere abattoirs

The mean Value of total heterotrophic bacteria and fungi of waste water samples from both abattoirs is represented in Table 3.

Table 3: Mean microbial count of water sample isolates from Agege and Surulere abattoirs

Abattoirs	Mean bacteria count (cfu/l)	Mean fungi count (cfu/l)
Agege	2.42×10^6	4.36×10^3
Surulere	1.60×10^6	3.67×10^3

Table 4 shows the coliform counts for underground water (well) around the vicinity of Agege and Surulere abattoir were studied with respect to the distance of the well from the stream.

Table 4: Coliform counts for underground water (well)

Distance of wells from stream	Agege abattoir Coliform count(cfu/ml)	Surulere abattoir Coliform count(cfu/ml)
50 m	1.10×10^2	1.10×10^2
100 m	1.10×10^2	0.00
150 m	0.00	0.00

The presence of *Escherichia coli* and *Faecal streptococci* in water samples at close proximity to the abattoirs shows that the groundwater within the abattoir and about 100 meters from the abattoir is harmful to human health and can cause urinary tract infection, diarrhoea or meningitis. The groundwater (located about 150 meters from the abattoir) pose little or no threat at both abattoirs.

Micro-organisms isolated from abattoir liquid wastes and their microbial counts

The mean total heterotrophic bacteria, fungi and coliform count were high for water samples from the two studied abattoirs (Tables 2, 3, 4 and 5). The WHO (2008) recommends 0cfu/100ml for all faecal bacteria and by this set guideline; any water contaminated to this level is neither good for domestic use nor is it supposed to be discharged directly into the environment without treatment.

Table 5: Micro-organisms isolated from abattoir liquid wastes and their microbial counts

Samples	Blood	Faeces	Urine	Intestinal content
Bacteria isolates	<i>Bacillus spp.</i> , <i>E. coli</i>	<i>Bacillus spp.</i> , <i>E. Coli</i> , <i>Klebsiella spp.</i>	<i>Bacillus spp.</i> , <i>E. Coli</i> , <i>Klebsiella spp.</i>	<i>Bacillus spp.</i> , <i>E. Coli</i>
Fungi isolates	<i>Saccharomyces spp.</i> , <i>Mucor spp.</i>	<i>Saccharomyces spp.</i>	<i>Aspergillus spp.</i>	<i>Rhizopus stolonife</i>
Total heterotrophic bacteria count (cfu/ml)	2.1×10^5	3.2×10^5	1.5×10^5	1.3×10^5
Total heterotrophic fungi count (cfu/ml)	13.0×10^3	12.0×10^3	9.0×10^3	1.0×10^3
Total coliform count	1.2×10^2	1.7×10^2	1.4×10^2	1.3×10^2

High level of pollution of the surface and nearby groundwater close to these abattoirs as revealed in this study further confirmed the dangers associated with discharging untreated wastewater to the environment and the need for adequate treatment to minimise its impact on the environment.

Impact on health of residents

This study revealed that abattoir activities and management have direct and indirect effects on the built-up environment and health of people especially residents in abattoir vicinity. 100 residents of buildings located about 150 meters radius to the two abattoirs were randomly selected for questionnaire survey using relevant indicators to investigate effects on their health. Offensive odour emanating from the abattoir as a result of decomposing animal waste, manure and carcasses as well as burning of hide and skin of animals was reported to constitute air quality impairment by the respondents. Ninety percent of the respondents reported that smoke from nearby abattoir affects breathing, causes respiratory ailments like cough and asthma as well as poor ventilation because many residents close their windows especially in the direction of the abattoir. Almost all residents reported the incidence of large number of house flies and rodents due to their close proximity to the abattoir, and these have been found to be causative agents of diseases such as typhoid fever, dysentery and diarrhoea. The quality of health of residents living in close proximity to these abattoirs was found to be poor due to the effect of pollutants from abattoir activities located in their neighbourhood.

The abattoir management system in Lagos should include a waste management plan designed for abattoir operation. Laws on land use, and waste regulation to control the location and management of abattoirs should be enforced. Environmental impact assessment for abattoirs should be enforced. There is the need for the treatment of the abattoir waste waters before they are discharged into the nearby surface waters and drainages in order to minimize the pollution of

the groundwater around the abattoir and reduce the health risk of the residents in such neighborhoods.

REFERENCES

- Adesemoye A.O., and Adedire C.O (2005). Use of cereals as basal medium for the formulation of alternative culture media for fungi. *World J. Microbiol. Biotechnol.* 21: 329-336.
- Adesemoye, A.O., Opere, B.O., and Makinde, S.C.O. (2006). Microbial content of abattoir waste water and its contaminated soil in Lagos, Nigeria *African Journal of Biotechnology*, 5(20), 1963-1968.
- Adeyemo, O.K., Ayodeji, I.O., and Aiki-raji, C.O. (2002). The water quality and the sanitary conditions in a major abattoir (Bodija) in Ibadan. *African Journal of Biomedical Research*, 5, 51-55
- Adeyemo, O.K. (2002). Unhygienic operation of a city abattoir in south western Nigeria: Environmental implication. *AJEAM/RAGEE*. 4(1), p 23-28.
- Akinro, A., Ologunagba, I.B., and Olotu (2010). Environmental implications of unhygienic operation of a city abattoir in Akure, Western, Nigeria. *ARPN Journal of Engineering and Applied Sciences*. 4(9): 311-314.
- Alonge, D.O. (2001). Textbook of Meat hygiene in the tropics, 5th edition, Farmcoe press Ibadan, Nigeria, p 61.
- APHA (2005) Standard Methods for the Examination of Water and Waste Water. 21st Edition. American Public Health Association. Washington D.C., p 1325.
- Atlas, R. M., and Bartha, R. (2007). *Microbial Ecology: Fundamentals and Applications*, Benjamin/Cummings Publishing Company Inc, India.
- Bello, Y. O. and Oyedemi, D. T. A. (2009) The Impact of Abattoir Activities and Management in Residential Neighbourhoods: A Case Study of Ogbomoso, Nigeria. *J Soc Sci*, 19(2): 121-127
- Boulter J.I, Trevor J.T, and Boland G.J (2002). Microbial studies of compost: bacterial identification and their potential for turfgrass pathogen suppression. *World J. Microbiol. Biotechnol.* 18: 661-671.
- Chukwu O., Mustapha, H.I., Gafar, H.B. (2006). The effect of Minna abattoir wastewater on surface water quality. *I. Environ Res J.* 3: p 334-338.
- FEPA/FMEnv, 1991. Guidelines and standard for Environmental Pollution Control in Nigeria. Federal Ministry of Environment Publications, p 206.
- Magaji, J.Y., Chup, C.D. (2012). The effects of abattoir waste on water on water quality in Gwagwalada-Abuja, Nigeria. *Ethiopian Journal of Environmental Studies and Management*. Vol. 5 no.4
- Rabah, A.B., Oyeleke, S.B., Manga, S.B., Hassan, L.G., and Ijah, U.J.J. (2010). Microbiological and physicochemical assessment of soil contaminated with abattoir effluents in Sokoto Metropolis, Nigeria. *Science World Journal*. Vol 5 (No 3): 1-4.
- Sangodoyin, A.Y. (1992). Environmental study on surface and groundwater pollutants from abattoir effluents *Bioresource Technology*, 41: p 193-200.
- World Health Organization (2003). Heterotrophic Plate Counts and Drinking-water Safety. Edited by J. Bartram, J. Cotruvo, M. Exner, C. Fricker, A. Glasmacher. Published by IWA Publishing, London, UK. ISBN: 1 84339 025 6.
- World Health Organisation (2008) "Guidelines for Drinking Water Quality" W.H.O. Geneva.

ISOLATION OF COLIFORMS IN VEGETABLES FROM SUBSISTENCE GARDENS IN LAGOS STATE

Omotayo, A.E., Simeon, O.M. & Amund, O.O.

Department of Microbiology, Faculty of Science, University of Lagos
elizabethomotayo@yahoo.com , simeon_oladapo@yahoo.com , kay_amund@yahoo.com

ABSTRACT

The presence of coliforms in vegetables from gardens in Lagos State was examined. The vegetables sampled include cabbage, waterleaf, carrot, lettuce and cucumber collected from five sites representing five geographical zones in Lagos State. The vegetables were highly contaminated with coliforms. Cabbage, waterleaf, carrot, lettuce and cucumber had coliform counts of 1.10×10^8 cfu/g, 6.90×10^7 cfu/g, 5.50×10^7 cfu/g, 1.06×10^8 cfu/g and 4.70×10^4 cfu/g respectively. The populations of faecal coliforms and *Salmonella/Shigella* species were equally high. The faecal coliform population range was between 3.63×10^6 and 1.90×10^9 cfu/g, while the *Salmonella* and *Shigella* species ranged from 1.40×10^2 - 3.16×10^4 cfu/g. *Escherichia coli* O157:H7 was not isolated from any of the sites. The following bacterial isolates obtained which includes, *Staphylococcus aureus*, *Yersinia pestis*, *Staphylococcus equorum*, *Enterobacter asburiae*, *Serratia fonticola*, *Photobacterium asymbiotica*, *Providencia alcalifaciens*, *Plesiomonas shigelloides*, *Enterobacter cancerogenus* were hemolytic, while *Staphylococcus xylosum*, *Proteus mirabilis*, *Salmonella enterica*, *Enterobacter gergoviae*, *Escherichia fergusonii*, *Escherichia coli*, *Salmonella enterica*, *Enterobacter amnigenus* were non-hemolytic. The study shows the prevalence of coliforms in vegetables before harvesting.

Keywords: Bacteria, Coliforms, Gardens, Prevalence, Vegetables

INTRODUCTION

Coliform bacteria are a commonly used bacterial indicator of sanitary quality of foods and water. Coliforms are not normally causes of serious illness, they are easy to culture and their presence is used to indicate that other pathogenic organisms of faecal origin may be present (Kim and Harrison, 2008). Coliforms can be found in aquatic environment, in the soil and on vegetation.

Vegetables and fruit are vital to our health and well-being, providing essential vitamins, minerals and fiber. Fresh fruits and vegetables once were thought to be relatively free of disease-producing pathogens (Beuchat and Ryu, 1997). However, according to the Centers for Disease Control and Prevention in the US (CDC), food-borne illnesses linked to fruits and vegetables have become more common (FDA, 2004). Outbreaks of food-borne illnesses on vegetables have been linked to *Escherichia coli*, *Escherichia coli* O157:H7, *Listeria monocytogenes*, *Shigella* and *Salmonella* (Johnston *et al.*, 2005; NSW, 2007). Changes in microorganisms have undoubtedly contributed to this increase. Vegetables can become contaminated with pathogenic organisms during growth, harvesting, post-harvest handling, or distribution (McMahon and Wilson, 2001). Use of untreated wastewater in irrigation also represents an important route for transmission of these pathogenic organisms. The aim of this study was therefore to evaluate the prevalence of coliforms in vegetables in Lagos State, Nigeria.

METHODS

Sample Source

The vegetables were obtained from different vegetable gardens from five sites representing five geographical zones of Lagos State. The samples were collected in sterilized polythene bags and taken to the laboratory for analysis.

Sample Preparation

The vegetable samples were soaked for one minute in 70% alcohol so as to eliminate surface microorganism and then shredded to pieces. The vegetables were aseptically homogenized in distilled water using sterile pestle and mortar.

Isolation and Identification of Microorganisms

Aliquots of 0.1 ml from ten-fold dilutions were inoculated in triplicates into freshly prepared growth medium using the spread plate technique. MacConkey (MAC) Agar, Eosine methylene blue (EMB) Agar and Salmonella Shigella (SSA) Agar were incubated at 37^oC for 24 hours. After incubation, the colonies that developed were enumerated. The bacterial isolates that grew on EMB Agar and SSA Agar were identified using morphological, biochemical and Analytical Profile Index 20E and 20SA kit.

Isolation of *Escherichia coli* 0157:H7

Escherichia coli 0157:H7 was isolated using Sorbitol MacConkey Agar which supports its growth. All the isolates that grew on EMB Agar were streaked on Sorbitol MacConkey Agar and incubated at 37^oC for 24 hours. After the incubation, the plates were observed for growth and colour change. Pink coloration on the plate indicates the growth of other stains of *Escherichia coli*, while colourless growth indicates the growth of *Escherichia coli* 0157:H7.

Heamolysis Test

This test is dependent on the presence of a substance called heamolysin, which breaks down red blood cells. The bacterial isolates were streaked on Blood Agar, incubated at 37^oC for 24-28 hours and observed for haemolysis of red blood cells.

RESULTS

The populations of coliforms (4.70×10^4 - 1.10×10^8 cfu/g) and faecal coliforms (3.63×10^6 - 1.90×10^9 - cfu/g) were generally high in all the vegetables as presented in Figure 1. The population of *Salmonella/Shigella* spp. was however low (1.40×10^2 - 3.16×10^4 cfu/g) in all the samples compared with the coliform counts. Statistically, there was no significant difference in the bacterial populations among the vegetables for both coliform and faecal coliform counts.

None of the isolates that grew on EMB Agar plates were *E. coli* 0157:H7 (Table 1). Isolates EMB 5,6,7,9 and 10 produced pink pigmentation after fermenting sorbitol, while isolates EMB 1,2,3,4,8 were colourless.

The following isolates displayed complete haemolysis on blood agar plates. They include; *Staphylococcus aureus*, *Yersinia pestis*, *Staphylococcus equorum*, *Enterobacter asburiae*, *Serratia fonticola*, *Photobacterium asymbiotica*, *Providencia alcalifaciens*, *Plesiomonas shigelloides* and *Enterobacter cancerogenus*, while *Staphylococcus xylosum*, *Proteus mirabilis*, *Salmonella enterica*, *Enterobacter gergoviae*, *Escherichia fergusonii*, *Escherichia coli*, *Salmonella enterica*, *Enterobacter amnigenus* were all negative to the test (Table 2).

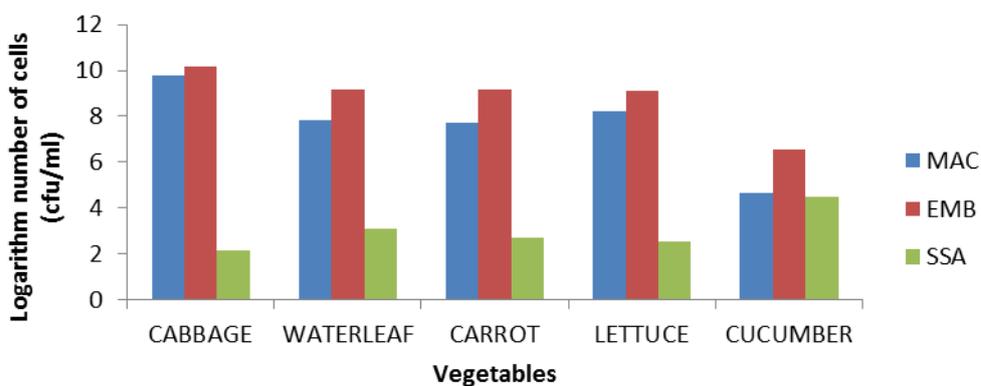


Figure 1. Population of coliforms in different vegetables from subsistence gardens in Lagos State.

MAC, MacConkey Agar for the growth of total coliforms; EMB, Eosin methylene blue Agar for growth of faecal coliform; SSA, Salmonella-Shigella Agar for growth of *Salmonella* and *Shigella* species.

Table 1: Growth of isolates obtained from Eosin methylene blue Agar on Sorbitol MacConkey Agar for the isolation of *Escherichia coli* 0157:H7

ISOLATE CODE	ISOLATES	COLONIAL GROWTH COLOUR
EMB 1	<i>Staphylococcus auricularis</i>	Colourless
EMB 2	<i>Staphylococcus xylosus</i>	Colourless
EMB 3	<i>Proteus mirabilis</i>	Colourless
EMB 4	<i>Salmonella enteric</i>	Colourless
EMB 5	<i>Yersinia pestis</i>	Pink
EMB 6	<i>Enterobacter gergoviae</i>	Pink
EMB 7	<i>Staphylococcus equorum</i>	Pink
EMB 8	<i>Enterobacter asburiae</i>	Colourless
EMB 9	<i>Escherichia fergusonii</i>	Pink
EMB 10	<i>Escherichia coli</i>	Pink

TABLE 2: Hemolysin production by coliforms isolated from vegetables in Lagos State

S/N	ISOLATE CODE	ISOLATE IDENTITY	HEAMOLYSIS
1	EMB 1	<i>Staphylococcus auricularis</i>	+
2	EMB 2	<i>Staphylococcus xylosus</i>	-
3	EMB 3	<i>Proteus mirabilis</i>	-
4	EMB 4	<i>Salmonella enterica</i>	-
5	EMB 5	<i>Yersinia pestis</i>	+
6	EMB 6	<i>Enterobacter gergoviae</i>	-
7	EMB 7	<i>Staphylococcus equorum</i>	+
8	EMB 8	<i>Enterobacter asburiae</i>	+
9	EMB 9	<i>Escherichia fergusonii</i>	-
10	EMB 10	<i>Escherichia coli</i>	-
11	SSA 11	<i>Salmonella enterica</i>	-
12	SSA 12	<i>Serratia fonticola</i>	+
13	SSA 13	<i>Photobacterium asymbiotica</i>	+
14	SSA 14	<i>Providencia alcalifaciens</i>	+
15	SSA 15	<i>Plesiomonas shigelloides</i>	+
16	SSA 16	<i>Enterobacter cancerogenus</i>	+
17	SSA 17	<i>Enterobacter amnigenus</i>	-

EMB, Eosine methylene blue Agar; SSA, Salmonella Shigella Agar; +, positive; -, negative.

DISCUSSION

This study has shown that coliforms are abundant on the surfaces and within the tissues of tested vegetables. The coliform counts of the vegetables were high and far above the recommended standards for ready-to-eat vegetables which should be less than 10 coliform bacteria per gram (FAO, 1979). These high counts could be attributed to the unhygienic practices in the gardens, the water used in irrigation, soil and other environmental contaminations. Also, the high population density in these vegetables are not surprising since most often, the source of water for irrigation of the gardens in these communities are usually runoff waters and sewage water from domestic sources.

High levels of bacteria and coliforms in vegetables have been reported by Aliyu *et al.* (2005) and Seow *et al.* (2012). According to Peterside and Waribor (2006), bacterial load on leafy vegetables increase with time during storage and also their exposure to contaminated water and soil. If the microbial loads on vegetables are high then they pose dangers to consumers. A potential hazard exists for persistent pathogenic bacterial populations to be transferred to harvested vegetables indirectly through contaminated water or by direct cross contamination by

proximity to animal production compounds or facilities, or from inadequately composted animal manure and biosolids (Committee on the Use of Treated Municipal Wastewater Effluents and Sludge in the Production of Crops for Human Consumption 1996; FDA 1998). Kim and Harrison (2008) demonstrated that *Escherichia coli* and *Salmonella enterica* also obtained from this study can be transferred to vegetables even through iced water.

Escherichia coli O157:H7 strains were not isolated from the sampled sites. The severe consequences of *Escherichia coli* O157:H7 if isolated can affect all age groups. The very young and very old are most vulnerable to long-term complications (Beuchat and Ryu, 1997). The haemolytic nature of coliforms isolated in this study confirms the pathogenicity of some members of this group and their potential health hazards to consumers.

In conclusion, this study has revealed that vegetables are contaminated even before harvesting. Therefore, it is advisable to properly sterilize vegetables before consumption either by steaming or by other means of sterilization. The contamination of vegetables can also be reduced by using irrigation water that meets the WHO standards ($\leq 10^3$ faecal coliform bacteria/100 ml) and also by avoiding cross contamination that may arise as a result of close proximity to animals and waste dumps.

REFERENCES

- Aliyu, Y.U., Basse, S.E. and Kawo, A.H. (2005). Bacteriological quality of vegetables sold in some shops around Kano metropolis, Nigeria. *Biological and Environmental Sciences Journal for the Tropics* **2**(1): 145 – 148
- Beuchat, L.R. and Ryu, J. (1997). Produce Handling and Processing Practices. *Emerging Infectious Diseases* **3**(4): 459-465.
- Committee on the Use of Treated Municipal Wastewater Effluents and Sludge in the Production of Crops for Human Consumption (1996). Water Science and Technology Board, Commission on Geosciences Environment and Resources, National Research Council, (1996). Public health concerns about infectious disease agents. Use of reclaimed water and sludge in food crop production. Washington, DC: National Academy Press. Pp 89-99.
- FDA (Food and Drug Administration) (1998). Center for Food Safety and Applied Nutrition. Guide to minimize microbial food safety hazards for fresh fruits and vegetables [Guidance for Industry].
- FDA (Food and Drug Administration, US) (2004). Produce safety from production to consumption: 2004 Action plan to minimize food borne illness associated with fresh produce consumption.
- Food and Agricultural Organization (FAO) (1979). Manuals of food Quality Control 4: Microbiological Analysis. FAO of the United Nations Publications, Rome, Italy. *FAO and Nutrition paper* **14**(4): C11-C12.
- Johnston, L.M., Jaykus, L., Moll, D., Martinez, M.C., Anciso, J., Mora, B. and Moe, C.L. (2005). A field study of the microbiological quality of fresh produce. *Journal of Food Protection* **68**(9): 1840-1847.
- Kim, J.K. and Harrison, M.A. (2008). Transfer of *Escherichia coli* O157:H7 to Romaine lettuce due to contact water from melting ice. *Journal of Food protection* **71**(2): 252- 256.
- McMahon, M.A.S. and Wilson, I.G. (2001). The occurrence of enteric pathogens and Aeromonas species in organic vegetables. *International Journal of Food Microbiology* **70**(1-2):155-162.
- NSW Food Authority (2007). Microbiological quality of fresh cut vegetables. NSW/FA/CP019/0903.
http://www.foodauthority.nsw.gov.au/Documents/corporate_pdf/microbiological-quality-fresh-leaves-CP019-0903.pdf ACCESSED ON 30 August 2013

- Peterside, F.N. and Waribor, O. (2006). Bacteria associated with spoilage of fluted pumpkins leaves and their effect on the chlorophyll content. *Nigerian Journal of Microbiology* **20**(1): 751 – 756.
- Seow, J., Ágoston, R., Phua, L. and Yuk, H. (2012). Microbiological quality of fresh vegetables and fruits sold in Singapore. *Food Control* **25**(1): 39-44.

IMPACTS OF SPENT ENGINE OIL ON THE GROWTH POTENTIAL OF FLUTED PUMPKIN (*Telfairia occidentalis*) AND SOIL BIOTA

Omotayo Ahmed Idowu & Akinlolu Micheal Olaniyan

Department of Zoology, University of Lagos, Akoka, Yaba, Lagos.

*ormorteey32@yahoo.com, makoniyani2002@yahoo.co.uk

ABSTRACT

Pollution is one of the major factors that has impacted the distribution and abundance of plants in nature. This engenders this research which seeks to assess the effect of spent engine oil polluted soil on the growth potential of fluted pumpkin (*T. occidentalis*) and soil biota. Five seeds of *T. occidentalis* were planted in three replicates on various concentrations of spent oil contaminated soil at 0, 10, 30, 50, 70 and 90ml/kg. The following parameters were determined; seed germination, number of leaves and leaf area, stem height, dry weight of leaf, stem and root. At termination of the experiment, earthworm count was taken. The result showed that 100% germination was obtained in the control, 10ml/kg and 30ml/kg spent oil treated soil while germination was inhibited at all other concentrations. Additionally, germination was delayed in the 50ml/kg, 70ml/kg and 90ml/kg spent oil treated soil. Also, the number of leaves, leaf area, stem height and dry weight were significantly lower $P < 0.05$ at 50, 70, and 90ml/kg spent oil treated soil when compared with the control. The number of earthworm was highest in the control and 10ml/kg treatment followed by a significant reduction in their number with increasing concentration of spent oil. The heavy metal in soil and earthworm treated with various level increased with increase in concentration of spent oil. Consequently, the study showed that soil contaminated with above 10ml/kg spent engine oil hinders the growth of *T. occidentalis* as well as normal activity of soil biota.

Keywords: *Telfairia occidentalis*, spent engine oil, seed germination, plant parameters

INTRODUCTION

The continued existence of plant species in any given habitat is only possible when the complexities of environment factors of the habitat, lies within the limit of physiological tolerance of the species. It is reported that distribution and abundance of plants in nature depends not only on efficient seed dispersal but also on the quality of the habitat considering the limits of physiological tolerance of the species (Barnard, 1964; Okunsanya, 1970). Pollution of the soil with petroleum derivatives is often observed in Municipal soils, around industrial plants and in areas where petroleum and natural gas are obtained (Adam *et al.*, 2002; Clark, 2003). Used oil is defined by the U.S. Environmental Protection Agency as "any oil that has been refined from crude oil or any synthetic oil that has been used and as a result of such use is contaminated by physical or chemical impurities (USEPA, 1996). Spent lubricant, otherwise called waste engine oil, is usually obtained after servicing and subsequent draining from automobile and generator engines and usually discarded into the environment (Anoliefo and Vwioko, 2001). Pollution from spent engine oil is one of the most cosmopolitan environmental problems and is reported to be more widespread than crude oil pollution (Odjegba and Sadiq, 2002). There are relatively large amounts of hydrocarbons in the used oil, including the highly toxic polycyclic aromatic hydrocarbons (Wang *et al.*, 2000). Also, Ekundayo *et al.* (1989) have shown that a marked change in properties occurs in soils polluted with petroleum hydrocarbons, affecting the physical, chemical and microbiological properties of the soil. Oil pollution of soil leads to build up of essential (organic C, P, Ca, Mg) and non-essential (Mg, Pb, Zn, Fe, Co, Cu) elements in soil and the eventual translocation in plant tissues (Vwioko *et al.*, 2006).

In Nigeria and some developing countries, about 20 million gallons of waste engine oil are generated annually from mechanic workshops and discharged carelessly into the environment (Faboya 1997; Adegoroye 1997). According to USEPA (1996), only 1 litre of used engine oil is enough to contaminate one million gallons of freshwater. Used engine oil also renders the environment unsightly and constitutes a potential threat to humans, animals, and vegetation (ATSDR 1997; Edewor *et al.* 2004; Adelowo *et al.* 2006).

Telfairia occidentalis is a tropical vine grown in West Africa for its leaves which is used as vegetable and edible seeds. Common names for the plant include Fluted gourd, fluted pumpkin and Ugwu. The plant is a drought tolerant, dioecious, perennial plant that is usually grown trellised. *Telfairia occidentalis* is an important leaf and vegetable indigenous to Southern Nigeria and grown in the forest zone of west and central Africa (Olaniyi and Oyerele, 2012). The leaf is of high nutritional, medicinal and industrial value, rich in protein (29%), fat (18%), minerals and vitamins (20%) (Akanbi *et al.*, 2006). The nutritional value of the seed is different from that of leaves. The protein contents of seeds and leaves are 20.5g and 2.9g, respectively (FAO, 1988). The soil biotas that are essential component of the soil involved in natural enrichment of the soil may be negatively affected when polluted with spent oil, which in turn affect the growth potential of the plant. One of such biota is the earthworm. Earthworms have great potential for use as bioassay/biomonitor organisms in studies of contaminant uptake and possess many characteristics that make it ideally suited for this purpose (Ma, 1982). Considering the extent of pollution of the soil with spent engine oil, this research seeks to study the impacts of spent engine oil contaminated soil on the development of *Telfairia occidentalis* and soil biota.

METHODS

Study Site

The study was carried out at the Botanical Garden of the University of Lagos, Nigeria.

Sources of Experimental Material

The seeds of *Telfairia occidentalis* used in the study were obtained from vegetable leaf sellers at Oyingbo market, Ebute Metta, Lagos, Nigeria. The source of spent oil used for the study was obtained from AP filling station at the University of Lagos, Akoka, Lagos. The soil sample was collected from the rich alluvial area of the botanical garden of the University of Lagos.

Soil Treatment with Spent Oil

Eighteen (18) four litre pots were filled with 2.5kg treated soil. Three pots each were treated with 25cc, 75cc, 125cc, 175cc, 225cc which represent 10, 30, 50, 70 and 90ml/kg contamination respectively. The pots were divided into six (6) groups, (A-F) with 3 pots in each group labeled as 1, 2, 3 i.e each group having 3 replicates. Group A represent the control with no spent engine oil while group B, C, D, E and F were treated with 10, 30, 50, 70 and 90ml/kg spent engine oil respectively. The soil was thoroughly mixed with the spent oil using hand trowel. The soil was left for six days before planting of seeds. Each pot was watered daily at 6.00 GMT.

Determination of Seed Germination

Five seeds of *Telfairia occidentalis* were sown into each of the pots. The number of seedlings that emerged from each bucket was counted on odd days from the 7th day till the 21st day after planting and the percentage germination was calculated using the formula.

$$\% \text{ germination} = \frac{\text{Number of seedlings that emerged from soil}}{\text{Number of seeds sown}} \times 100$$

Determination of Plant Parameters

The number of leaves, leaf area and stem height were observed and recorded weekly for 6 weeks after planting. The plant height was measured with meter rule. The leaf area of the plant is the product of the length and breadth of the leaf measured with the meter rule according to (Pearcy *et al.* 1989).

Dry Weight Analysis

Dry weight analysis was carried out by destructive sampling method as adapted by Ekpo and Odu (2000).

Determination of Heavy Metal Concentration in Soil

The soil was analyzed for heavy metal content by first ashing the soil and then analyzed by flame atomic absorption spectrophotometer. Heavy metal concentration analysis in earthworm was also carried out as above.

Statistical Analysis

Data generated were analyzed for Analysis of variance (ANOVA) using graph pad prism software. Dunnett multiple comparison test was further used to determine significant difference ($P < 0.05$) among the mean values.

RESULTS

Germination Study

Germination was generally delayed as the level of spent oil increased in the soil, however there was no difference in germination of seed between the lowest treatment of 10ml/kg and control in which 100% germination was obtained. Also, 100% germination was obtained in the 30ml/kg soil treatment, however, germination of the seed did not take place until day 11, Table 4.1. Additionally, as the level of spent oil increased there was a corresponding decrease in the percentage germination, where only 60% germination was recorded in the 50ml/kg treatment and 40% occurred in the 70 and 90ml/kg soil treatment. Germination of seeds occurred in the control and 10ml/kg concentration on the 7th day while in the 30ml/kg and 50ml/kg soil treatment, germination did not occur until the 11th day. In the 70 and 90 ml/kg soil treatment, germination was delayed until the 17th and 15th day respectively (Table 4.1).

Growth Parameters

There was a corresponding decrease in mean number of leaves, mean leaf area and mean stem height with increasing level of spent oil concentration in the soil. There was no development in *T. occidentalis* in the soil treated with the highest concentration (Table 4.2). However, there was no difference in the number of leaves between the control and the lowest concentration treatment but leaf area between the control and lowest treatment was significantly different. The leaf area in the control was 1.6 times higher than leaf area in the 10ml/kg soil treatment. There was significant difference in the leaf area at $P < 0.05$ between the control and all other concentrations. Considering stem height, there was no significant difference between the control and 10ml/kg and 30ml/kg soil treatment, contrary to the difference between the control and other higher concentrations which was significant.

Dry Weight Study

The mean dry weight of leaf, stem and root showed no significant difference between the control and 10ml/kg spent oil treatment. However as concentration of spent oil increases there was a corresponding decrease in the dry weight of leaf, stem and root. (Table 4.3)

Heavy Metal Component of Soil Treated with Spent Oil

Table 4.4 revealed that the heavy metal concentration increased with increase concentration of spent oil in the soil. In the 90ml/kg soil treatment Cu, Fe, and Pb are about 2times, 2.5times, and 3times higher respectively in concentration than the 10ml/kg treatment. Generally Zn was highly concentrated in soil as concentration of spent oil increased in the soil, Zn concentration in the 90ml/kg concentration was 5times that of the 10ml/kg concentration.

Earthworm Study

Higher numbers of earthworm were found in the control and 10ml/kg treatment. There was however a decrease in number of earthworm thereafter with increase in concentration of spent oil (Table 4.5). No earthworm was seen in the 70ml/kg. There was no recognisable trend in the concentration of heavy metal in the earthworm with increase in spent oil concentration in soil.

DISCUSSION

The effect of spent oil on growth potential of fluted pumpkin (*T. occidentalis*) showed that germination potential of the plant was inhibited and there was delayed emergence especially in the 50, 70 and 90ml/kg spent oil treated soil. The poor emergence obtained at higher contamination levels of the soil may be attributed to poor aeration of the soil as insufficient aeration and reduced soil microbial activity are associated problems of soil polluted with spent engine oil (Udo and Fayemi, 1975; Anoliefo and Vwioko, 1995). In addition, the inhibition of germination especially at the 90ml/kg treatment level may be due to absorption of oil by the seeds, which made the seeds swollen and slimy, as observed when the ungerminated seeds were dugged out from the treated soil. The findings agrees with the work of Amakin and Onofeghara (1978) who reported that crude oil affected the germination of *Zea mays* and *Capsicum frutescens* and noted a significant decrease in the rate of germination. They attributed the inhibition primarily to the physical surface characteristics of the oil, which reduced contact of the seeds with water and oxygen.

The study also revealed that the mean number of leaves, mean leaf area of *T.occidentalis* (Table 4.2) were significantly affected ($P<0.05$) especially at the 50, 70, 90ml/kg when compared with the control and 10ml/kg treatment. There was marked impairment in growth and development of the plant, chlorosis of the leaves, stunted growth and wilting of the plant with increase in concentration. Dwarfing of plant became pronounced with increase in concentration of spent oil in the soil. Some of this symptoms have been associated with the presence of heavy metals especially Zn in spent oil contaminated soil by Lepp (1981).

Also, dry matter of the leaf, stem and root at higher levels of contamination was significantly ($P>0.05$) lower compared to the control and the 10ml/kg spent oil treatment. There was continuous reduction in leaf number with increase in concentration of spent oil contamination. The reduction in dry matter at higher levels of contamination may be attributed to accumulation of heavy metals present in spent engine oil (Wang, 2002) which in turn affect metabolic processes in the plant (Prasad and Prasad, 1987).

Additionally, the 10ml/kg spent oil treatment had better growth than the control (uncontaminated soil). This is because at lower level of contamination, the degradation capacity of soil biota matches up with the available spent oil in the soil, thereby enhancing the fertility of the soil with the degraded spent oil which now acts as nutrient rather than pollutant as reported by Odu (1981).

The number of earthworm also decreased with increase in concentration of spent oil contamination (Table 4.5). The earthworm cast showed more activity of earthworm in the control than in other concentrations. The reduction in number of earthworm and absence of other soil biota is due to poor aeration of the soil. The earthworms also accumulated a certain level of

heavy metal (Table 4.5) in their tissue, though the level was not significant when compared with other treatments. Ireland (1979) reported that earthworms are known to suffer significant morbidity responses and direct mortality from exposure to organochlorides and heavy metals. Also, they may accumulate the residues in their tissues even above the amount in the soil they inhabit (Curry, 1994). Heavy metals have been confirmed to affect sexual development and cocoon production (Cikutovic et al., 1993). Specifically, heavy metals such as zinc, lead, cadmium, manganese and high concentration of sodium chloride as metal compounds affect reproduction in earthworms (Fisher et al., 1997).

The negative impacts of spent oil on the growth potential of fluted pumpkin plants may have also resulted from increase in temperature due to the dark nature of the contaminated soils. It was observed that the contaminated soils were darker than the control, and dark soils absorb more heat making them unsuitable for optimum plant growth. (Donahue *et al.*, 1990)

Reasonably, contamination of soil by spent oil at lower concentrations (10ml/kg and below) are beneficial to both plants and soil biota, specifically the test crop *T. occidentalis*. Soil organism inhabiting habitats contaminated with above 10ml/kg were negatively affected. Consequently, the need to encourage the protection of our environment and farmlands against indiscriminate disposal of high concentrations of spent oil. Therefore, it is necessary for all stakeholders to guard against unwarranted pollution of our environment with spent engine oil and to promote a healthy environment for sustainable agricultural yield.

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REFERENCES

- Adelowo, O. O., Alagbe, S. O. and Ayandele, A. A. (2006). Time-dependent stability of used engine oil degradation by cultures of *Pseudomonas fragi* and *Achromobacter aerogens*. *African Journal of Biotechnology*, **5**(24), 2476–2479.
- Adegoroye, G. (1997). Environmental considerations in property design, urban development and renewal. In O. Akinjide (Ed.), *Dimensions of environmental problems in Nigeria* Washington: Friedrich Ebert Foundation. pp. 12–25.
- Adam G, Gamoh K, Morris D.G, Duncan H (2002). Effect of alcohol addition on the movement of petroleum hydrocarbon fuels in soil. *Science Total Environment*. **286**(1/3): 15-25.
- Akanbi W.B, Adebooye C.O, Togun A.O, Ogunrinde J.O and Adeyeye S.A (2006). Growth, herbage, seed yield and quality of *Telfairia occidentalis* quality as influenced by cassava peel compost and mineral fertilizer. *World Journal of Agricultural Sciences*, **3**(4): 508-516.
- Amakin J.O and Onofeghara F.A (1978). Effect of crude oil pollution on the germination of *Zea mays* and *Capsicum frutescens*. Ser. *Environmental Pollution* **35**: 157-167.
- Anoliefo, G.O. and Vwoko, D.E. (1995). Effect of spent lubricating oil on the growth of *capsium annum* and Remedial response at hazardous wastes sites. *lycopersium*. *Pollution*, **88**: 361-364.
- ATSDR (Agency for Toxic Substances and Disease Registry), (1997). Toxicology profile for used mineral based crankcase oil. Department of health and human Services, Public health Service Press, Atlanta, GA, USA.
- Barnard C (1964). *Grasses and grasslands*, Macmillan Company, New York. 269pp.
- Clark C.S (2003). Field detector evaluation of organic clay contaminated with diesel *Environment Florescence*, **4**(3): 167-173.

- Cikutovic, M. A. *et al*, (1993) Spermcount in earthworms (*Lumbricus terrestris*) as a biomarker for environmental toxicology: Effects of cadmium and chlordane. *Environmental Pollution*, **81**, 123-125.
- Curry, J. P (1994): Grassland Invertebrates: Ecology, influence on soil fertility and effects on plant growth. Chapman and Hall, London, Glasgow and New York. p. 437.
- Donahue R. L, Miller R.W, Shickluna J. C (1990). An introduction to soils and plants growth. Prentice-Hall Inc., U.S.A. 667 pp.
- Edewor, T. I., Adelowo, O. O., and Afolabi, T. J. (2004). Preliminary studies into the biological activities of a broad spectrum disinfectant formulated from used engine oil. *Pollution Research*, **23**(4), 581–586.
- Ekundayo, J A; Aisueni, N; Benka-Coker, M O (1989). The Effects of drilling fluids in some waste and burrow pits in western operational areas of Shell Petroleum Development Company of Nigeria Limited on the soil and water quality of the areas. Environmental Consultancy Service Group, Consultancy Services Unit, University of Benin, Benin City, Nigeria.
- Ekpo M.A. and Odu C.T.I. (2000). Effect of drilling mud additives on dry matter production and yield of maize (*Zea mays*). *Journal Applied Science*. **4**:1885-1894
- Faboya, O. O. P. (1997). Industrial pollution and waste management. In O. Akinjide (Ed.), Dimensions of environmental problems in Nigeria (pp. 12–25). Washington: Friedrich Ebert Foundation.
- FAO (1988). Traditional Food Plant. Food and Agricultural Organization of the United Nations, Rome, Italy.
- Fisher, E., Molnar L. and Edwards C. A.: (1997). Growth and reproduction of *Eisenia foetida* (Oligochaeta, Lumbricidae) in semi natural soil containing various metal chlorides. *Soil Biological Biochemical*, **29**, 667-670
- Ireland, M. P. (1979): Metal accumulation by earthworms *Lumbricus rubellus*, *Dendrobaena veneta* and *Eisenia tetraedra* living in heavy metal polluted sites. *Environmental Pollution*, **13**, 66-69.
- Lepp, N W (1981). Effect of heavy metals pollution on plants. Applied Science Publishers Ltd., England. 352 pp.
- Ma W.C., (1982). The influence of soil properties and worm-related factors on the concentration of heavy metals in earthworms. *Pedobiologia* **24**, 109-119.
- Odu C.T.I, Babalola O, Udo E.J, Ogunkunle A.O, Bakare T.A, Adeoye G.O (1986). Laboratory manual for agronomic studies in soil, plant and microbiology. Department of Agronomy, University of Ibadan, Ibadan, Nigeria.
- Odjegba, V.J. and A.O. Sadiq, (2002). Effect of spent engine oil on the growth parameters, chlorophyll and protein levels of *Amaranthus hybridus* L. *The Environmentalist*, **22**: 23-28.
- Okonokhua B.O, Ikhajiagbe B., Anoliefo G.O and Emede T.O (2007). The Effects of spent engine oil on soil properties and growth of Maize (*Zea mays* L.). *Journal of Applied Science and Environmental Management*, **11** (3) 147 – 152
- Okunsanya O.T (1970). Comparative ecology studies of *Paspalum Vaginatium* and *Paspalum orbiculare* in Nigeria. *Journal of Tropical Ecology* **6**: 103- 114
- Olaniyi J.O and Oyerele T.A (2012). Growth, yield and nutritional compositions of Fluted Pumpkin (*Telfairia Occidentalis*) as affected by fertilizer types in Ogbomoso, South West Nigeria. *Bulletin of Environment, Pharmacology and Life Sciences*, **1**(9): 81 – 88
- Pearcy R.W, Ehleringer J.R, Mooney H and Rundel P.W (1989). Plant physiological ecology: Field methods and instrumentation. Chapman and Hall, New York. pp. 301-306.
- Prasad, D.D.K and Prasad, A.R.K (1987). Ecological aspect of metal toxicity. *Journal of Plant Physiology*, **127**: 241-249.

- Udo, E.J. and Fayemi A.A.A., (1975). The effect of oil pollution on soil germination, growth and nutrient uptake of corn. *Journal of Environmental Quality*, **4**: 537-540
- USEPA. (1996). Recycling used oil: What can you do? Cooperation Extension Services ENRI, 317, 1-2.
- Vwioko, D E; Anoliefo G O and Fashemi, S D (2006). Metals concentration in plant tissues of *Ricinus communis* L. (Castor Oil) grown in soil contaminated with spent lubricating oil. *Journal of Applied Science and Environmental Management*, **10**: 127-134
- Wang J., Jia C.R., Wong C.K and Wong P.K, (2000). Characterization of polycyclic aromatic hydrocarbon created in lubricating oils. *Water, Air and Soil Pollution*, **120**: 381-396.
- Wang Q.R, Liu X.M, Cui Y.S, Dong Y.T and Christie P (2002). Responses of legume and non-legume crop species to heavy metals in soils with multiple metal contamination. *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances and Environmental Engineering*, **37**:611-621

TABLES

Table 4.1: Daily mean germination and percentage germination of *T.occidentalis* at various levels of spent oil contamination in soil.

Conc/Days	Day 7	Day 9	Day11	Day1 3	Day1 5	Day1 7	Day1 9	Day2 1	T.ger m	Germ %
Control	1	2	2	0	0	0		0	5	100
10ml/kg	1	0	2	0	2	0	0	0	5	100
30ml/kg	0	0	2	0	1	2	0	0	5	100
50ml/kg	0	0	1	0	1	1	0	0	3	60
70ml/kg	0	0	0	0	0	1	1	0	2	40
90ml/kg	0	0	0	0	1	0	0	1	2	40

Table 4.2: Mean number of leaves, leaf area and stem height of *T.occidentalis* in soil treated with different concentrations of spent oil for seven weeks after planting.

Concentration(ml/kg)	Mean Number of Leaves	Mean Leaf Area	Mean Stem Height
Control	14.5±4.16 ^b	93.0± 4.43 ^c	119.0±15.70 ^b
10	14.6±4.62 ^b	36.0±18.34 ^b	137.3±58.33 ^b
30	11.0±1.00 ^a	53.9± 8.05 ^b	73.6± 5.69 ^b
50	8.6 ±2.52 ^a	39.0± 9.60 ^a	58.3± 12.01 ^a
70	6.6± 2.80 ^a	17.8± 2.44 ^a	31.0 ±9.64 ^a
90	5.0± 0.00 ^a	5.0± 3.24 ^a	5.0± 4.20 ^a

Mean followed by same alphabet are not significant at P<0.05

Table 4.3: Mean percentage of dry weight of stem, leaf and roots of *T.occidentalis* at the end of planting/harvesting.

Concentration(ml/kg)	Stem	Leaf	Root
Control	19.4±1.72 ^c	20.2±1.60 ^c	16.9±0.99 ^d
10	19.9±2.13 ^c	20.9±2.33 ^c	16.8±3.11 ^d
30	12.1±1.20 ^b	13.5±1.09 ^b	11.1±1.22 ^c
50	10.5±0.90 ^b	12.3±0.92 ^b	11.4±0.93 ^c
70	5.6±1.40 ^a	4.3±1.44 ^a	2.8±1.41 ^b
90	3.2±1.14 ^a	2.1±1.41 ^a	0.91±1.01 ^a

Mean followed by same alphabet are not significant at P<0.05

Table 4.4: Total hydrocarbon content and heavy metals concentration in soil treated with spent oil.

Contamination (ml/kg)	Total Hydrocarbon Content %	Cu (Mg/kg)	Fe (Mg/kg)	Pb (Mg/ kg)	Zn (Mg/kg)
Control	0.2523	0.73	1.28	0.34	1.64
10	1.6756	2.38	2.42	1.56	5.73
30	2.0221	2.74	3.86	2.21	3.82
50	3.1145	3.25	4.11	2.82	18.54
70	7.1305	3.86	4.79	3.35	22.68
90	10.0786	4.32	6.56	5.42	27.30

Table 4.5: Heavy metal concentration and number of earthworm in soil.

Concentration	Number of Earthworms	Cu (Mg/Kg)	Fe (Mg/Kg)	Pb (Mg/Kg)	Zn (Mg/Kg)
Control	6	0.02	0.03	0	0.03
10	6	0.03	0.05	0	0.09
30	3	0.07	0.12	0.02	0.13
50	2	0.08	0.14	0.01	0.014
70	0	0	0	0	0
90	1	0.12	0.16	0.03	0.17

SYSTEMATIC IDENTIFICATION OF AFRICAN SAPINDACEAE USING DNA BARCODING

Onuminya, T.O. & Ogundipe, O.T.

Molecular Systematics Laboratory, Department of Botany,
University of Lagos, Akoka, Lagos, Nigeria.
topssy4u@yahoo.co.uk

ABSTRACT

Sapindaceae Jussieu is a family of flowering plants in the order Sapindales. They exist as trees and shrubs, and tendril-bearing vines with about 140-150 genera and 1400-2000 species worldwide. They are economically, medicinally and aesthetically useful. This research aimed at exploring the diversity of Sapindaceae in western and central Africa with particular emphasis on identification of the plant samples as well as generation of DNA barcodes with a view to sharing the DNA barcode sequence in a public database. This was achieved following standard protocols. Extracted DNA samples (119) were deposited at the DNA Bank of the Royal Botanic Gardens, Kew, Richmond and voucher specimens were deposited at the University of Lagos Herbarium, Lagos, Nigeria. Silica gel dried specimens' yielded good quality DNA unlike the old dried herbarium leaf samples. DNA samples were sent to International Barcode of Life (IBOL) Centre in Guelph, Canada for analysis of the barcode region and sixty-nine (69) DNA barcodes were generated. Barcode data which was hinged on matK and rbcL sequence data have been deposited at the Barcode of Life database (BOLD) website and GenBank for public use. This research can be seen as a basis for further taxonomic research on the family Sapindaceae especially in Africa.

Keywords: *Africa, Bio-conservation, DNA barcodes, Identification, Sapindaceae.*

INTRODUCTION

The biological diversity of each country is a valuable and vulnerable natural resource while knowledge about biodiversity and the ability to identify organisms that come with it are global public goods e.g. controlling Agricultural pest; identify disease vectors and environmental sustainability and many other Millennium Development goals. Africa's biodiversity is one of the most extraordinary in the world, but also one of the most threatened by human activities (population growth, over-exploitation, logging) and global change (desertification, climatic warming). Among the first steps towards protecting and benefiting from biodiversity are sampling, identifying and studying biological specimens. While biodiversity is disappearing alarmingly fast, there have also been fantastic technological developments that can help reverse biodiversity loss, one of these is DNA barcoding. 'DNA barcoding' is a revolutionary diagnostic technique in which short DNA sequence is used for species identification (Powell *et al.*, 2008). It is increasingly being tested in many areas as a cost-effective tool for identifying and regulating agricultural pests, invasive and disease-carrying species, trade and sale of endangered species, and many other species of concern to governments and society. The goal of barcoding is that anyone, anywhere, anytime be able to identify quickly and accurately any species whatever its condition (Stoeckle *et al.*, 2005). This technology is being promoted by the International Consortium for Barcoding of Life (CBOL) to enable the rapid and inexpensive identification of the estimated 10 million species on earth. It has enormous benefits and brings huge gain to countries rich in biodiversity including: rapid species identification, including any life stage or fragment, providing insight into the diversity of life, quick and cheap identification of specimens as well as ability to control the movement of species across national borders (Stoeckle *et al.*, 2005).

Sapindaceae is a family of flowering plants in the order Sapindales. They exist as trees and shrubs, and tendril-bearing vines widely distributed throughout the warm sub-tropical and tropical regions of the world. Sapindaceae is economically, medicinally and aesthetically useful (Odugbemi and Akinsulire, 2006; Sofidiya *et al.*, 2007, 2008; Adesegun *et al.*, 2008; Muanya and Odukoya, 2008; Pendota *et al.*, 2008; Antwi *et al.*, 2009; Ripa *et al.*, 2010). Although members of the family Sapindaceae have been recorded to be widely distributed in Africa, their occurrence is being threatened by high rate of deforestation and agricultural practices leading to loss of forest and threatened status of the family as recorded in the IUCN R.L. (2008). Members of Sapindaceae are known to be difficult to identify, particularly when they are sterile, which makes them an ideal model group in which to test DNA barcoding techniques. Moreover, the family has problems of synonymy, taxa misidentification, doubtful specific status and grouping dissimilar taxa in the same higher taxonomic rank (Buerki *et al.*, 2009). Hence, the aim of this research is to explore the diversity of Sapindaceae in western and central Africa with particular emphasis on identification of the plant samples as well as generation of DNA barcodes with a view to sharing the DNA barcode sequence in a public database.

METHODS

Study Area

Five African countries were visited in this study namely: Nigeria, Ghana, Ethiopia, western Cameroon and Madagascar.

Taxon Sampling

Species names, voucher information, and GenBank accession numbers for all sequences are provided in table 1. The sampling strategy encompasses the majority of subfamilies, tribes and genera of the family as recognized by the existing classifications of Radlkofer (1933), Müller and Leenhouts (1976) and Thorne (2007). In-group sampling comprised 120 specimens representing 40% of the generic diversity while the family Anacardiaceae (*Sorindeia* sp.; defined as outgroup in all analyses; Savolainen *et al.*, 2000a; Muellner *et al.*, 2007) and Simaroubaceae (*Harrisonia abyssinica*) were included as out-groups. Herbarium, fresh and silica-gel dried samples were used for the study. The national herbaria as well as local herbaria in the study area were visited to examine and collect samples. Silica-gel dried samples (Chase and Hills, 1991) were collected in the field by the authors and complemented with materials from the DNA banks of the Royal Botanic Gardens, Kew (London, UK). Preliminary identification in the field was achieved with the aid of floras including that of Hutchinson and Daziell (1958), Fouilloy and Hallé (1973) and Cheek *et al.* (2000). Voucher specimen were deposited at the University of Lagos herbarium while further authentication was carried out at the Forestry Herbarium, Ibadan.

DNA Extraction and Quantification

Total DNA was extracted from herbarium or silica dried leaf material (0.1–0.3 g) using the 2-cetyltrimethylammonium bromide (CTAB) procedure of Doyle and Doyle (1987) with minor modifications (see Muellner *et al.*, 2005) followed by additional purification using a caesium chloride/ethidium bromide gradient (1.55 g/ml) and a dialysis procedure. The quality of the DNA samples obtained was checked on 1% agarose gel stained with 10mg/ml ethidium bromide and run on 0.5x TBE (Tris Borate EDTA) buffer at 75volts for 1 h 30 mins. This is then viewed with ultraviolet (UV) trans-illuminator and photographed with Polaroid film. Furthermore, the concentration and absorbance of the DNA samples were measured using an eppendorf biophotometer.

PCR Amplification

Two coding plastid DNA regions (matK and rbcL) were amplified. Primers used include 390F and 1326R for maturase K (matK) (specific primer for the Dodonaeoideae was designed by Harrington *et al.*, 2005) as well as 1F and 1460R for ribulose 1,5, biphosphate carboxylase large subunit (rbcL) (Savolainen *et al.*, 2000b). Also the fragment size amplified was between 870 – 910 bp for matK and 1436 – 1460 bp for rbcL. Amplification of selected regions were achieved in a 25 µl reaction mixtures containing 22.5 µl PCR premix, 0.5 µl BSA (bovine serum albumin), 0.5 µl forward primer, 0.5 µl reverse primer and 1.0-2.0 µl total genomic DNA. The amplification of the matK region was improved by the addition of 4% DMSO in the total volume of the PCR mix. Polymerase chain reaction (PCR) amplification was carried out in a Gene Amp[®] PCR System 9700 thermal cycler (Applied Biosystems Inc. (ABI), Foster City, U.S.A.) using the following programme: initial denaturation for 3 min at 94° C followed by one cycle of denaturation for 1.00 min at 94° C, followed by 35 cycles of annealing for 45 s at 52° C and extension for 2 min 30 s at 72° C. The amplification was completed by holding the reaction mixture for 7 min at 72° C to allow complete extension of the PCR products and a final hold of 4° C. PCR products were visualized on Agarose gel followed by purification on QIA quick silica column (QIAGEN Ltd) following manufacturers protocol.

Sequence of Barcode Region

DNA sequencing was carried out following a modification dideoxy cycle sequencing with dye terminators (Sanger *et al.*, 1977). Cycle sequencing reactions was achieved in a 10 µl reaction mixtures containing 0.5 µl pink juice (Big Dye Terminator, Applied Biosystems Inc.), 3.0 µl 5X sequencing buffer (BioLoin), 0.75 µl primer (1:10 dilution: forward or reverse for each primer pair) and 40 ng cleaned PCR product, made up to 10 µl with sterile distilled water. The amplification of the matK region was improved by the addition of 4% dimethyl sulfoxide (DMSO) in the total volume of the sequencing mix. Cycle sequencing was carried out in a Gene Amp[®] PCR System 9700 thermocycler (Applied Biosystems Inc.) using the following programme: initial denaturation for 30 s at 95° C followed by one cycle of denaturation for 1.00 min at 95° C, annealing for 30 s at 55° C and extension for 60 s at 72° C this was ran for 30 cycles and the cycle was completed by holding the reaction mixture for 7 min at 72° C to allow complete extension of the PCR products with a final hold of 4° C. The products were purified using ethanol precipitation to remove any excess dye terminator. Cleaned cycle sequencing products were then directly sequenced on a 3130 *xl* Genetic Analyzer (Applied Biosystems Inc.). Purified cycle sequencing products were sequenced in an automated sequencer (ABI PRISM[®] 3730 DNA Analyzer) following the manufacturer's instructions.

Sequence Alignment and Analyses

The program Sequencher version 4.5 was used to assemble complementary strands and verify software base-calling and the bases were aligned manually in PAUP* v. 4.0b1 (Swofford 1998). Cladistic analyses were performed using the parsimony algorithm of the software package PAUP* version 4.0b10. The partition homogeneity test was performed using heuristic search methods and 1000 replications, simple stepwise addition, tree bisection-reconnection (TBR) branch swapping, and MULTREES on (Keeping multiple shortest trees), but holding only 10 trees per replicate to reduce the time spent in swapping on large numbers of suboptimal trees. After the 1000 replicates, the shortest trees from the first round were used as starting trees for a search with a tree limit of 10,000. Robustness of clades was estimated using the bootstrap (Felsenstein, 1985) involving the use of 1000 replicates with simple sequence addition and SPR branch swapping. For visual assessment of the data sets, the bootstrap trees were considered incongruent only if they displayed “hard” (i.e. with high bootstrap support > 85%) rather than “soft” (with low bootstrap support < 85%) incongruence (Seelanan *et al.*, 1997; Wiens, 1998).

The following arbitrary scale for describing bootstrap support was applied: 50 - 74% weak, 75 - 84% moderate and 85 - 100% high. DNA barcoding of samples was carried out at the International Barcode of Life (IBOL) Centre in Guelph, Canada using *matK* and *rbcL* primers.

RESULTS

Extracted DNA samples (119) were deposited in the DNA bank at the Royal Botanic Gardens Kew. A few taxa could not be amplified for *matK* and *rbcL* due to low DNA yield during extraction however seventy samples were successfully amplified during PCR. Of the seventy (70) DNA samples, thirty-four (34) DNA barcode sequences were generated from the *matK* region while thirty-five (35) barcode sequences were generated from the *rbcL* region. In total, sixty-nine (69) DNA barcode sequences were generated and deposited at the Genbank. The DNA barcode sequences were 833bp long in the *matK* region and 555bp in the *rbcL* region.

From these sequences, phylogenetic trees were generated to show the relationships existing between each taxa in the family Sapindaceae and closely related taxa of family Fabaceae; this relationship was the same irrespective of the barcode region i.e. either *matK* or *rbcL*. Phylogenetic analysis of the samples with closely related taxa of family Fabaceae revealed that *Allophylus conraui*, *Allophylus griseotomentosus*, *Cardiospermum corindum*, *Chytranthus carneus* and *Deinbollia kilimandscharia* are more distantly related to *Lessertia* species than other members of the family Sapindaceae (Fig. 1 and 2). Also, phylogenetic analyses revealed that Sapindaceae is monophyletic but paraphyly and polyphyly were shown at subfamilial and tribal levels. The recent suggestion on the taxonomic position of *Xanthoceras sorbifolia*, Aceraceae and Hippocastanaceae as belonging in the family is corroborated (Figure 3). The family can be subdivided into four (4) subfamilies: Sapindoideae, Dodonaeoideae, (57% bp) Hippocastanoideae (66% bp) (including Aceraceae) and a monotypic Xanthoceroideae. *Xanthoceras* is sister to the rest of the family while Hippocastanoideae is sister to subfamily Sapindoideae and Dodonaeoideae. A high degree of paraphyly and polyphyly is also highlighted at subfamilial level, especially in subfamilies Dodonaeoideae and Sapindoideae.

DISCUSSION

Although members of the family Sapindaceae have been recorded to be widely distributed in Africa, their occurrence is being threatened by high rate of deforestation and agricultural practices leading to loss of forest and threatened status of the family as recorded in the IUCN R.L. (2008). However, our sampling revealed that there are 28 genera and 119 species in Africa in contrast to the twenty four (22) genera recorded by Burkhill (2000). The other six genera include *Aphania*, *Atalaya*, *Ganophyllum*, *Haplocoelum*, *Laccodiscus* and *Litchi*. Taxa sampling within Sapindaceae was difficult especially as DNA was extracted from herbarium materials. Though the herbarium materials were readily available, the problem was how they were preserved and what kinds of chemicals were present in the samples. The method of plant collection and duration of drying the material is important for the survival of the DNA. Some of the materials were oven dried and the old material had been exposed to pesticides, these could have degraded the quality of DNA. Nevertheless, good quality DNA was successfully extracted from 48% of the samples most of which were silica gel dried samples. This study supports previous studies by Harrington *et al.* (2005) and Buerki *et al.* (2009) on a broadly defined Sapindaceae including the family Aceraceae and Hippocastanaceae. Also in the *matK* gene analysis, *Xanthoceras* was found to be sister to all other Sapindaceae. While Sapindaceae occurs as a monophyletic family, paraphyly is observed at subfamilial level and this supports previous reports given by Harrington *et al.* (2005) and Buerki *et al.* (2009). Also, *Laccodiscus* species was shown to be more closely related to one of the out-group taxa from the family Anacardiaceae – *Sorindea* species suggesting misidentification of the sample and this was supported with 56% bp. Generally, the *matK* gene gave a better resolution in identification of members of sapindaceae

and this supports the report of Kress and Erickson (2007) that *matK* is one of the most rapidly evolving plastid coding regions and it consistently showed high levels of discrimination among angiosperm. A particular strength of the barcoding approach is that these identifications can be made with small amounts of tissue from sterile, juvenile or fragmentary materials from which morphological identifications are difficult or impossible (Little and Stevenson, 2007). In addition, it is important to emphasize that the discriminatory power of this standard barcode will be higher in situations that involve geographically restricted sample sets, such as studies focusing on the plant biodiversity of a given region or local area (Valentini *et al.*, 2008). A future challenge for DNA barcoding in plants is to increase the proportion of cases in which unique species identifications are achieved.

CONCLUSIONS

This work is probably the first record of DNA Barcoding of Sapindaceae in Africa and this can be seen as a major contribution to the TREEBOL Africa and Genbank.

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REFERENCES

- Adesegun, S.A., Coker, H.A.B. and Hamann, M.T. (2008). Antifungal triterpenoid saponins from *Lecaniodiscus cupanioides*. *Research Journal of Phytochemistry* **2**: 93-99.
- Buerki, S., Forest, F., Acevedo-Rodríguez, P., Callmander, M.W., Nylander, J.A.A., Harrington, M., Sanmartín, I., Küpfer, P., and Alvarez, N. (2009). Plastid and nuclear DNA markers reveal intricate relationships at subfamilial and tribal levels in the soapberry family (Sapindaceae). *Molecular Phylogenetics and Evolution* **51**: 238-258.
- Chase, M.W. and Hills, H.H. (1991). Silica-gel – an ideal material for field preservation of leaf samples for DNA studies. *Taxon* **40**: 215-220.
- Cheek, M., Onana, J.M. and Pollard, B.J. (2000). *The Plants of mount Oku and the Ijim ridge, Cameroon: A Conservation Checklist*. Royal Botanic Gardens, Kew, London. 211pp.
- Doyle, J.J. and Doyle, J.L. (1987). A rapid DNA isolation procedure for small quantities of fresh leaf tissue. *Phytochem. Bull. Bot. Soc. Amer.* **19**: 11-15.
- Felsenstein, J. (1985). Confidence limits on phylogenetic: an approach using the bootstrap. *Evolution* **39**: 783-791.
- Fouilloy, R. and Hallé, N. (1973). *Flora of Cameroon: Sapindaceae*. Volume 16. National Museum of Natural History, Paris. 202pp.
- Harrington, M.G., Edwards, K.J., Johnson, S.A., Chase, M.W., Gadek, P.A. (2005). Phylogenetic inference in Sapindaceae sensu lato using plastid *matK* and *rbcl* DNA sequences. *Systematic Botany* **30**: 366–382.
- Hutchinson, J. and Daziel, J.M. (1958). *Flora of West Tropical Africa*. Volume 1, Part 2. Crown Agents for Oversea Government and Administrations, Millbank, London. 828pp.
- IUCN (2008). The IUCN red list of threatened species. International Union for Conservation of Nature and Natural Resources. <http://www.iucnredlist.org/>.
- Kress, W.J. and Erickson, D.L. (2007). A two-locus global DNA barcode for land plants: The coding *rbcl* gene complements the non-coding *trnH-psbA* spacer region. *PLoS ONE* **2**:e508.
- Little, D.P. and Stevenson, D.W. (2007). A comparison of algorithms for the identification of specimens using DNA barcodes: Examples from gymnosperms. *Cladistics* **23**: 1–21.
- Müller, J. and Leenhouts, P.W. (1976). A general survey of pollen types in Sapindaceae in relation to taxonomy. In: Ferguson, I.K. and Müller, J. (Eds.) *The Evolutionary Significance of the Exine*. Academic Press, London. Pp. 407–445.

- Muellner, A.N., Samuel, R., Chase, M.W., Pannell, C.M. and Greger, H. (2005). *Aglaia* (Meliaceae): an evaluation of taxonomic concepts based on DNA data and secondary metabolites. *American Journal of Botany* **92**: 534–543.
- Muellner, A.N., Savolainen, V., Samuel, R. and Chase, M.W. (2006). The mahogany family “out-of-Africa”: divergence time estimation, global biogeographic patterns inferred from plastid rbcL DNA sequences, extant, and fossil distribution of diversity. *Molecular Phylogenetics and Evolution* **40**: 236–250.
- Muellner, A.N., Vassiliades, D.D. and Renner, S.S. (2007). Placing Biebersteiniaceae, a herbaceous clade of Sapindales, in a temporal and geographic context. *Plant Systematics and Evolution* **266**: 233–252.
- Muanya, C.A. and Odukoya, O.A. (2008). Lipid peroxidation as index of activity in aphrodisiac herbs. *Journal of Plant Science* **3**: 92-98.
- Odugbemi, T. and Akinsulire, O. (2006). Medicinal plants according to Family names. In: Odugbemi, T. (Ed.) *Outlines and Pictures of Medicinal Plants from Nigeria*. University of Lagos Press, Akoka, Yaba, Nigeria. Pp 117-161.
- Pendota, S.C., Grierson, D.S. and Afolayan, A.J. (2008). An ethnobotanical study of plants used for the treatment of eye infections in the Eastern Cape province, South Africa. *Pakistan Journal of Biological Sciences* **11**: 2051-2053.
- Radlkofer, L. (1933). Sapindaceae. In: Engler, A. (Ed.) *Das Pflanzenreich: Regni Vegetabilis Conspectus (IV) 165 (Heft 98ah)*. Leipzig, Verlag von Wilhelm, Engelmann. Pp 983-1002.
- Sanger, F., Nicklen, S. and Coulson, A.R. (1997). DNA sequencing with chain-terminating inhibitors. *Proceedings of the Academy of Science, USA* **74**: 5473-5467
- Savolainen, V., Chase, M.W., Hoot, S.B., Morton, C.M., Soltis, D.E., Bayer, C., Fay, M.F., De Bruijn, A.Y., Sullivan, S. and Qui, Y.L. (2000a). Phylogenetics of flowering plants based upon a combined analysis of plastid atpB and rbcL gene sequences. *Systematic Biology* **49**: 306–362.
- Savolainen, V., Fay, M.F., Albach, D.C., Backlund, M., Van der Bank, M., Cameron, K.M., Johnson, S.A., Lledo, L., Pintaud, J.C., Powell, M., Sheenan, M.C., Soltis, D.E., Soltis, P.S., Weston, P., Whitten, W.M., Wurdack, K.J. and Chase, M.W. (2000b). Phylogeny of the eudicots: A nearly complete familial analysis of the rbcL gene sequences. *Kew Bulletin* **55**: 257–309.
- Seelanan, T., Schnabel, A. and Wendel, J.F. (1997). Congruence and consensus in the cotton tribe (Malvaceae). *Systematic Botany* **22**: 259-290.
- Sofidiya, M.O., Odukoya, O.A. Afolayan, A.J. and Familoni, O.B. (2007). Survey of anti-inflammatory plants sold on herb markets in Lagos Nigeria. *International Journal of Botany* **3**: 302-306.
- Stoeckle, M., Waggoner, P. and Ausubel, J. (2005). Barcoding Life Illustrated: Goals, Rationale and Results. *Consortium for the Barcode of Life Leaflet* **3**: 1-2.
- Swofford, D.L. and Sullivan, J. (2009). Phylogeny inference based on Parsimony and other methods using PAUP*. In: Philippe, L., Marco, S. and Anne-Mieke, V. (Eds.) *The Phylogenetic Handbook: A practical approach to phylogenetic Analysis and Hypothesis Testing*. 2nd edition, Cambridge University Press, UK. Pp 267-312.
- Thorne, R.F. (2007). An update classification of the class Magnoliopsida (“Angiospermae”). *Botanical Reviews* **73**: 67–182.
- Valentini, A., Pompanon, F. and Taberlet, P. (2008). DNA barcoding for ecologists. *Trends in Ecology and Evolution* **24**: 110–117.
- Wiens, J.J. (1998a). Does adding characters with missing data increase or decrease phylogenetic accuracy? *Systematic Biology* **47**: 625–640.

Table 1: Voucher information and GenBank accession number of taxa used in the phylogenetic analysis of family Sapindaceae s.l.
 Abbreviations: FHI – Forestry Research Institute, Ibadan, Nigeria; LUH – University of Lagos, Lagos, Nigeria; SFRK/HNC – National Herbarium Yaounde, Cameroon; ABU – Ahmadu Bello University, Zaria, Nigeria, GCH – University of Ghana, Legon, Ghana.

S/No	Species	Voucher	Country	Herbarium	Gen Bank Accession Nos.	
					matK	rbcL
1.	<i>Allophylus africanus</i>	Adeyemi, T.O 1194	Cameroon	LUH	JN191100	JN191136
2.	<i>Allophylus bullatus</i>	Adeyemi, T.O 1185	Cameroon	LUH	JN191101	JN191137
3.	<i>Allophylus conraui</i>	Chapman, 78107	Nigeria	FHI	JN191102	JN191138
4.	<i>Allophylus griseotomentosus</i>	ATO 043	Cameroon	FHI	JN191103	JN191139
5.	<i>Allophylus hirtellus</i>	Adeyemi, T.O 1190	Cameroon	LUH	-	JN191140
6.	<i>Allophylus sp</i>	Adeyemi, T.O 3441	Cameroon	LUH	-	JN191135
7.	<i>Allophylus spicatus</i>	Adeyemi, T.O 3442	Nigeria	LUH	JN191104	JN191141
8.	<i>Allophylus welwitschii</i>	Adeyemi, T.O 1192	Cameroon	LUH	JN191105	JN191142
9.	<i>Blighia sapida</i>	Adeyemi, T.O 1196	Nigeria	LUH	JN191106	-
10.	<i>Blighia welwitschii</i>	Adeyemi, T.O 3315	Cameroon	LUH	JN191107	JN191143
11.	<i>Cardiospermum corindium</i>	Daramola, B.O 049		FHI	JN191108	JN191144
12.	<i>Cardiospermum grandiflorum</i>	Adeyemi, T.O 1189	Nigeria	LUH	JN191109	JN191145
13.	<i>Chytranthus carneus</i>	Abbiw & Hall, J.B. 4650	Ghana	GCH	-	JN191148
14.	<i>Chytranthus macrobotrys</i>	Adeyemi, T.O 1187	Cameroon	LUH	JN191110	JN191149
15.	<i>Chytranthus setosus</i>	Adeyemi, T.O 3444	Cameroon	LUH	JN191111	JN191150
16.	<i>Chytranthus sp1</i>	Adeyemi, T.O 3445	Cameroon	LUH	JN191112	JN191147
17.	<i>Chytranthus sp2</i>	Adeyemi, T.O 3446	Cameroon	LUH	JN191113	JN191146
18.	<i>Chytranthus talbotii</i>	Adeyemi, T.O 3447	Nigeria	LUH	JN191114	JN191151
19.	<i>Deinbollia grandifolia</i>	Hall, J.B. 47068	Ghana	GCH	JN191115	JN191153
20.	<i>Deinbollia kilimandscharia</i>	De WILDE, J.J & De WILDE, B.E 7781.	Ethiopia	GCH	JN191116	JN191154
21.	<i>Deinbollia sp</i>	Adeyemi, T.O 3448	Cameroon	LUH	JN191117	JN191152
22.	<i>Dodonaea viscosa</i>	Adeyemi, T.O 037	Nigeria	LUH	JN191118	-
23.	<i>Eriocoelum kertstingii</i>	Ibhanesebhor 77683	Nigeria	FHI	JN191119	-
24.	<i>Eriocoelum macrocarpum</i>	Adeyemi, T.O 1195	Cameroon	LUH	JN191121	-
25.	<i>Eriocoelum microspermum</i>	Adeyemi, T.O 069	Cameroon	FHI	JN191120	JN191155
26	<i>Laccodiscus ferrugineus</i>	Adeyemi, T.O 1183	Cameroon	LUH	-	JN191156
27	<i>Laccodiscus pseudostipularis</i>	Florey, J.J. 39252	Cameroon	FHI	JN191122	JN191157

28	<i>Lecaniodiscus cupanioides</i>	Adeyemi, T.O 3451	Nigeria	LUH	JN191123	JN191158
29	<i>Litchi chinensis</i>	Adeyemi, T.O 3452	Madagascar	LUH	JN191125	JN191160
30	<i>Majidea fosterii</i>	Adeyemi, T.O 1718	Cameroon	LUH	JN191124	JN191159
31	<i>Pancovia atroviolaceus</i>	Adeyemi, T.O 1182	Cameroon	LUH	JN191126	JN191162
32	<i>Pancovia sp1</i>	Adeyemi, T.O 1188	Cameroon	LUH	JN191127	-
33	<i>Pancovia sp2</i>	Adeyemi, T.O 1186	Cameroon	LUH	JN191128	JN191161
34	<i>Paullinia pinnata</i>	Adeyemi, T.O 1193	Cameroon	LUH	JN191129	JN191163
35	<i>Placodiscus leptostachys</i>	Adeyemi, T.O 3454	Cameroon	LUH	JN191130	JN191165
36	<i>Placodiscus sp1</i>	Adeyemi, T.O 3455	Cameroon	LUH	JN191131	JN191164
37	<i>Radlkofera sp2</i>	Adeyemi, T.O 3459	Nigeria	LUH	JN191132	JN191167
38	<i>Radlkofera sp3</i>	Adeyemi, T.O 3460	Cameroon	LUH	JN191133	JN191166
39	<i>Zanha golugensis</i>	Adeyemi, T.O 3462	Nigeria	LUH	JN191134	JN191168

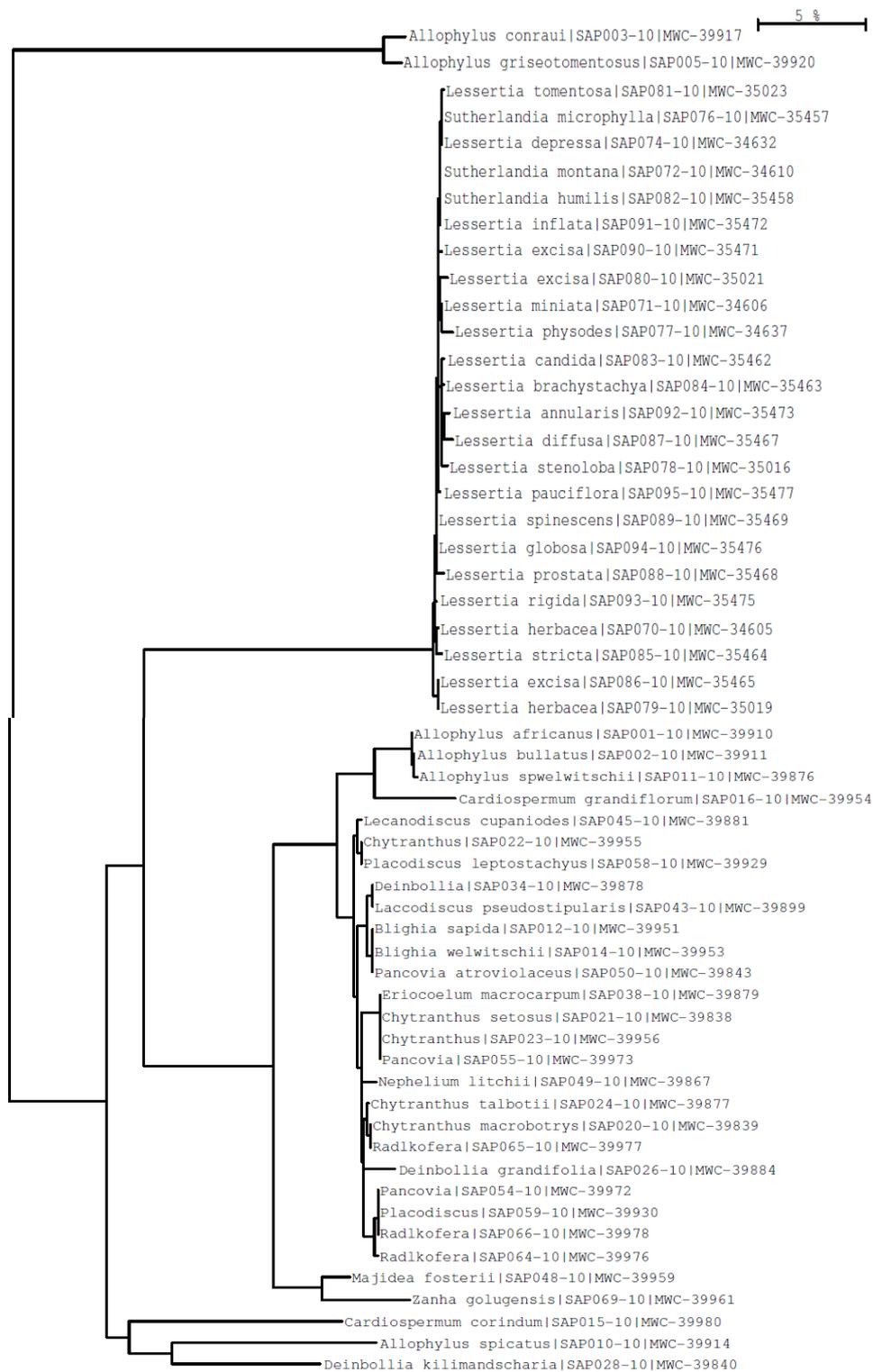


Figure 1: Phylogenetic relationship within Sapindaceae based on matK barcode sequence data

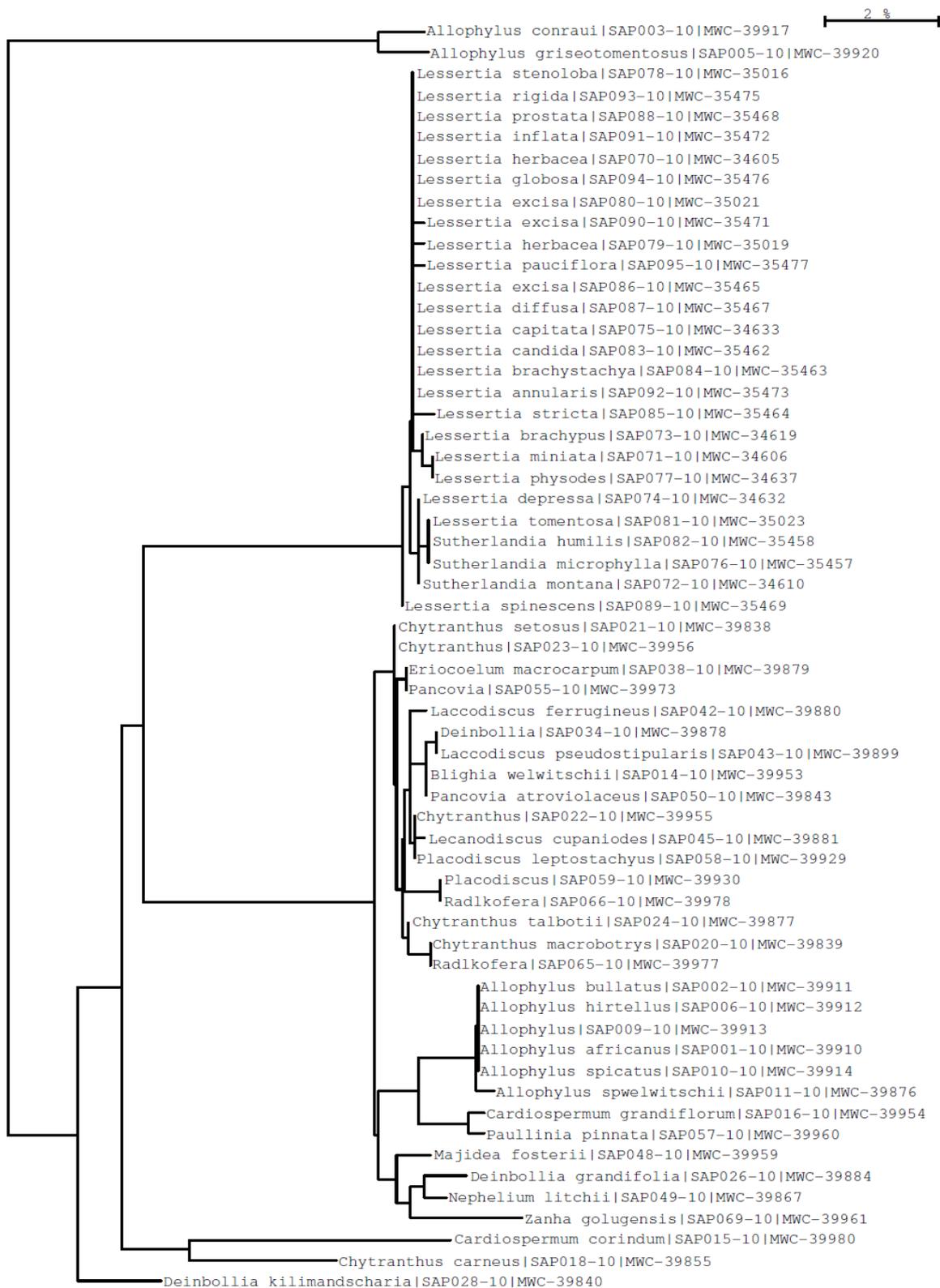


Figure 2: Phylogenetic relationship within Sapindaceae based on rbcL barcode sequence data

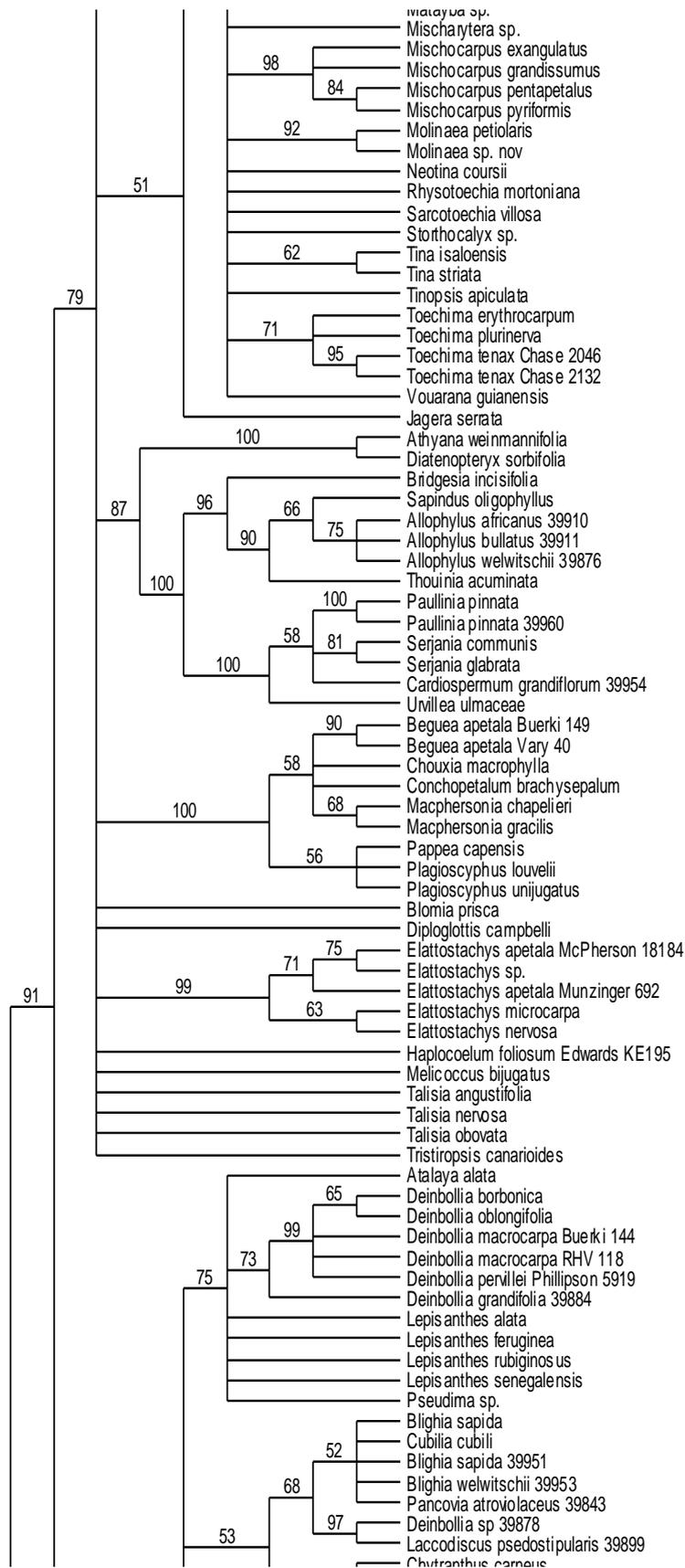


Figure 3: Phylogenetic Relationships within Sapindaceae based on matK data. Bootstrap supports are indicated above branches.

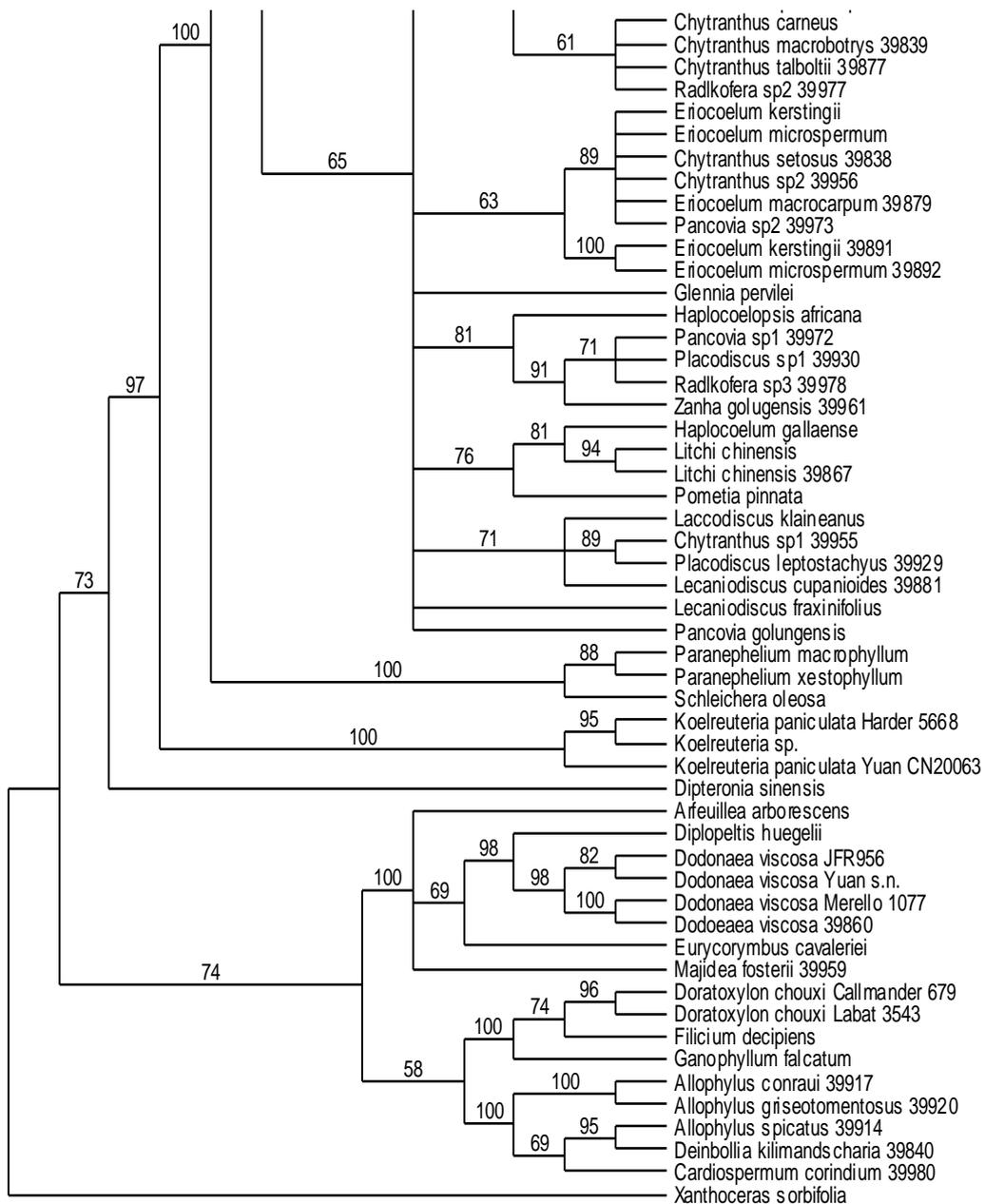


Figure 3: Phylogenetic Relationships within Sapindaceae based on matK data. Bootstrap supports are indicated above branches (cont'd).

AN EMPIRICAL ANALYSIS OF AGRICULTURE AND COMMERCIAL BANK CREDIT IN NIGERIA (1982-2007)

Onyeka-Ubaka, J. N.¹, Adewara, J. A.² & Ofili, O. E.¹

¹Department of Mathematics, University of Lagos, Akoka, Lagos, Nigeria.

²Distance Learning Institute, University of Lagos, Akoka, Lagos, Nigeria.

Jonyeka-ubaka@unilag.edu.ng

ABSTRACT

There is a general agreement that Nigerian agriculture is grossly underfunded and the pattern of agricultural sector spending hardly represent the best and most effective use of public resources. In line with the structure of the funding problem, we address two dimensions here volume of funding/agricultural share of capital budget and the quality/impact of agricultural sector funding/spending. The study employs Ordinary Least Squares (OLS) method of estimation. Preliminary test of stationarity and co-integration of variables using the Augmented Dickey Fuller (ADF) test were conducted. The respective test shows that some of the variables including the dependent variable were stationary at second differenced except real interest rate which was stationary at first differenced. The accompanied co-integration test provided no evidence of co-integration among the variable. However, the empirical results established that agricultural output as well as commercial banks credit to agriculture and real interest rate contributed immensely to economic growth in Nigeria. These findings can be traced with a look at the public spending on agriculture in Nigeria over time.

Keywords: Agriculture, Bank Credit, OLS, Stationarity and Co-integration

INTRODUCTION

Agriculture is the first and most thriven occupation of mankind. Nigerian agriculture is divided into two types, the subsistence agriculture and commercial agriculture:- The subsistence agriculture is the type of farming which involves only the farmer and his family. That is, the farmer produces for himself and his family with little or none to sell in the market. It involves only a little amount of money to practice unlike commercial farming that involves huge amount of money to practice. It does not involve the machine to carry out, since the land is very small and fragmented.

The second type is commercial agriculture, and this is where a farmer produces his crops and sells them in the market. It is carried out in large scale with enough land and machines. These machines are used in cultivating crops. It involves a lot of capital and time, and also increases the farmer's income. Commercial farming helps farmers to engage in the cultivation of different varieties of crops, since the money, land and equipment could easily be used.

Several researches have shown that Nigeria is endowed with huge expanse of fertile agricultureland, rivers, streams, lakes, forest and grassland, as well as a large active population that can sustain a high productive and profitable agricultural sector. Wells, Carl. and Eicher (1970), Adubi (2000) and Obadan, I.M. (2000) admit that this enormous resource base if well managed could support a vibrant agricultural sector capable of ensuring self-sufficiency in food and raw materials for the industrial sector as well as providing gainful employment for the population and generating foreign exchange through exports.

In spite of these endowments, the sector has continued to record a declining productivity. The capacity of the sector to fulfill its role in the Nigerian economy has been constrained by various social-economic and structural problems such as:

- (a) Unavailability of credits to local farmers
- (b) The civil war of the late 1960's
- (c) Thesevere drought of the early 1970's and 1980's
- (d) The discovery of oil
- (e) High interest rates on loans to farmers
- (f) Rural-urban migration
- (g) Ineffective institutions charged with policy implementations.

LITERATURE REVIEW

Agriculture in Nigeria is the most dominant sector and major source of livelihood for the populace. It accounts for about 70% of employment, and in spite of this Amechi (2004) say it has not been able to achieve the major objectives of agricultural development which the World Bank (1997) identified to include; (i) increase in food production and family income, (ii) make household food, water and energy secure and (iii) restore and maintain the natural resources. They stated further that the failure of agriculture to meet these objectives is due to limited use of purchased inputs and mechanization. This limitation is tied to undercapitalization or lack of credit. Hence, since the availability of adequate credit is central to improvement in agricultural productivity in an economy, this chapter is devoted to the impacts of credits on Agricultural outputs especially in Nigeria.

Finance is one input required for agricultural development as it represents the power to purchase all other inputs and thus, it is not the single determinant of the level of development in agriculture. According to IjaiyaandAbdulraheem (2000), the availability of credits to local farmers pose a serious problem. This is because of the rate of defaulting cases among small farmers. Muftau (2003) also revealed that commercial banks in Nigeria were willing to grant to large-scale farmers credit because it has noticed that small farmers default. Mostly in the act of loan repayment, they also have no provision for collateral security required by banks. It is in light of this that the government has always maintained that commercial banks should not neglect agricultural and allied activities since they are the chief agent of mobilization of savings. Notwithstanding, the unsuitability of commercial banks for financing agriculture in general and small scale farmers in particular, studies carried out by Ijere (1975) pointed out the need for raising the volume of loan resources available to the credit constitutions so as to permit increase in lending to the individual borrowers. However, Garba (2000) attributed most of the shortcomings and institutional credits in Nigeria to the facts such as: ineffective supervision or monitoring, insufficient funds, political interference, cumbersome and time consuming loan processing and gearing absence of financial projections.

Agricultural credit in Nigeria dates back to the 1930s but organized credit to farmers did not start until 1972 when the Nigeria Agricultural and Cooperative Bank (NACB) was established, Adekanye(1986). He further said that agriculture is the largest sector of Nigerian economy, though its contribution to the Gross Domestic Product (GDP) has declined from 67% in 1950 to 18% in 1980. According to the Federal Ministry of Agriculture Publication (1980) and Aku(1995) , 58% of farming- related borrowings was obtained from family and friends; 24% from professional private money lenders, 15% from merchant and only 3% from commercial banks and other institutional sources. As Garba (2000) noted, they are grossly, inadequate and unsatisfactory for the credit needs of the farmers. Thus, there is the need for larger credit sources.

The importance of project supervision or monitoring of facilities is to ensure that all conditions attached to the approval of credits facilities are complied with. Credit supervision is also aimed at identifying emergent problems before they got out of control. Problems detected earlier

CBC= commercial bank credit
 β_0 = Constant term
 β_1 = Coefficient of parameter
 ε_i = Stochastic error term
 $GDP = \beta_0 + \beta_1 AOP + \beta_2 RINTR + \varepsilon_i$

(2)

where

GDP = Gross domestic product
 AOP = Agricultural output
 RINTR = Real Interest Rate
 β_0 = Constant term
 β_1, β_2 = parameters to be estimated
 ε_i = Stochastic error term

This normality test was carried out to check whether the error term follows the normal distribution. The normality test adopted is the Jarque-Bera (JB) Test of normality. The JB test of normality is an asymptotic, or large-sample test and it is based on the OLS residuals and uses the chi-square distribution.

RESULTS AND DISCUSSION

The data were sourced from the Central Bank of Nigeria (CBN), Statistical Bulletin, Federal Government of Nigeria National Accounts and Supplemented with Federal Office of Statistics Annual Abstract of Statistics and Digest of Statistics and analyzed by first plotting the data to track the trend.

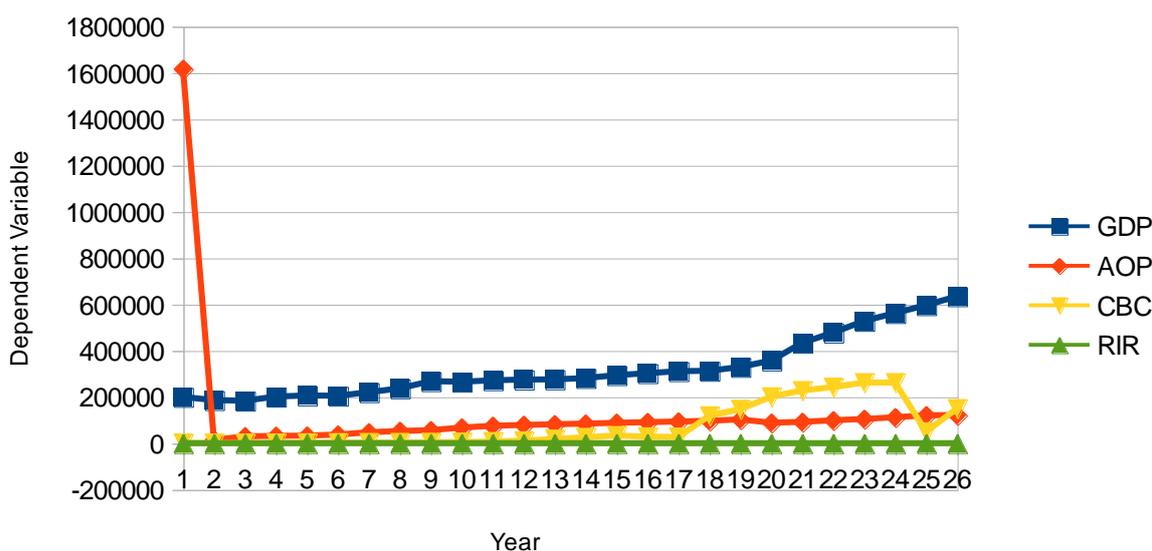


Fig. 2: GDP, AOP, CBC and RIR of Nigeria (1982-2007)

The unit root test of stationarity using the augmented dickey-filler (ADF) test was conducted. The result is presented below. This is because loading of the endogenous variable is sufficient when in fact a long-run relationship exists between the dependent variable and the economic fundamentals driving it. Thus, each of the variables would be examined for unit root and co-integration. The empirical result of this analysis is in two model and the two models will be analyzed together. The first is in log linear model which examines a simple relationship of

agricultural output and commercial banks credit, while the second is also a log linear model that seeks to know the relationship shown by agricultural output to economic growth.

Unit Root Test

The unit root test of stationarity using the augmented dickey-filler (ADF) test was run on the variables up to their 2nd differences. The results show that real interest rate was stationary at first differenced, while gross domestic product, agricultural output and commercial banks credit to agricultural sector were stationary at second differenced. The summary results are presented in table 4.1 below.

Table 4.1: ADF Unit Root Test on the Annual Series

Variable	DDL GDP	DDL AOP	DDL CBC	DRIR
1~(d)	2	2	2	1
Lag	2,1,0	2,1,0	2,1,0	2,1,0
t-ADF	-4.0192* -3.9066** -6.3923**	-6.0393* -6.9775** -6.3362**	-4.2488* -5.5409** -7.5291**	-4.5463** -4.7982** -4.8954**
5% & 1% Critical Values	-1.958 -2.682	-1.958 -2.682	-1.958 -2.682	-1.957 -2.676

Where ** indicates significance at both 5% and 1% critical value D, DD indicates the order of stationarity.

This observation of order of stationarity as indicated above, led us to a possible suspicion of co-integration between the dependent variables and those of explanatory variables that have the same order with them. Hence we proceed to co-integration test.

Co-integration test

This test is conducted to check whether there is evidence of the co-integration between the explanatory variables having the same order of stationarity with the dependent variables. As a result, we estimate their linear combination at their level form without the constant term and obtain their residual which was further subjected to unit root test of stationarity. The result is also presented in Table 4.2.

Table 4.2: Co-Integration Result

	t-ADF	1% critical value	5% critical value
Residual	-2.3061(2)	-2.672	-1.957
Residual	-2.2487(1)	-2.672	-1.957
Residual	-2.5050 (0)	-2.672	-1.957

Where **ADF** – augmented dickey-filler

The result shows a slight evidence of co-integration. This is because the residual obtained from the linear combination of the variables under consideration were statistically significance at 5% but not at 1% critical values, reading from lag lengths 2, 1 and 0. The outcomes of the co-integration test did not invalidate the former specified model of log linear model and on this ground; we present the summary of the estimated models.

Test for Normality

This test was carried out to check whether the error term follows the normal distribution. The normality test adopted is the Jarque-Bera (JB) Test of Normality. The test computes the skewness and Kurtosis measures of the OLS residuals and the Chi-square distribution, Gujarati (2004)

The null hypothesis, $H_0: \sigma_1 = 0$ (the error term follows a normal distribution) against the alternative hypothesis, $H_1: \sigma_1 \neq 0$ (the error term does follow a normal distribution) at $\alpha = 5\%$ with 2 degrees of freedom was tested.

The Test statistics:

$$\text{Residual (JB)} = n \left[\frac{s^2}{6} + \frac{(k-3)^2}{24} \right] = 1.4077$$

Where; n = sample size,

s = Skewness coefficient, and

k = Kurtosis coefficient

From the result obtained from Jarque-Bera (JB) Test of Normality, JB= 1.4077 and from Chi-square table $\chi_{tab}^2 = 5.99147$. Therefore, since $\chi_{cal}^2 = 1.4077 < \chi_{tab}^2 = 5.99147$ at 5% level of significance, we accept H_0 and conclude that the error term follows a normal distribution.

The summary of the results for the two models were obtained using Pc-Give version 8.0.

Table 4.3: Modeling Log of AOP by OLS

Variable	Coefficient	Std. Error	T-value	T-prob	Part R ²
Constant	9.2653	0.23922	38.732	0.0000	0.9862
LCBC	0.19419	0.023295	8.336	0.000	0.7679

$$R^2 = 0.767931, F(1, 21) = 69.49 [0.0000],$$

$$DW = 1.573$$

Table 4.4: Modeling log of GDP by OLS

Variable	Coefficient	Std. Error	T-value	T-prob	Part R ²
Constant	4.5479	1.0902	4.172	0.0000	0.4653
LAOP	0.72742	0.097012	7.498	0.0000	0.07376
RIR	0.0043151	0.0019970	2.161	0.0430	0.1893

$$R^2 = 0.752486, F(2, 20) = 30.402 [0.0000], DW = 1.573$$

Our analysis is centered on the statistical criteria. The elasticity coefficient observed from the two models presented above, shows that any unit adjustment in the variables will transmit to positive or negative adjustment to the dependent variable to the tune of the values of the elasticity coefficient in each variable. However, the result from the first model showed a great significant relationship between agricultural output and commercial bank credit. This was observed following a "2-t Rule of thumb," a variable is statistically significant if its t-value is greater than 2 in absolute value at any percent level of significance. In other hand, it statistically insignificant if its t-value is less than 2 in absolute value at any percent level of significance, Gujarati(2004). The coefficient shows that every unit increase in commercial bank credit to agriculture sector will relatively contribute a 0.19419 unit increase to the output of agricultural sector, all things being equal.

Also judging from the second model, the result equally shows that agricultural output and real interest rate is two major macroeconomic indicators that exact much pressure on the growth variation of the economy. It shows that every unit increase in agricultural output will on average bring about 0.72742 unit increase to the economic growth. Also, the coefficient of real interest

rate shows that every unit changes in real interest rate will cause the economic growth indicator to change by 0.0043151 units, all things being equal.

CONCLUSION

Agricultural sector funding comes from the federal government, state government, organized private sector, informal sector and international development partners including bilateral and multilateral agencies. Perhaps, because the society sees agriculture as a small-farmer activity, less than 1% of Nigeria's annual GDP is ploughed back into agriculture as productive investment. The study therefore re-affirms the fact that one of the most important functions of the commercial banks and other monetary authorities is to make credit available to the investors at affordable rate most especially the agricultural sector. This is because low credit or high lending rate will amount to low level of investment which transmits to low agricultural output. There is also the need for clarification of the roles of the three tiers of government in agricultural services delivery.

The government through its relevant authorities should design a favourable monetary policy that will enable commercial bank to make credit more available to the agricultural sector for mass development of that sector. This is because, the fiscal posture for the reform period, and monetary policy outcomes will depend largely on the government's fiscal stance. The disparity between monetary targets and outcomes is wide, largely because of the statutory financing of budget deficits and the inability of the apex bank to sterilize the liquidity effects of government expenditure. Thus, monetary policy intervention has been basically reactionary and term, leading to missed targets and ineffectiveness in performance towards increasing the agricultural output in Nigeria, and except urgent measures are taken, the present economic objectives in Nigeria may not be achieved in the nearest future.

REFERENCES

- Adekanye, F. (1986). *Practice of Banking*. London: Collins Publishing Company.
- Aku, P.S. (1995). Comparative Analysis of NAC and ACGSP loan Disbursement to Agriculture in Nigeria. *Journal of Social and Management Studies*. 1(34).
- Amechi, N.F. (2004). *Model Agricultural Science*. Oko: Federal Polytechnic press.
- Emmanuel .O.E. (2008). Macroeconomic Environment and Agricultural Sector Growth in Nigeria. *World Journal of Agricultural Sciences*. 8(16).
- Garba, P.K. (2000). *An Analysis of the Implementation and Stability of Nigeria Agricultural Policies*. Accra: AEC Publishers.
- Ijaiya, G.T. & Abdulraheem, A. (2000). Commercial Banks Credits to the Agricultural Sector and Poverty Reduction in Nigeria. A Calibration Analysis. *Nigeria Journal of Agricbiz and Rural Development*. Vol.XL, No.12.
- Ijere, M.O. (1986). *New perspectives in Financing Nigeria Agriculture*. Benin: Dimension Publishers.
- Muftau, A.I. (2003). Commercial Bank Credit to the Agricultural Sector and the Nigerian Economy. An Analysis of the Future Trend. *A Journal of Department of Business Administration* .28(32).
- Obadan, I.M. (2000). *Prospect for Diversification in Nigeria Export Trade*. Benin: Dimension Publishers.
- Ojo, M.O. (1994). *Non Oil Export-led growth in Economic Development*. Lagos: Longman Nigeria Plc.
- Wells, J. C. Carl, K. and Eicher, L. (1970). *Nigerian Development Plan In Growth and Development of the Nigerian Economy*. USA: Michigam State University Press.

WATER-DISPERSIBLE MAGNETITE NANOPARTICLES OBTAINED BY CO-PRECIPITATION AND THERMAL DECOMPOSITION METHODS.

Khadijat. O. Abdulwahab,^{1†} Mohammad A. Malik¹ & Paul O'Brien^{1,2}

¹School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

²School of Materials, University of Manchester, Grosvenor Street, Manchester, M1 7HS, UK.

[†]Department of Chemistry, University of Lagos, Lagos state Nigeria.

khidother@yahoo.co.uk

ABSTRACT

Water-dispersible magnetite (Fe₃O₄) nanoparticles were synthesised by the co-precipitation of iron salts (dual-source) and the hot injection thermolysis of iron pivalate complex (single source). The iron pivalate complex was thermolysed in a mixture of polyvinylpyrrolidone (PVP) as capping agent and triethylene glycol (TREG) as solvent at the boiling point of the solvent (285 °C). The co-precipitation method involved precipitating iron(II) and iron(III) salts with ammonium hydroxide at room temperature. This was then followed by the addition of polyallylamine hydrochloride (PAH).

The p-XRD patterns obtained for the nanoparticles revealed that magnetite was synthesised by both methods. TEM showed that the magnetite nanoparticles obtained from the thermal decomposition method are more monodispersed (4.1 ± 0.3 nm) than those obtained from co-precipitation method (7.0 ± 1.0 nm).

The nanoparticles were characterised by powder X-ray diffraction (p-XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED).

Keywords: Magnetite, Nanoparticles, Colloidal, water dispersible, Co-precipitation, Monodisperse.

INTRODUCTION

Magnetite nanoparticles have attracted a lot of attention recently due to their unique magnetic properties. Magnetite has an inverse spinel structure in which the divalent cations occupy the octahedral site while the trivalent cations occupy both tetrahedral and octahedral sites.¹ Studies have shown that magnetite nanoparticles with diameters in the range of 5-20 nm are usually superparamagnetic.^{2,3} This in turn has led to a wide range of applications including drug delivery,^{4,5} magnetic resonance imaging (MRI),^{4,6-8} hyperthermia treatment,^{7,9} data storage,¹⁰ ferrofluids,¹¹ environmental remediation^{12,13} and catalysis.^{14,15} Magnetite nanoparticles are well suited for biomedical applications because they have high saturation magnetisation values and can be functionalised with appropriate molecules for tagging biological specimens.^{16,17} In addition, the phenomenon of superparamagnetism makes it possible for controlling the movement of these nanoparticles to specific targets when placed under an external magnetic field. More often, such applications require the magnetite nanoparticles to be monodisperse. As such, various synthetic and functionalisation methods have been employed to synthesise magnetite nanoparticles suitable for such applications. The co-precipitation method is commonly used for the synthesis of magnetite and other ferrite nanoparticles because it is easy to use and scalable.^{12,13,18-32} However, nanoparticles obtained from this method tend to have a broad size distribution and poor crystallinity, hence, other non-hydrolytic methods have been employed to synthesise these nanoparticles.³³⁻³⁵

The biological methods have been used to synthesise water soluble iron oxide nanoparticles.³⁶⁻

⁴⁶A major challenge with this route is that the success of getting monodisperse nanoparticles depends on environmental parameters such as temperature, redox potential and pH which are often difficult to control.¹

Thermal decomposition methods have been proven to produce monodisperse crystalline nanoparticles^{47,48} but the shortcoming of this method is that most often the nanoparticles are not soluble in water because of the hydrophobicity of the capping agents employed. As a result of this, the nanoparticles have limited applications in biomedical and environmental fields. To overcome this problem, there has been ongoing research into preparing water dispersible ferrite nanoparticles with desirable properties. Methods proposed to achieve this goal are either direct synthesis or post synthesis by ligand exchange to obtain the desired surface modification.

A lot of post synthesis surface modification/ ligand exchange techniques have been employed to disperse the nanoparticles obtained from thermal decomposition in aqueous medium⁴⁹⁻⁵³ but one of the major shortcomings of this approach is the incomplete replacements of ligand that leads to reduced stability in aqueous solution. More often the ligand exchange procedures are tedious. Consequently, the direct synthesis of highly-crystalline ferrite nanoparticles that can be dispersed in water is a preferable alternative.

A direct synthesis of water dispersible ferrite nanoparticles has been investigated by different synthetic routes including hydrothermal/solvothermal method⁵⁴⁻⁵⁸ and the thermal decomposition method has been further developed to produce water dispersible ferrite nanoparticles by using strong polar capping agents such as 2-pyrrolidone and glycols.⁵⁹⁻⁶³

In this paper, we compared the results obtained for magnetite nanoparticles synthesised by two different methods: co-precipitation of iron(II) and iron(III) salts and the hot injection thermolysis of iron pivalate complex in polyvinylpyrrolidone and triethylene glycol.

METHODS

Synthesis of Precursor

The synthesis of $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{O}_2\text{C}^t\text{Bu}).\text{HO}_2\text{C}^t\text{Bu}$ was carried out as described in the literature.³⁴

Synthesis Of Nanoparticles

Two methods were employed: the co-precipitation and thermal decomposition methods.

Co-precipitation method

In a typical reaction, a mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2703 g, 1 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.099 g, 0.5 mmol) was added slowly into ammonium hydroxide (0.05 M, 50 mL) at room temperature and stirred vigorously for 30 minutes under nitrogen. The black precipitate was collected with a magnetic stirrer and washed with deionised water. This was followed by the addition of polyallylamine hydrochloride (PAH) and ultrasonication for 15 minutes.

PAH was prepared as follows: Polyallyl amine (M_w 17,000, 20% solution, 10 mg) was diluted with 10 mL deionised and adjusted to pH 3 with Hydrochloric acid (HCl). 1 mL of this solution was further diluted 5 times and added to 0.1 mL suspension of the magnetite nanoparticles.

Thermal decomposition method.

Polyvinylpyrrolidone PVP (M_w 40,000 0.25 g) and triethylene glycol TREG (15 mL) was degassed at 100 °C under vacuum for 30 minutes and then heated to the boiling point of the solvent (TREG) under nitrogen. The precursor, $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{O}_2\text{C}^t\text{Bu}).\text{HO}_2\text{C}^t\text{Bu}$ (0.275 g, 0.25 mmol) was dispersed in TREG (10 mL) and injected into the solution of the hot mixture. The reaction was maintained at 230 °C for 2 hours. The dark mixture was allowed to cool and acetone was added to precipitate the nanoparticles which were then isolated by centrifugation. The residue was washed with acetone three times and then re-dispersed in deionised water.

Characterisation of Nanoparticles.

Powder X-ray diffraction studies were performed on a Bruker Discover 8 diffractometer with a Co- $K\alpha$ radiation. TEM samples were prepared by placing 1 or 2 drops of the nanoparticles dispersion on a holey carbon copper grids. High resolution transmission electron microscopy (HRTEM) was performed using a Tecnai F30 FEG TEM instrument at an accelerating voltage of 300 kV.

RESULTS

The p-XRD nanoparticles obtained from both methods were matched with cubic magnetite (Fe_3O_4) (ICDD Card No: 00-019-0629) (Fig. 1). This demonstrates that the samples are in inverse spinel structure with a face centred cubic phase.

The average nanoparticle sizes estimated using the Scherrer equation are 5 nm (from the thermal decomposition method) and 6.5 nm (from the co-precipitation method). Statistical data from the TEM was also used to calculate the average diameters which gave 4.1 ± 0.3 nm and 7.0 ± 1 nm for magnetite nanoparticles synthesised by the thermal decomposition and co-precipitation methods respectively.

DISCUSSION

In comparison, the magnetite nanoparticles synthesised from the thermal decomposition method have a narrow size distribution and are well dispersed than those nanoparticles obtained from co-precipitation. This has been attributed to the fact that in the thermal decomposition method, the addition of capping agent is in-situ which is better at suppressing further particle growth compared to the co-precipitation approach in which the stabilisation was done after synthesis.⁶⁴

The nanoparticles obtained from thermal decomposition are spherical and highly crystalline as observed in the lattice fringes and the selected area electron diffraction (Fig. 2(A) and (C)) whilst those synthesised by the co-precipitation method are pseudo-spherical (Fig. 2(B)). This observation is due to the fact that the shape and size distribution of the nanoparticles obtained from co-precipitation are strongly influenced by pH.⁶

The d -spacing measured from the lattice fringes of the nanocrystallite correspond to a value of 2.54 Å which can be indexed to the (311) reflection plane of magnetite (ICDD Card No: 00-019-0629). It is worth mentioning that the average d - spacing of the nanoparticles was calculated from a number of lattice fringes by drawing a perpendicular line across the fringes which produced a line profile from which the spacing is estimated (Fig. 2(D)). The SAED pattern (Fig. 2(C)) contains information from a large number of magnetite nanoparticles (from thermal decomposition method) and the observed strong diffraction rings can be indexed to (220), (311) and (400) planes. This also confirms the formation of face centred cubic magnetite.

CONCLUSION

Water-soluble magnetite nanoparticles have been synthesised by both the hot injection thermolysis of iron pivalate complex and the co-precipitation of iron salts. The magnetite nanoparticles obtained from the thermal decomposition method have a better size distribution and are more crystalline than those obtained from the co-precipitation approach. The nanoparticles produced were of pure single phase as evident in their p-XRD, SAED and HRTEM images. The nanoparticles dispersion was stable (no visible precipitation) for several months at room temperature. Our investigation revealed that these nanoparticles could have potential use in the biomedical applications. Hot injection thermolysis of iron pivalate complex in PVP and TREG has proven to be a good route for the synthesis of monodisperse water soluble magnetite nanoparticles and this method can also be extended to produce other ferrite nanoparticles.

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REFERENCES

1. R. K. Abhilash and B. D. Pandey, *Bull. Mater. Sci.*, 2011, **34**, 191.
2. P. Guardia, A. Labarta, and X. Batlle, *J. Phys. Chem. C*, 2011, **115**, 390.
3. J. Santoyo Salazar, L. Perez, O. de Abril, L. Truong Phuoc, D. Ihiwakrim, M. Vazquez, J.-M. Greneche, S. Begin-Colin, and G. Pourroy, *Chem. Mater.*, 2011, **23**, 1379.
4. P. Majewski and B. Thierry, *Crit. Rev. Solid State Mater. Sci.*, 2007, **32**, 203.
5. R. Mout, D. F. Moyano, S. Rana, and V. M. Rotello, *Chem. Soc. Rev.*, 2012, **41**, 2539.
6. R. Qiao, C. Yang, and M. Gao, *J. Mater. Chem.*, 2009, **19**, 6274.
7. J. Jang, H. Nah, J. H. Lee, S. H. Moon, M. G. Kim, and J. Cheon, *Angew. Chemie Int. Ed.*, 2009, **48**, 1234.
8. H. J. Lee, K. S. Jang, S. Jang, J. W. Kim, H. M. Yang, Y. Y. Jeong, and J. D. Kim, *Chem. Commun.*, 2010, **46**, 3559.
9. S. W. Lee, S. Bae, Y. Takemura, I. B. Shim, T. M. Kim, J. Kim, H. J. Lee, S. Zurn, and C. S. Kim, *J. Magn. Magn. Mater.*, 2007, **310**, 2868.
10. R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, and D. R. Huffman, *Science*, 1992, **257**, 219.
11. K. Raj, B. Moskowitz, and R. Casciari, *J. Magn. Magn. Mater.*, 1995, **149**, 174.
12. Y. G. Li, H. S. Gao, W. L. Li, J. M. Xing, and H. Z. Liu, *Bioresour. Technol.*, 2009, **100**, 5092.
13. I. Safarik, L. F. T. Rego, M. Borovska, E. Mosiniewicz-Szablewska, F. Weyda, and M. Safarikova, *Enzyme Microb. Technol.*, 2007, **40**, 1551.
14. A. Hu, G. T. Yee, and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 12486.
15. A. H. Lu, W. C. Li, A. Kiefer, W. Schmidt, E. Bill, G. Fink, and F. Schüth, *J. Am. Chem. Soc.*, 2004, **126**, 8616.
16. D. L. Leslie-Pelecky and R. D. Rieke, *Chem. Mater.*, 1996, **8**, 1770.
17. T. Suzuki, M. Shinkai, M. Kamihira, and M. Kobayashi, *Biotechnol. Appl. Biochem.*, 1995, **21**, 335.
18. J. Mürbe, A. Rechtenbach, and J. Töpfer, *Mater. Chem. Phys.*, 2008, **110**, 426.
19. P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy, and C. Muthamizhchelvan, *Mater. Lett.*, 2011, **65**, 483.
20. R. T. Olsson, G. Salazar-Alvarez, M. S. Hedenqvist, U. W. Gedde, F. Lindberg, and S. J. Savage, *Chem. Mater.*, 2005, **17**, 5109.
21. I. Martínez-Mera, M. E. Espinosa-Pesqueira, R. Pérez-Hernández, and J. Arenas-Alatorre, *Mater. Lett.*, 2007, **61**, 4447.
22. K. Maaz, A. Mumtaz, S. K. Hasanain, and A. Ceylan, *J. Magn. Magn. Mater.*, 2007, **308**, 289.
23. F. Dang, N. Enomoto, J. Hojo, and K. Enpuku, *J. Cryst. Growth*, 2010, **312**, 1736.
24. C. Yang and H. Yan, *Mater. Lett.*, 2012, **73**, 129.
25. Y. Qi, Y. Yang, X. Zhao, X. Liu, P. Wu, F. Zhang, and S. Xu, *Particuology*, 2010, **8**, 207.
26. Y. Sahoo, A. Goodarzi, M. T. Swihart, T. Y. Ohulchansky, N. Kaur, E. P. Furlani, and P. N. Prasad, *J. Phys. Chem. B*, 2005, **109**, 3879.
27. R. F. Fakhrullin, J. García-Alonso, and V. N. Paunov, *Soft Matter*, 2010, **6**, 391.
28. X. M. Guo, B. Guo, Q. Zhang, and X. Sun, *Dalt. Trans.*, 2011, **40**, 3039.
29. C. Wilhelm, C. Billotey, J. Roger, J. N. Pons, J. C. Bacri, and F. Gazeau, *Biomaterials*, 2003, **24**, 1001.

30. Z. Lu, G. Wang, J. Zhuang, and W. Yang, *Colloids Surf. Physicochem. Eng. Asp.*, 2006, **278**, 140.
31. X. Liu, M. D. Kaminski, Y. Guan, H. Chen, H. Liu, and A. J. Rosengart, *J. Magn. Magn. Mater.*, 2006, **306**, 248.
32. M. M. Lin, S. Li, H. H. Kim, H. Kim, H. B. Lee, M. Muhammed, and D. K. Kim, *J. Mater. Chem.*, 2010, **20**, 444.
33. K. O. Abdulwahab, M. A. Malik, P. O'Brien, G. A. Timco, F. Tuna, C. A. Muryn, R. E. P. Winpenny, R. A. D. Patrick, V. S. Coker, and E. Arenholz, *Chem. Mater.*, 2014, **26**, 999.
34. K. Abdulwahab, M. A. Malik, P. O'Brien, K. Govender, C. A. Muryn, G. A. Timco, F. Tuna, and R. E. P. Winpenny, *Dalt. Trans.*, 2013, **42**, 196.
35. K. O. Abdulwahab, M. A. Malik, P. O'Brien, G. A. Timco, F. Tuna, R. E. P. Winpenny, R. A. D. Patrick, V. S. Coker, and E. Arenholz, *J. Mater. Chem. C*, 2014, **2**, 6781.
36. W. Li, L. Yu, P. Zhou, and M. Zhu, *World J. Microbiol. Biotechnol.*, 2007, **23**, 1489.
37. C. T. Lefèvre, F. Abreu, M. L. Schmidt, U. Lins, R. B. Frankel, B. P. Hedlund, and D. A. Bazylinski, *Appl. Environ. Microbiol.*, 2010, **76**, 3740.
38. W. Zhou, W. He, S. Zhong, Y. Wang, H. Zhao, Z. Li, and S. Yan, *J. Magn. Magn. Mater.*, 2009, **321**, 1025.
39. T. Perez-Gonzalez, C. Jimenez-Lopez, A. L. Neal, F. Rull-Perez, A. Rodriguez-Navarro, A. Fernandez-Vivas, and E. Iañez-Pareja, *Geochim. Cosmochim. Acta*, 2010, **74**, 967.
40. Y. Amemiya, A. Arakaki, S. S. Staniland, T. Tanaka, and T. Matsunaga, *Biomaterials*, 2007, **28**, 5381.
41. L. W. Yeary, L. J. Love, J. R. Thompson, C. J. Rawn, and T. J. Phelps, *IEEE Trans. Magn.*, 2005, **41**, 4384.
42. A. Bharde, D. Rautaray, V. Bansal, A. Ahmad, I. Sarkar, S. M. Yusuf, M. Sanyal, and M. Sastry, *Small*, 2006, **2**, 135.
43. V. S. Coker, C. I. Pearce, C. Lang, G. van der Laan, R. A. D. Patrick, N. D. Telling, D. Schüler, E. Arenholz, and J. R. Lloyd, *Eur. J. Mineral.*, 2007, **19**, 707.
44. A. P. Philipse and D. Maas, *Langmuir*, 2002, **18**, 9977.
45. D. A. Bazylinski, R. B. Frankel, and H. W. Jannasch, *Nature*, 1988, **334**, 518.
46. V. S. Coker, J. A. Bennett, N. D. Telling, T. Henkel, J. M. Charnock, G. van der Laan, R. A. D. Patrick, C. I. Pearce, R. S. Cutting, I. J. Shannon, J. Wood, E. Arenholz, I. C. Lyon, and J. R. Lloyd, *ACS Nano*, 2010, **4**, 2577.
47. T. Hyeon, S. S. Lee, J. Park, Y. Chung, and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798.
48. S. Sun and H. Zeng, *J. Am. Chem. Soc.*, 2002, **124**, 8204.
49. Y. Li, M. Afzaal, and P. O'Brien, *J. Mater. Chem.*, 2006, **16**, 2175.
50. C. Yu, J. Zhao, Y. Guo, C. Lu, X. Ma, and Z. Gu, *J. Biomed. Mater. Res.*, 2008, **87**, 364.
51. Y. Wang, J. F. Wong, X. Teng, X. Z. Lin, and H. Yang, *Nano Lett.*, 2003, **3**, 1555.
52. Y. W. Jun, Y. M. Huh, J. S. Choi, J. H. Lee, H. T. Song, S. Kim, S. Yoon, K. S. Kim, J. S. Shin, J. S. Suh, and J. Cheon, *J. Am. Chem. Soc.*, 2005, **127**, 5732.
53. Y. M. Huh, Y. Jun, H. T. Song, S. Kim, J. Choi, J. H. Lee, S. Yoon, K. Kim, J. S. Shin, J.-S. Suh, and J. Cheon, *J. Am. Chem. Soc.*, 2005, **127**, 12387.
54. H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, and Y. Li, *Angew. Chemie Int. Ed.*, 2005, **44**, 2782.
55. N. Guan, J. Xu, L. Wang, and D. Sun, *Colloids Surf. Physicochem. Eng. Asp.*, 2009, **346**, 221.
56. L. Zhu, H. Xiao, W. Zhang, G. Yang, and S. Fu, *Cryst. Growth Des.*, 2008, **8**, 957.
57. W. Cheng, K. Tang, and J. Sheng, *Chem. Eur. J.*, 2010, **16**, 3608.
58. D. Caruntu, G. Caruntu, Y. Chen, C. J. O. Connor, G. Goloverda, and V. L. Kolesnichenko, *Chem. Mater.*, 2004, **16**, 5527.

59. Z. Li, H. Chen, H. Bao, and M. Gao, *Chem. Mater.*, 2004, **16**, 1391.
60. Z. Li, L. Wei, M. Y. Gao, and H. Lei, *Adv. Mater.*, 2005, **17**, 1001.
61. F. Q. Hu, L. Wei, Z. Zhou, Y. L. Ran, Z. Li, and M. Y. Gao, *Adv. Mater.*, 2006, **18**, 2553.
62. F. Hu, Z. Li, C. Tu, and M. Gao, *J. Colloid Interface Sci.*, 2007, **311**, 469.
63. X. Lu, M. Niu, R. Qiao, and M. Gao, *J. Phys. Chem. B*, 2008, **112**, 14390.
64. C. Ravikumar and R. Bandyopadhyaya, *J. Phys. Chem. C*, 2011, **115**, 1380.

FIGURE CAPTIONS

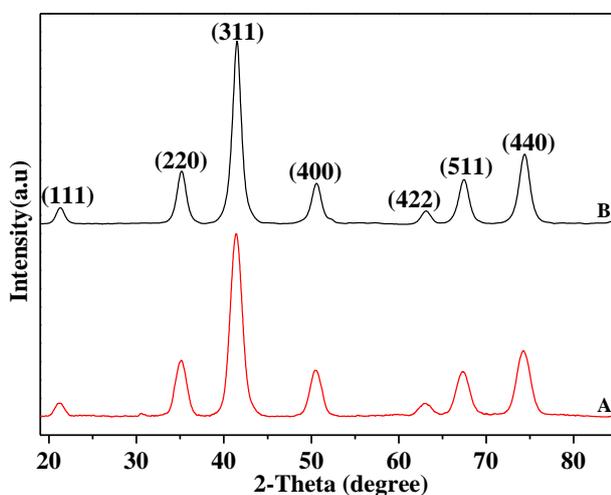


Fig. 1 The p-XRD pattern for magnetite (Fe_3O_4) nanoparticles obtained from (A) the thermolysis of $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{O}_2\text{C}^t\text{Bu})\cdot\text{HO}_2\text{C}^t\text{Bu}$ in PVP and TREG, (B) co-precipitation of Fe^{2+} and Fe^{3+} with PAH as stabiliser.

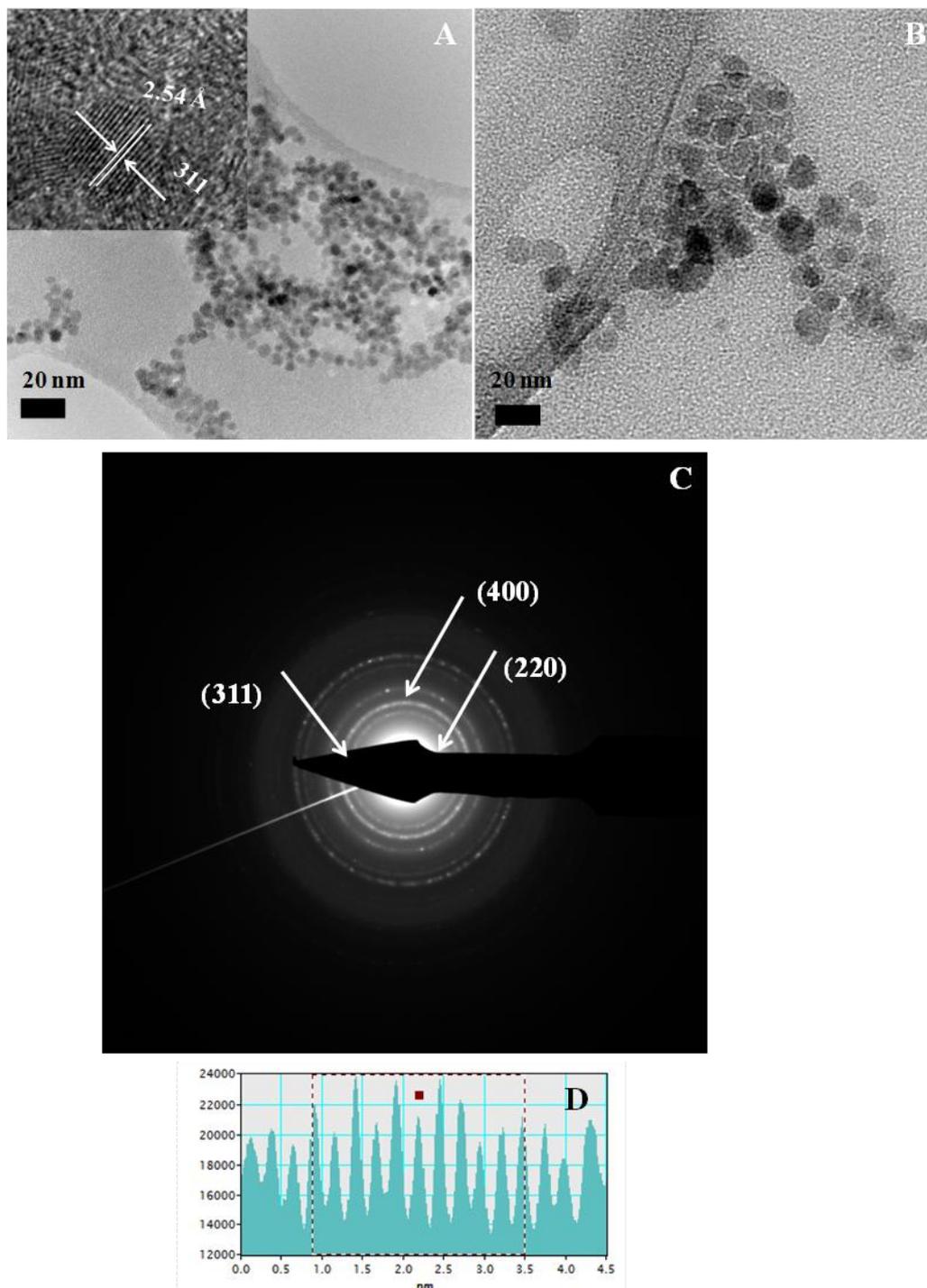


Fig. 2 (A) and (B) are TEM images obtained for magnetite (Fe_3O_4) nanoparticles obtained from the thermal decomposition and co-precipitation methods respectively. (C) SAED of (A). (D) Line profile obtained by drawing a perpendicular line across the fringes in (A) from which the d -spacing is estimated.

GC-MS ANALYSIS OF ESSENTIAL OIL EXTRACT FROM THE ROOTS OF *CARPOLOBIA LUTEA*

Osibote, Elizabeth Adejoke & Lawal Abdufatai

Chemistry Department, University of Lagos, Lagos, Nigeria.
eosibote@unilag.edu.ng

ABSTRACT

Several plants are used in folk medicine to treat infections that cause male infertility. *Carpolobia lutea* (G. Don) (Polygalaceae) is a plant used by practitioners of alternative medicine in South West Nigeria for the management of infertility gonorrhoea, gingivitis, infertility, ulcer and malaria. This study is to extract and analyze essential oil from the roots of *Carpolobia lutea*. The fresh roots were air-dried, pulverized and the essential oil extracted into hexane by hydro-distillation over 4hr period. The hexane in the extract was evaporated off and dried with anhydrous sodium sulphate. The essential oil obtained was analysed with GC model 7890 A and MS model 5975C of capillary column size 30m x 250µm x 0.25µm film thickness which was packed with HP-5MS 5% Phenyl methyl siloxane. Helium was the carrier gas at a flow rate of 1ml/min. The mass spectrometer (MS) was fitted with Chem.-Station software for processing the data. The temperature program of the column was initially 50°C held at same temperature for 17 minutes, gradually increased to 200°C at 4°C /minute and finally increased to 240°C at 15°C /minute. Mass spectra were recorded using ionization energy of 70 eV. The molecular ions detected were identified by the MS library. Some of the compounds identified in the extract are dodecanoic acid, n-hexadecanoic acid, 13-octadecenal and oleic acid. The presence of fatty acids in the essential oil may be useful for the management of bacterial and fungal infections which may be implicated in male infertility factor. Thus the plant extract may be useful in the management of male infertility factor arising from bacterial/microbial infection.

Keywords: *Carpolobia lutea*, male infertility, essential oil, analyses, herbal treatment.

INTRODUCTION

There are several medicinal plants commonly used by traditional medicine in the South-Western Nigeria to manage genitourinary infectious diseases that cause infertility in male and *Carpolobia lutea* is among. The plant *Carpolobia lutea* is a shrub or small tree about 15ft high. It is widely distributed in west and central areas of tropical Africa (Mitaine - Offer *et al.*, 2002). Its common names are Cattle stick-English, *Abekpok ibuhu* (Eket), *Ikpafum*, *ndiyan*, *nyanyanga* (Ibibio), *Agba* or *Angalagale* (Igbo) and *Egbo oshunshun* or *Egbo amureju* (Yoruba).

Practitioners of Alternative Medicine from these tribes use the root decoction in locally-made alcohol as an aphrodisiac; also for the treatment of genitourinary infections and waist pain (Etebong & Nwafor, 2009). The root decoction is also said to be useful in the treatment of internal heat.

The leaf extract of *Carpolobia lutea* is a natural source of ingredients that could aid the management of gastric ulcers, hemorrhoid, wound healing and diarrhea. The plant has been reported to possess anti-inflammatory and anti-arthritis properties; it contains triterpene saponins, possesses anti-microbial activities as well as anti-diarrhea and anti-ulcerogenic properties.

The root is used to facilitate childbirth treat worm infection, sterility, headache, and also has aphrodisiac and stimulant properties. The stem is used as chewing stick (Kayode and Omotoyinbo, 2008); the root is also used as chewing stick because of its aphrodisiac potentials.

The leaf is used traditionally among the Efik, Ibibio and Yoruba ethnic group in Nigeria in the treatment of wound and in the management of diarrhea, fever, leprosy and snake bite.

A list of plants used to manage infertility problems include *Apium graveolens* (celery), *Massularia acuminata* (Ijebu chewing stick), *Garcinia afzelii* (mangostreen), *Ficus capensis* (African mustard tree), *Euphorbia laterifolia* (little cactus) and *Cissus populnea* (*ogbolo* in Yoruba), *Phyllanthus amarus* (small leaves) (*eyin olobe*, *eyinbisowo* in Yoruba), *Sesamum radiatum* (*ewe ekuku* in Yoruba) and *Musa paradisiaca* (plantain) (Ogunlesi *et al.*, 2010; Osibote, 2013).

The main objective of this research work is to authenticate the use of the herb as profertility plant as it is being used by the practitioners of alternative medicine in South-West Nigeria.

EXPERIMENTAL

The fresh roots of *Carpolobia lutea* were obtained from Abatadu Village in Osun State. The plant was identified and authenticated by Mr Olabanji Adewole of Department of Botany; University of Lagos and voucher number LUH 5585 was assigned and the specimen deposited in the herbarium. The roots were cut into small pieces and weighed before and after air-drying in a dust free environment for 4 weeks and pulverized into semi-powdered form. The extraction of the essential oil was carried out by hydro-distillation in four hour at a stretch into hexane. The essential oil in the hexane was dried with anhydrous sodium sulphate to remove any water that may be present in the mixture. The hexane was allowed to evaporate off leaving the essential oil of *Carpolobia lutea*.

GC-MS Analysis of the Essential Oil

The essential oil obtained was analysed with GC model 7890 A and MS model 5975C (Agilent Technologies) of capillary column size 30m x 250 μ m x 0.25 μ m film thickness which was packed with HP-5MS 5% (PhenyI methyl siloxane). Helium was the carrier gas at a flow rate of 1ml/min. The mass spectrometer (MS) was fitted with chem.-station software for control of the program and processing of the data. The extract was diluted with hexane prior to the injection into Gas Chromatography. The mass spectrometer (MS) was fitted with Chem.-Station software for processing the data. The temperature program of the column was initially 150 $^{\circ}$ C held at same temperature for 17 minutes, gradually increased to 200 $^{\circ}$ C at 4 $^{\circ}$ C /minute and finally increased to 240 $^{\circ}$ C at 15 $^{\circ}$ C /minute. Mass spectra were recorded using ionization energy of 70 eV. The molecular ions detected were identified by the MS library.

RESULTS

The result of the analysis of the GC-MS analysis of the essential oil is hereby presented in Figure 1 and Table 1.

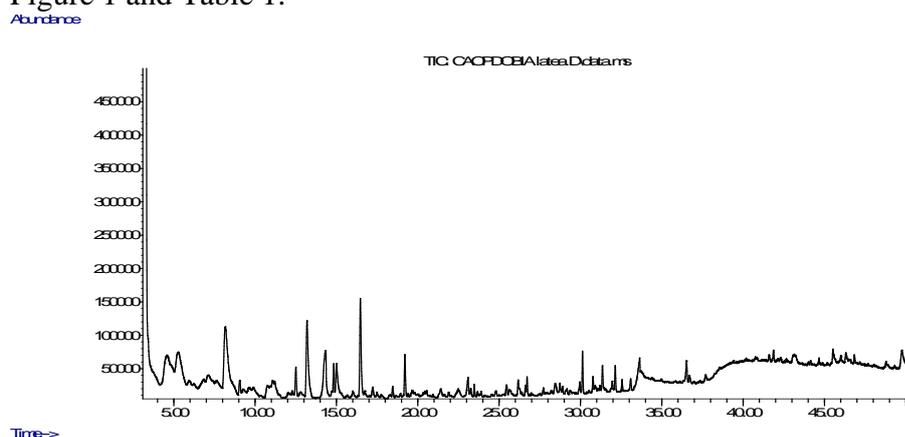


Figure 1: GC-MS chromatogram of the essential oil from the roots of *Carpolobia lutea*

Table 1: The constituents present in the GC-MS analysis of the essential oil from the dried roots of *Carpolobia lutea* with their possible medicinal/environmental applications

S/N	R _t (Min)	Name of Compound	Abund (%)	Medicinal / Environmental Application
1.	4.57	1-ethyl-3-methylBenzene	3.39	As fragrance agents ⁽³⁾
2.	8.19	Nonanal	22.90	As flavour and fragrance agents Used in food flavouring (NIST, 1969)
3.	12.51	2,4–Nonadienal	3.11	It is mainly used as spices in the preparation of meat and poultry flavor
4.	23.10	Dodecanoic acid	2.24	Antifungal and antibacterial properties (McGraw <i>et al.</i> , 2002, Sujatha <i>et al.</i> , 2014)) Increases total serum cholesterol, (the ‘good’ blood cholesterol (Nakatsuji <i>et al.</i> , 2009).
5.	26.72	Oxirane, tetradecyl-	2.24	It is used as a chemical intermediate for surface-active agents, fabric softeners, cosmetic ingredients, textile finishes and synthetic waxes ⁽⁶⁾
6.	31.35	13 – Octadecenal	2.29	It is a sex pheromone component of the rice stem borer (Lepidoptera) ⁽⁷⁾
7.	32.14	Pentadecanoic acid 14 – methyl ester	2.12	Antibacterial and anti-fungi properties. Anti-trypanosomal compounds (Agoramoorthy <i>et al.</i> 2007)
8.	32.14	Hexadecanoic acid, methyl ester.	2.12	Anti-oxidant, flavor and Hypocholesterolemic. Anti-fungal and anti-bacterial properties Agoramoorthy <i>et al.</i> 2007)
9.	33.64	n-Hexadecanoic acid	2.41	Anti-microbial and anti-oxidant properties anti-inflammatory, anti-fungal and anti-bacterial properties (Sujatha <i>et al.</i> , 2014; McGraw <i>et al.</i> , 2002)
10	36.52	Oleic acid	2.52	Oleic acid (C 18:1) has been found to be fungistatic against a wide spectrum of saprophytic moulds and yeasts (McGraw <i>et al.</i> , 2002)

Some of the compounds identified from the essential oil extract of *Carpolobia lutea* were Nonanal (22.90%), 2,4–Nonadienal (3.11%), Dodecanoic acid (2.24%), 13 – Octadecenal (2.29%), pentadecanoic acid, 14-methyl ester (2.12%), n-hexadecanoic acid (2.41%) and oleic acid (2.52%). Some of these compounds have medicinal applications.

DISCUSSION

The constituents identified in the essential oil sample included saturated fatty acids namely n-hexadecanoic acid, dodecanoic acid, pentadecanoic acid, 14 methyl ester and hexadecanoic acid, methyl ester and unsaturated fatty acids like oleic acid. n-Hexadecanoic acid (Palmitic acid) has antimicrobial and antioxidant properties. It is an inhibitor of phospholipase A(2), hence, an anti-inflammatory agent. Dodecanoic acid (Lauric acid) has an antimicrobial property against propionic-bacterium acnes. It has a therapeutic potential for inflammatory acne vulgaris. It increases total serum cholesterol (the “good” blood cholesterol) (Nakatsuji *et al.*, 2009).

Pentadecanoic acid, 14 methyl ester and hexadecanoic, methyl ester (palmitic acid methyl ester) have antibacterial and antifungal activities. Pentadecanoic acid, 14 methyl ester is an anti-trypanosomal compound. Hexadecanoic acid, methyl ester is an antioxidant and

Hypocholesterolemic. Unsaturated fatty acids have antimicrobial and anti-inflammatory properties (Li *et al.*, 2004). Oleic acid has been found to be fungistatic against a wide spectrum of saprophytic moulds and yeasts ((Davidson, *et al.*, 1999; McGraw *et al.*, 2002). anti-cancer, anti-tumor, antioxidants (Osibote, 2013). Antioxidants are an inhibitor of the process of oxidation, even at relatively small concentration and thus have diverse physiological role in the body – the potential to reduce oxidative stress related diseases. n-Hexadecanoic and dodecanoic acid present in the essential oil of the root of *Carpolobia lutea* may contribute to the pro-fertility effect of the plant- they are fatty acids and have antimicrobial potentials. It has been reported that infections could be implicated in male infertility factor.

The constituents with antibacterial, antifungal properties can help reduce infertility by removing causes due to bacterial infections; those with antitumor properties may help to remove abnormal cells from the system. The anti-inflammatory agents may treat other health problems different from infertility and the antioxidants can be scavenger for abnormal cells.

Therefore the presence of these constituents in the essential oil from the plant may be useful for the management of the male infertility factor thus may jointly corroborate the use of the plant as a pro-fertility herb.

REFERENCES

- Agoramoorthy G., Chandrasekaran M., Venkatesalu M. J., Itsu (2007) “Antibacterial and antifungal properties of pentadecanoic acid, 1 4-methylester. *Braz. J. Microbial* 38
- Ajibesin, K. K., Ekpo, A. B., Bala, D. N., Essien, E. E., Adesanya, S. A. (2007). Ethnobotanical survey of Awa Ibom State of Nigeria. *J. Ethnopharmacology* 115, 387-408
- Bero J., Ganfon H., Jonville M.C., Frédérick M., Gbaguidi F., DeMol P., Moudachirou M., Quetin-Leclercq J. (2009). *In vitro* antiplasmodial activity of plants used in Benin in traditional medicine to treat malaria. *J. Ethnopharmacology* 122 (2009) 439– 444
- Davidson, W. S., Saxena, R. K. & Gupta, R. (1999a) The Fungistatic Action of Oleic Acid. *Current Science-Bangalore* 76, 1137-1139.
- Etebong, E. & Nwafor, P. 2009 “*In-vitro* antimicrobial activities of extract of *Carpolobia lutea* root,) *Pak. J. Pharm. Sci.* 22 (3); 335-338
- Kayode J & Omotoyinbo, MA. (2008). Cultural erosion and biodiversity: conserving chewing stick knowledge in Ekiti State, Nigeria. *African Scientist* 9 (1) 41-51.
- Lucky Legbosi Nwidu, Eduardo Maffud Cilli, Wagner Vilegas, “Amino acid anti-oxidant and iron profiles of *Carpolobia* leaf, (2012), *Tropical J. Pharm. Res.* 11; 807-813
- Mcgraw, L. J, Jager, A. K, Van Staden, J (2002). Isolation of Antibacterial Fatty Acids From *Schotia Brachypetala*. *Fitoterapia*, 73: 431-433.
- Mitaine-Offer A.C., Miyamoto, T., Khan, I.A., Delaude C and Lacaille-Dubois, M.A. (2002). Three new triterpene saponins from two species of *Carpolobia*. *J. Nat. Prod.* 65: 553–557.
- Nakatsuji T., Kao M. C., Fang J. Y., Zouboulis C. C., Zhang L., Gallo R. L., Huang C. M., (2009) “Antimicrobial properties of lauric acid against propionibacterium acnes, its therapeutic potential for inflammatory acne vulgaris”, (2009), *J. Invest. Derma.* 129; 2480-2488
- Nwidu, L. L., Nwafor, P. A. and Vilegas, W. (2012) Antimicrobial Activity of *Carpolobia Lutea* Extracts and Fractions. *Afr J Tradit Complement Altern Med.* 9(3):323-328. doi.org/10.4314/ajtcam.v9i3.4
- Ogunlesi, M., Okiei, W. and Osibote, E. A. (2010). Analysis of the essential oil from the leaves of *Sesamum radiatum*, a potential medication for male infertility factor, by gas chromatography – mass spectrometry. *African Journal of Biotechnology* Vol. 9(7), pp. 1060-1067. ISSN 1684–5315 © 2010 Academic Journals
- Osibote E.A.S. (2012) “Chemical analysis and bioassays of extract from selected tropical profertility plant”. Ph.D Thesis

Sujatha, Karthika, Sivakamasundari, Mariajancyrani and Chandramohan (2014) GC-MS Analysis of Phytochemicals and Total Antioxidant Activity of Hexane Extract of *Sinapis alba* International Journal of Pharmaceutical, Chemical and Biological Sciences 4(1), 112-117 ISSN: 2249-9504

EVALUATION OF ASCORBIC ACID CONTENT OF FRESH FRUIT DRINKS, PACKAGED FRUIT JUICES AND DRINKS IN THE NIGERIAN MARKET

***Oyeyiola, O.A & Adetunde, O.T**

Department of Chemistry
University of Lagos Akoka, Yaba, Lagos, Nigeria
*aaderonke8@yahoo.com; aoyeyiola@unilag.edu.ng

ABSTRACT

Ascorbic acid (Vitamin C) is usually affected by availability of fruits and vegetables due to seasonal variations. To ensure its availability all year round, fruits juices and drinks are often preserved and packaged. This study compared quality of various packaged fruit juices and drinks sold in the Nigerian market with some fresh fruit juices. The pH of the juices were measured by the potentiometric method while their ascorbic acid content were measured using the titrimetric method. Fresh orange, mango, pineapple, pawpaw and watermelon juices had ascorbic acid concentration of 80mg/100ml, 76mg/100ml, 50mg/100ml, 44mg/100ml and 42mg/100ml respectively, while packaged orange, pineapple, mango and apple juices had concentrations range of 10.0 - 38.6mg/100ml, 5.6 -25.2mg/100ml, 15.3-17.3mg/100ml and 4.4 -15.0mg/100ml respectively. Apple, mango, mixed fruits, orange, pineapple and strawberry packaged fruit drinks had ascorbic acid content in the range of 3.7 - 10.9 mg/100ml, 6.9 - 7.6 mg/100ml, 1.8 - 12.16 mg/100ml, 0.9 - 12.2 mg/100ml, 2.5 - 25.7mg/100ml and 6.7 - 14.8mg/100ml respectively. The pH values of all the drinks and juices samples in this study had values between 2.6 and 4.8. This study showed that higher amounts of ascorbic acid are derived from fresh fruit juices followed by the packaged fruit juices and then the packaged fruit drinks. Over 200ml (children) and 400ml (adult) of the packaged fruit juices and drinks will be required to meet the Recommended Dietary Allowances (RDAs) of 45mg/day, 75mg/day and 95mg/day for children, women and men respectively while about 100ml of fresh juice will meet the RDAs for all.

Keywords: Ascorbic acid, Fruit juice, Recommended Dietary Allowances,

INTRODUCTION

Ascorbic acid sometimes called vitamin C is of both synthetic and natural origin. Natural ascorbic acid is found in a wide variety fresh fruits and vegetables (Moffat, 1986) especially citrus fruits such as oranges etc. Factors that affect the vitamin C contents of citrus fruits include, production factors and climate conditions, maturity state and position on the tree, type of fruits (species and variety) handling and storage, type of container (Naggy, 1980).

L-enantiomer of ascorbic acid is a stable solid that does not react with air; however, it is readily oxidized on exposure to air, light and when in aqueous solution. The product of this oxidation is dehydroascorbic acid. Dehydroascorbic acid ($C_6H_6O_6$) and ascorbic acid ($C_6H_8O_6$) together give the total amount of vitamin C. However, dehydroascorbic acid is not readily absorbed (bio available) across the intestinal mucosa and supplemental dehydroascorbic acid has little antiscorbutic activity (Johnston and Hale, 2002). It also gradually darkens upon exposure to light, however slight coloration does not impair the therapeutic activity of ascorbic acid injection (Boostani et al., 2004, Mason, 2007).

Ascorbic acid is odourless with pleasant and sharp acid taste. It is soluble in water, sparingly soluble in ethanol and practically insoluble in chloroform and ether. Ascorbic acid has pka value of 4.2 and 11.6. A solution of ascorbic acid in water has pH of 2.2 - 2.5 (i.e. strongly acidic). Ascorbic acid exists as colorless white to yellowish crystalline powder with a melting point of

about 190⁰C and boiling point is 553⁰C while the density is 1.694g/cm³ (Moffat, 1986). Vitamin C is an antioxidant, along with vitamin E, beta-carotene and other plant – based nutrients. Antioxidants block some of the damage caused by free radicals, which occur naturally when our bodies transform food into energy. The build-up of the free radicals overtime may be largely responsible for the ageing process and can contribute to the development of health conditions such as cancer, heart disease, and arthritis (Laight et al., 2000). Getting enough vitamin C an anti oxidant, from diet may help reduce the risk of developing some of these conditions (Hamrick and Counts, 2008). Metabolizing of carbohydrate, resisting infections and healing the body by immune system require certain quantities of ascorbic acid (Gritsanapun et al., 2002). Vitamin C cannot be synthesized by human body and must be consumed regularly. Severe form of vitamin C deficiency is known as scurvy (Lykkesfeldt, 2000). Deficiencies of vitamins are classified as either primary or secondary. A primary deficiency occurs when an organism does not get enough of the vitamins in its food while secondary deficiency may be due to an underlying disorder that prevents or limits the absorption or use of the vitamin, due to a “lifestyle factor”, such as smoking, excessive alcohol consumptions, or the use of medications that interfere with the absorption or uses of the vitamin (Venturi et al., 2000). The Federal Nutrition Board of the United States (FBN) has set recommended dietary allowance in mg /day for humans as 40 to 120mg/day but not more than 2000mg/day (upper limits) (IOM, 2000). Established upper limits of vitamin C intake for food and supplements refer levels above which adverse effect may occur.

Ascorbic acid an important food component for human nutrition is usually affected by availability of fruits and vegetables due to seasonal variation. To ensure its availability, all year round, fruits and vegetables are often preserved and packaged for sale to the public in form of juices and drinks. American Academy of Pediatrics (AAP) has defined fruit juice as 100% concentrate of fruit extract without the addition of sweetener and drinks as containing less than 100% concentrate. Drinks are also referred to as beverages or cocktails. They are usually calorically sweetened and contain small percentage of concentrate or fruit flavours (Gupta and Gupta 2008). Fruit juice is produced by the macerating or mechanically squeezing fruit or vegetable without the application of heat or solvents (Saha et al, 2011). Several techniques like high performance liquid chromatography (HPLC) (Anna et al, 2002, Saeed et al 2008), micellar electrokinetic capillary chromatographic method (MECC) (Catherine and Craige, 1995), electrophoresis with electrochemistry detection (CE-ED) developed by Ting et al (2007) and the classical titrimetry (Kabasakalis et al, 2000) have been used in the determination of Vitamin C (ascorbic acid). The titrimetric method is based on iodometry.

In Nigeria several brands of packaged fruit juice and drinks exists. Insufficient nutritional information is usually provided. Even when given, vitamin C concentration and pH values are usually not given. Vitamin C is recommended by medical practitioners for treatment and prevention of scurvy, pneumonia. Plenty of vitamin C also helps in reducing the toxicity. Low pH of drinks has also been linked to dental erosion. (Cheng, et al 2009). The aim of this study is to compare the pH and concentration of ascorbic acid of various packaged fruit juices and drinks sold in the Nigerian market with some fresh fruit juices in other to determine how the products meet consumer’s daily requirement for vitamin C.

METHODS

Sampling

Five different fruits namely; Orange (*Citrus sinensis*), Pineapple (*Ananas comosius*), Pawpaw (*Carica papaya*), Mango (*Magnifera indica*), and Water melon (*Citrullus vulgaris*) were purchased from Oyingbo market in Lagos state, Nigeria. These fruits were selected based on their availability and the choice of market was based on its central location and because it is

often visited by majority of the city resident for fruits. Purchased fruits were washed, peeled and chopped into small pieces and juiced with the aid of a juice extractor.

Packaged fruit juices and drinks of different fruit types and brands, were purchased from different super markets Lagos state, Nigeria. The various samples were purchase in good conditions with the expiring date still valid before it was analyzed. . The various packaged drinks and juices brands and types are as shown in Table1.

Table 1: Lists of packaged fruit juices and drinks sampled

Sample Types	Packaged Fruit Drinks	Package (cartoon or sachet) Volume (ml)	Packaged Fruit Juices (package volume;1litre)
Apple	Capri-sona	200	Ceres
	California	200	Frutta
	Healthilife	200	Chivita
	Royal fruta	200	Fumman
	Vita-vite	200	Fresh
	Zico	200	5alive
			Don Simon
Tropika			
Mango	Capri-sona	200	Frutta
	Zico	200	Chi Exotic
Mixed fruits	Capri-sona	200	
	California	200	
	Chi-vita active	230	
	Happy hour	200	
	Healthilife	200	
	Royal fruta	200	
	Vita-vite	200	
Orange	Caprisone	200	Ceres
	Healthilife	200	Frutta
	Royal fruta	200	Chivita
	Piko	200	Fumman
	Vita-vite	200	Fresh
			5 Alive
			Don Simon
			Topika
Healthi life			
Pineapple	Caprisone	200	Ceres
	Healthilife	200	Frutta
	Yoju	200	Chivita
			Fumman
			Fresh
			Tropika
Strawberry	Caprisone	200	
	Royal fruta	200	
	Zico	200	

Determination of ascorbic acid and pH in the fruit juices and drinks

Ascorbic acid content was determined as in Hesseini et al (2013) and Njoku et al (2011), using the oxidation-reduction titration method. Briefly, 50ml of sample and 25ml of standard KIO₃ solution were mixed together. To this mixture, 2g of potassium iodide, 0.1g of sodium

bicarbonate and 5ml of 0.5M sulphuric acid solution were added to liberate iodine. Standardised sodium thiosulphate was titrated against the generated iodine to pale straw colour. Starch indicator was introduced and the solution was titrated to a colourless endpoint. This was repeated for all the fifty six samples (fresh juice (5), packaged juice (24), and packaged fruit drinks (26)). The titration for every sample was done in triplicates. Calibrated pH meter (metrolum 826 pH mobile) was used to take the pH readings for aliquots of samples, as soon as the packages were opened while for the fresh juices the pH values were taken as soon as they were prepared. The pH measurements were also carried out in triplicates.

RESULTS

Vitamin C (ascorbic acid) concentration of the different juices and drinks were determined and the pH of the different juices and drinks were determined and the results are as seen in Tables 1, 5 and 6. Fresh fruit juices had ascorbic acid content of 42mg/100ml to 80mg/100ml and pH value in the range of 3.6 to 5.4. Ascorbic acid content of the packaged drinks and juices were lower than the fresh juices. Orange, pineapple, mango and apple packaged fruit juices from different brands had concentrations range of 10.0 - 38.6mg/100ml, 5.6 -25.2mg/100ml, 15.3-17.3mg/100ml and 4.4 -15.0mg/100ml respectively. The concentration of ascorbic acid content in different brands of apple, mango, mixed fruits, orange, pineapple and strawberry packaged fruit drinks were in the range of 3.7 - 10.9 mg/100ml, 6.9 – 7.6 mg/100ml, 1.8 – 12.16 mg/100ml, 0.9 – 12.2 mg/100ml, 2.5 – 25.7mg/100ml and 6.7 – 14.8mg/100ml respectively. The pH values of fresh orange, mango, pineapple, pawpaw and watermelon juices were 3.6, 4.2, 3.9, 5.4, and 4.2 respectively while orange, pineapple, mango and apple packaged fruit juices from different brands had values in the range of 3.6 – 4.6, 3.0 – 4.6 , 4.0 - 4.1 and 2.6 – 4.8. The pH value for different brands of apple, mango, mixed fruits, orange, pineapple and strawberry packaged fruit drinks were in the range of 2.9- 4.0, 2.9 -3.1, 2.80 – 4.2, 3.1 – 4.0, 2.7 - 3.6 and 3.4 -3.8 respectively.

Table 2: Result of pH and ascorbic acid content of fresh fruit juices

Fresh fruit juices	pH	Ascorbic acid (mg/100ml)	Ascorbic acid in 250ml	Ascorbic acid in 1litre
Mango	4.2	76	190	760
Orange	3.6	80	200	800
Pineapple	3.9	50	125	500
Pawpaw	5.4	44	110	440
Watermelon	4.2	42	105	420

Table 3: Result of pH and ascorbic acid content of packaged fruit Juices

Sample Types	Packaged Fruit Juices (1litres)	pH	Ascorbic acid (mg/100ml)	Ascorbic acid in two cups (500ml)	Ascorbic acid in 4 cups (1litre)
Apple	Ceres	4.0	21	105.5	211
	Frutta	4.0	15	75	150
	Chivita	3.5	5	25	50
	Fumman	3.2	8	37.5	75
	Fresh	2.6	4	22	44
	5alive	3.5	13	67	134
	Don Simon	3.7	20	101.5	203
	Tropika	4.8	6	30.5	61
Mango	Frutta	4.0	15	76.5	153
	Chi Exotic	4.1	17	86.5	173
Orange	Ceres	3.9	32	158	316
	Frutta	4.1	22	109	218
	Chivita	4.2	10	50	100
	Fumman	3.5	12	57.5	115
	5 Alive	3.9	24	122	243
	Don Simon	4.0	39	193	386
	Topika	4.6	14	70	140
	Healthi life	3.6	13	62.5	125
Pineapple	Frutta	3.6	21	106	212
	Chivita	4.0	7	33.5	67
	Fumman	3.8	10	50	100
	Fresh	3.0	6	28	56
	Tropika	4.6	8	38	75

Table 4: Result of pH and ascorbic acid content of packaged fruit drinks

Sample Types	Packaged Fruit Drinks	pH	Ascorbic acid (mg/100ml)	Ascorbic acid in (200ml) 1 pack	Ascorbic acid 5 packs (1litre)
Apple	Capri-sone	4.0	11	22	109
	California	3.2	11	22	109
	Healthylife	3.4	8	15	77
	Royal fruta	3.9	7	13	65
	Vita-vite	4.0	5	11	54
	Zico	3.0	4	7	37
	Capri-sone	2.9	6	12	60
Mango	Zico	3.1	8	15	76
	Capri-sone	3.5	7	15	74
Mixed fruits	California	4.2	7	13	65
	Chi-vita active	4.0	13	29	145
	Happy hour	2.8	2	9	46
	Healthilife	3.7	2	7	35
	Royal fruta	3.0	7	26	130
	Vita-vite	3.6	2	9	46
	Caprisone	3.3	12	49	243
Orange	Healthilife	3.1	1	4	18
	Royal fruta	3.5	4	15	74
	Piko	3.2	1	4	18
	Vita-vite	4.0	3	12	60
	Caprisone	3.6	2	10	49
Pineapple	Healthilife	3.6	3	13	67
	Yuju	2.7	26	103	514
	Caprisone	3.8	7	27	134
Strawberry	Royal fruta	3.4	14	57	285
	Zico	3.6	3	10	51

DISCUSSION

Generally the freshly prepared juices had higher amount of ascorbic acid compared to all the packaged juices and drinks. The package juices had more ascorbic acid compared to the drinks as shown in table 2, 3 and 4. This was consistent with the findings of Lee and Kader (2000), Johnston and Hale (2005) and Njoku et al (2011). Fresh juices were found to contain more vitamin C or ascorbic acid content compared to stored juices and drinks. The reduction may attributed to storage method, temperature at which the product were kept and the kind of containers (Njoku et al., 2011) especially containers that allowed oxygen get into the fruit juice. Fresh fruit juice from orange had the lowest average pH value of 3.6 but the highest ascorbic acid content of 80mg/100ml of all the freshly prepared juices. Ascorbic acid content in the fruit juices followed the order orange (80mg/100ml) > mango (76mg/100ml) > pineapple (50mg/100ml) > pawpaw (44mg/100ml) > watermelon (42mg/100ml). This order is similar to the findings of Akinwale, (2000), (cashew apple> orange> mango >pineapple) whose average values of vitamin C in 100ml juices of cashew apple, orange, mango, pineapple were 203.5mg,

54.7mg, 30.9mg and 14.7mg respectively. The orange packaged juices of the different packaged juices also consistently had higher ascorbic acid content compared to other type of packaged juice of the same brand as in the table 3.

Table5: Recommended Dietary Allowances (RDAs) for Vitamin C (IOM, 2000)

Age	Male	Female	Pregnancy	Lactation
0–6 months	40 mg*	40 mg*		
7–12 months	50 mg*	50 mg*		
1–3 years	15 mg	15 mg		
4–8 years	25 mg	25 mg		
9–13 years	45 mg	45 mg		
14–18 years	75 mg	65 mg	80 mg	115 mg
19+ years	90 mg	75 mg	85 mg	120 mg
Smokers	Individuals who smoke require 35 mg/day more vitamin C than non smokers.			

* Adequate Intake (AI)

Table 6: Tolerable Upper Intake Levels (ULs) for Vitamin C (IOM, 2000)

Age	Male	Female	Pregnancy	Lactation
0–12 months	Not possible to establish*	Not possible to establish*		
1–3 years	400 mg	400 mg		
4–8 years	650 mg	650 mg		
9–13 years	1,200 mg	1,200 mg		
14–18 years	1,800 mg	1,800 mg	1,800 mg	1,800 mg
19+ years	2,000 mg	2,000 mg	2,000 mg	2,000 mg

*Formula and food should be the only sources of vitamin C for infants.

The vitamin c content in a cup (250ml) (table 2) of each of the various fresh juices was found to contain sufficient vitamin C to meet the 45, 75 and 90mg/day RDA (table 5) for children, women and men respectively (IOM, 2000). More than 8cups (2000ml) of the fresh jucies will be required to exceed the UL of vitamin C (table 6) for both adults (male and female) and children. The various packaged juices required a minimum of two cups (500ml) (table 3), while the drinks required a minimum of four cups which is more than four pack/sachets (1litre) to provide the RDA for all groups (children and adults) as illustrated in table 4 except for Yoju pineapple drink which had up to 103mg in two packs of (400ml) which is 129mg in two cups (500ml). Ceres packaged juice had the highest amount of vitamin C of the apple and orange (21 and 32 mg/100ml) packaged juices sampled while for the sampled pineapple packaged juices, Frutta had the highest amount of vitamin C. A moderate daily consumption of two cups (250ml each) of the apple (Ceres, don Simon), four of the orange (Ceres, Frutta, 5 Alive and Don Simon) and one of the pinapple (Frutta) packaged juices will provide the WHO recommended vitamin C RDA for all age groups (45, 75 and 90mg/day for children, women and men respectively) as in table 5 and 6. Some of the packaged juices though contained less than 90mg in two cups had up to 75mg (apple Frutta, pinnapple Frutta, pineapple Chi Exotic) which will provide enough vitamin C RDA for women and children. Pineapple Fumman, orange Healthi life, orange Topika, Orange Fumman, orange Chivita and apple 5 Alive though had less than 90mg of vitamin C in two cups had up to 45mg in two cups and upto 90mg in four cups (1litre or one pack) which will provide the vitamin C RDA of 45mg/day for children and 90mg/day for adults respectively. Some of the

packaged juices such as apple chivita, apple Fresh, apple Fumman, apple Tropika, pineapple Fresh, pineapple Chivita, had less than 90mg even in 1litre (four cups) which implied that consumers will require more than four cups or one pack to meet the RDA. From the results, packaged fruit juices are useful as food supplements to prevent vitamin C deficiency. Since vitamin C is a water soluble vitamin, not stored in significant amounts because it is easily excreted from the body. Hence good sources of vitamin C are therefore required regularly to replenish body supplies for metabolic processes (Gritsanapun et al, 2002). From this study packaged fruit juices of Ceres, don Simon, frutta and 5-alive had higher vitamin C content, with their orange type having the highest amount of vitamin C. Two cups (500ml) of Ceres, Don Simon, frutta, and 5-alive are therefore recommended to the public.

The drinks sampled here because of the small package volume (200 to 230ml) are usually part of children launch packs hence consumed more by children in Nigeria. The vitamin C of each pack for the different drinks were not sufficient to provide the RDA of 45mg/day except in pineapple Yoju drink which had 52mg of ascorbic acid in it. More brands of mixed fruit drinks were analysed compared to other types of fruit drinks. This was due to their availability in market during sampling. The availability of mixed fruits in various brands may be due to harnessing of flavour and colour when different fruits are blended (Rutledge, 2001).

pH which is a measure of the hydrogen ion concentration, has been found to be related with the erosive capacity of fruit juices and beverages. Beverages and juices with lower pH values generally have greater erosive effects on tooth structure (Bamise and Bamise , 2007, Dawes, 2003). The results from this study indicate that all the freshly prepared juices, packaged juices and drinks evaluated had pH values below the critical pH (5.5) of enamel dissolution (Bamise and Bamise , 2007) but were higher than pH 3, below which a great potential for erosion exist (Dawes, 2003) except pineapple Yoju drink (2.7) and Happy hour (2.8).

CONCLUSION

This study showed higher amounts of ascorbic acid are derived from fresh fruit juices followed by the packaged fruit juices and packaged fruit juices had more ascorbic acid compared to the packaged fruit drinks. The concentration of ascorbic acid in the juices and drinks varied greatly from one type to the other even for the same brand. Over 200ml (children) and 400ml (adult) of the packaged fruit juices and drinks generally will be required to meet the Recommended Dietary Allowances (RDAs) of 45mg/day, 75mg/day and 95mg/day for children, women and men respectively while about 100ml of fresh juice will meet the RDA for both children and adults (men and women).

REFERENCES

- Anna, R., Ada, B., Sabrina, V. and Paola, E. (2002), Evaluation of sampling and extraction procedures for the analysis of ascorbic acid from pear fruit tissue. *Journal of Food Chemistry* 77 :257 – 263.
- Akinwale, T.O 2000. cashew apple juice: it is use in fortifying nutritional quanlity of some tropical fruit. *European food Research and Technology* 211(3)205-207.
- Bamise, C and Bamise O (2007). Quantifying the acidic content of commercial yoghurt drinks in Nigeria. *The Internet Journal of Dental Science*. 6 (1).
- Boostani, M.F., Hamidi, Z.E., and Sahari, M.A. (2004), Effect of low temperature on the ascorbic acid content and quality characteristics of frozen strawberry. *Food Chemistry*, 86:357 – 363.
- Catherine, T.O., and Craige, T.V. (1995), A rapid method for determination of total L – ascorbate. *Food chemistry*, 53:43 – 50.

- Cheng, Ran; yang, Hui, Shao, Mei-ying, Hu, Tao, Zhou, Xue-dong, (2009). Dental erosion and severe tooth decay related to soft drinks: a case report and literature review. *Journal of Zheijiang university science B* 10(5)395-399.
- Dawes, C (2003), What is the critical pH and why does a tooth dissolve in acid? *Journal of Canadian Dental Association*. 69(11):722–4
- Gritsanapun, W., Nilkamhank, S., Paochom, A., and Suntorusuk, L. (2002), Quantitation of Vitamin C content in herbal juice using direct titration. *Journal of Pharmaceutical Biomedicine Analytical* 28:849 – 855.
- Gupta, H and Gupta, P (2008), Viewpoint: Fruit Drinks How Healthy and Safe? *Indian paediatrics*, 45; 215-217
- Hamrick, I., and Counts, S.H., (2008), Vitamin and Mineral Supplements. *Wellness and Prevention*, 35(4): 729 – 747.
- Hesseini, S.M., Bahri, M.H., Rashidi, M and Niyazadeh, M (2013), Interactive Effects of Chemicals Materials Application and Storage Periods on Quality of Ambient Stored Lettuce. *Middle-East Journal of Scientific Research* 13(2); 248-253.
- IOM (2000). Food and Nutrition Board of the Institute of Medicine (IOM). Dietary Reference Intakes for Vitamin C, Vitamin E, Selenium, and Carotenoids. Washington, DC: National Academy Press.
- Johnston, C. S and Hale, J. C., (2002). Stability of Ascorbic Acid in Commercially Available Orange Juices. *Journal of the American Dietetic Association*. 102(4); 525–529
- Johnston, C. S and Hale, J. C., (2005). Oxidation of ascorbic acid in stored orange juice is associated with reduced plasma vitamin C concentrations and elevated lipid peroxides. *Journal of the American Dietetic Association*. 105(1): 106–109
- Kabasakalis, V., Siopidou, D., and Moshatou, F., (2000). Ascorbic acid content of commercial fruit juices and its rate loss upon storage. *Food Chemistry*, 70: 326 – 328.
- Laight, D.W., Carrier, M.J., and Anggavg, E.E. (2000), Antioxidants, diabetes and endothelial dysfunction. *Cardio-vascular. Resource*, 47: 457 – 464.
- Lee, S.K and Kader A.A., (2000), Preharvest and postharvest factors influencing vitamin C content of horticultural crops. *Postharvest Biology and Technology*, 20 (2000) 207 – 220
- Lykkesfeldt, J., Christen, S., Wallock, L.M., Chang, H.H., Jacob, R.A., and Ames, B.N. (2000). Ascorbate is depleted by smoking and replete by moderate supplementation; a study in male smokers and non-smokers with matched dietary antioxidant intakes. *American Journal of Clinical Nutrition*, 71(2): 530 – 536.
- Mason, J.B., (2007). Vitamins, trace minerals, and other micro nutrients. In: Goldman L, Ausiello D., eds, Cecil Medicine. 23rd ed. Philadelphia, Pa: Saunders Elsevier. Pp. 237.
- Moffat, A.C., (1986). Clark's Isolation and identification of drugs in pharmaceuticals, body fluids and post – mortem material. 2nd edition, pharmaceuticals, press, London, Pp. 105 – 140.
- Naggy, S., (1980). Vitamin c. contents of citrus fruits and their product: A review, *Journal of Agriculture and Food Chemistry*, 28: 8 – 18.
- Njoku, P.C, Ayuk, A.A and Okoye, C.V., (2011) Temperature Effects on Vitamin C Content in Citrus Fruits. *Pakistan Journal of Nutrition* 10 (12): 1168-1169.
- Rutledge, P. (2001). Production of non fermented fruit products. In: Arthey D, Ashurst PR, editors. Fruit processing: nutrition, products, and quality management. *Gaithersburg, Md.: Aspen Publishers. pp 85–109.*
- Saha, D., Hait, M., Patanwar, M., & Tamrakar, A., (2011). Studies on Surface Tension of Selected Juice Formulation by Drop Number Method Using Traube's Stalagmometer Technique. *Bulletin of Pharmaceutical Research*, 1(3);1-3.

- Saeed, N., Faezeh, K., Fatemeh, M., Atyeh, R., Armin, A., and Soheila C. (2008). Extraction and Quantitative determination of ascorbic acid during different maturity stages of Rosa Carina L. Fruit. *Journal of Food Composition and Analysis* 21: 300 – 305.
- Ting, W., Yueqing, G., and Jiannong, Y. (2004). Determination of flavonoids and ascorbic acid in grapefruit peel and juice by capillary electrophoresis with electrochemical detection. *Food Chemistry*, 100: 1573 – 1579.
- Venturi. S., Donati, F.M., Venturi, A., and Venturi, M. (2000). Environmental Iodine deficiency: A challenge to the evolution of terrestrial life. *Journal of the American Thyroid Association*, 10(8): 727 – 729.

ON THE CROSS CUTTER DESIGN PATTERN AND CONCURRENT PROGRAMMING

A.U.Rufai, E.P.Fasina, & C. O. Uwadia

Department of Computer Sciences, University of Lagos, Nigeria.

arufai@unilag.edu.ng

ABSTRACT

We present a novel design pattern as an alternative approach at separating crosscutting concerns in concurrent programming. The aspect-oriented programming paradigm has gained general acceptance in the software engineering community in separating crosscutting concerns. However it is characterized by the twin attributes of obliviousness and quantification which remain contentious issues in the community. These issues (obliviousness and quantification) sacrifice program understanding, modularity and control. Information Communication Technology (ICT) infrastructure is central to development, health and other areas of human endeavours. Software systems that drive the ICT infrastructure are better served with the use of a design pattern that allows a total control over software systems.

Keywords: Design, Patterns, Crosscutting concerns, Obliviousness, Quantification

INTRODUCTION

Separation of concerns (SoC) started with the advent of the structured programming paradigm that is remarkably different for the earlier paradigm that was characterized by the presence of *goto* statements. The structured programming paradigm aimed at providing greater clarity by the use of subroutines (sub-programs). It is often regarded as a top-down or bottom-up approach to programming. Structured programs can be composed by three simple structures: sequence, selection and repetition.

The object-oriented programming (OOP) paradigm is a further attempt at separating concerns by using an approach as close as possible to the real world view of a problem. The OOP is based on the notion of objects (which are instances of a class). There are also the notions of data, methods and their interactions. The OOP is characterized by the concept of inheritance, encapsulation, polymorphism, and data abstraction among others. Several methodologies abound in OOP to support the SoC. Gamma *et al.* (1995) came up with design patterns that offer repeatable solutions to commonly occurring problems in software engineering.

Despite the fact that OOP paradigm had revolutionized software engineering, the problem of cross-cutting concerns still remains. The term cross-cut was first used by Kiczales *et al.* (1997). It is characterized by the tangling of one or more concerns within a module aside from the core concern of the module and the scattering of one or more concerns over several modules. The Aspect-oriented programming (AOP) paradigm offers a solution to cross-cutting concerns by tackling the twin-problem of tangling and scattering in OOP. The idea behind this is that when aspects are isolated only the core concerns are implemented without the issues of tangling and scattering.

Tonella and Ceccato (2004) proposed the use of dynamic analysis in order to exercise the class methods involved in the main application functionalities. They subsequently considered the relationship between the execution traces associated with such functionalities and the class methods involved during each execution, by exploring the concept lattice produced by FCA.

Snelting (2006), presented three methods of the application of concept lattice in static and dynamic analysis of software. Ceccato (2006) proposed an automatic technique that can be used to support the migration of existing OOP code to AOP.

In this work, we investigated how crosscutting concerns in software systems can be separated using a novel design pattern within the context of the OOP technology and explore whether the design pattern can achieve the separation of concerns provided by the AOP technology. We further intent to scale up the design pattern for concurrent programming. The FCA is used to help detect common concerns which are the intents of concepts. This is one of the few works providing an approach in isolating cross cutting concerns without recourse to AOP technology.

THE CROSS CUTTER DESIGN PATTERN

The AOP paradigm improves modularity and the structure of codes. However, Steimann (2006) opined that, the ever-recurrent logging, tracing, debugging, etc. aspects are concerns a programmer has to deal with because she is programming. He believed that most of the programming problems addressed by AOP could either be solved by adding a corresponding feature to the integrated development environment (IDE) or by extending the language with suitable constructs.

The concept of obliviousness, which is often presented as a positive attributes of AOP, implies that a program has no knowledge of which aspect modify it. The notion of quantification denotes that aspects can affect arbitrary many different points in a program. These attributes have come under criticism mainly because it takes the control of the logic of the program from the programmer.

Steimann (2006) believes that while AOP has the merit of ensuring the compartmentalization of code belonging in one concern in one place, it required that locality in its expected module be sacrificed.

We propose the cross cutter design pattern, which is an attempt to ensuring the separation of concerns without the attendant loss of locality in the intended module that the concern affects. We are motivated by the example of the point and line used by Kiczales *et al.* (2001) in demonstrating the aspect-oriented programming paradigm. Our goal is to carry out coloring of the shapes and also move the shape from one location to another to illustrate the concerns that cross-cut all the shapes.

The Proposed Cross Cutter Design Pattern

The methodology for actualizing the Cross-cutter design pattern includes the use of the FCA to assist in the detection of common concerns in software. The concerns are then isolated. The FCA allows the discovering of common concerns on the basis of a rough description of the class. The Cross Cutter design pattern encapsulates these concerns without the attendant loss in program understanding and modularity. We demonstrate this pattern by using a simple example on shapes (circle, rectangle etc.) where the cross-cutting concerns are the coloring and the movement of shapes in the application. The pattern can be used for single threaded and multi-threaded applications. Shown in figure 2, below is the Unified Modelling Language (UML) diagram for the shapes example.

Concerns discovery using the FCA

For the application of FCA in the discovery of crosscutting concerns, we start with the elements (Point, Line, e.t.c) and the features of each of the elements as captured by the cross table below.

	x	y	x1	y1	x2	y2	rad	width	height	color	move
Point	X	X								X	X
Line			X	X	X	X				X	X
Circle	X	X					X			X	X
Rectangle	X	X						X	X	X	X

Table 1: The Cross Table.

In table 1, we consider the small application with the classes as objects and the fields and methods as the attributes. Using standard concept production algorithms to create the concept lattice from the table above resulted in the figure 5 below.

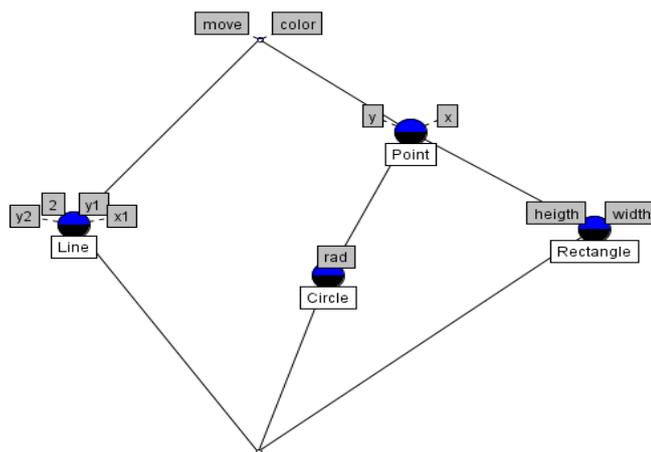


Figure 1: The Concept Lattice.

It is noteworthy that the set of all concepts of a given table forms a partial order. From the above, the supremum factors out common attributes, while the infimum factors out common objects. This indicates that the lattice can uncover a hierarchy of clusters that are otherwise implicit in the cross table (Snelting and Tip, 2000).

Generally, the underlying theorem for concept lattice by Hitzler and Scharfe (2009) in relation to subconcepts and superconcepts are given below:

$$\bigvee_{i \in I} (O_i, A_i) = ((\bigcap_{i \in I} A_i), (\bigcap_{i \in I} O_i))$$

As indicated above, the least common superconcept (join) of a set of concepts can be computed by obtaining the intersection of their intents. In a similar form, the meet can be obtained by:

$$\bigwedge_{i \in I} (O_i, A_i) = (\bigcap_{i \in I} O_i, (\bigcap_{i \in I} A_i))$$

Concepts are normally represented by a node and they are subsequently connected by an edge. Typically the lower concept is the sub-concept of the upper concept. The lattice top concept contains those attributes that apply to all objects. This can provide us with an insight on concerns that cross-cut the application. Notice that the top concept contains the Color and Move concerns. These are concerns that cross-cut the application. The bottom concept contains those objects that

possess all the attributes. In this case however, no object satisfies the condition; hence the bottom concept is empty.

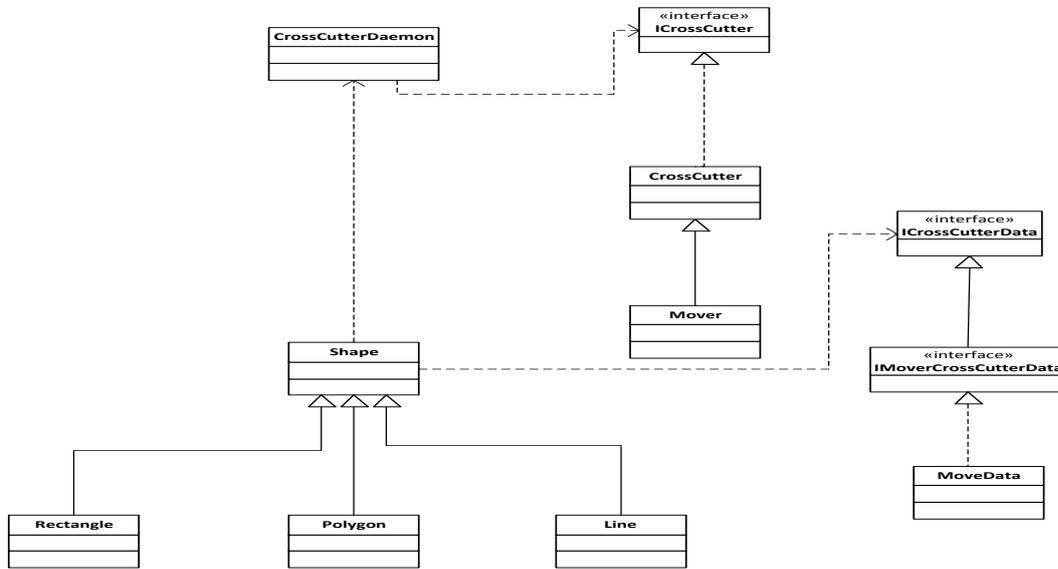


Figure 2: The Crosscutter Design Pattern for Shapes.

The Implementation of the Pattern in Java

The PaintBrush class extends JFrame. This class encapsulates the coloring and movement concerns.

```

public class PaintBrush extends JFrame
{
    private PaintBrushPanel paintBrushPanel = new PaintBrushPanel();

    public PaintBrush()
    {
        add (paintBrushPanel);
        paintBrushPanel.setFocusable(true);
    }

    static class PaintBrushPanel extends JPanel
    {
        private int x = 100;
        private int y = 100;
        private int displ = 5;
        public PaintBrushPanel()
        {
            addKeyListener(new KeyAdapter() {
                public void keyPressed(KeyEvent e) {
                    switch (e.getKeyCode()){
                        case KeyEvent.VK_DOWN:
                            y += displ;
                            break;
                        case KeyEvent.VK_UP:
                            y -= displ;
                            break;
                        case KeyEvent.VK_LEFT:
                            x -= displ;
                            break;
                        case KeyEvent.VK_RIGHT:
                            x += displ;
                            break;
                        default:
                            displ = e.getKeyCode();
                    }
                    repaint();
                }
            });
        }
        protected void paintComponent(Graphics g)
        {
            super.paintComponent(g);
            g.setColor(Color.BLUE);
            g.drawRect(x, y, 50, 20);
        }
    }
}

```

The canvas also extends JFrame. It implements the animation of the shapes.

```

public class Canvas extends JFrame
{
    private Shape shape;

```

```

private int xdispl = 0;
private int ydispl = 0;
private int unitTime = 1000;
private int ticks = 0;
public Canvas()
{
}
    public Canvas(int xdispl, int ydispl, int width, int height)
{
    setDispls(xdispl, ydispl);
    setSize(width, height);
}

public void add(Shape shape)
{
    this.shape = shape;
    super.add(shape);
}
public void setDispls(int xdispl, int ydispl)
{
    this.xdispl = xdispl;
    this.ydispl = ydispl;
}
public void start()
{
    Timer timer = new Timer(unitTime, new TimerListener());
    timer.start();
}
public void setUnitTime(int unitTime)
{
    this.unitTime = unitTime;
}
private class TimerListener implements ActionListener
{
    public void actionPerformed(ActionEvent e)
    {
        ++ticks;
        Mover mover = (Mover)ccdp.Graphics.CrossCutterDaemon.getMover();
        mover.setFrameHeight(getHeight());
        mover.setFrameWidth(getWidth());
        mover.setX(xdispl);
        mover.setY(ydispl);
        mover.setShape(shape);
        mover.o();
        shape.repaint();
    }
}
}

```

We create the interface for the CrossCutter. The CrossCutter class implements the interface above. The CrossCutterDaemon is created. The Mover class extends the CrossCutter class.

The MoveData class implements the IMoverCrossCutterData

```

public class CrossCutterDaemon
{
    private static CrossCutter mover;
    public static CrossCutter getMover()
    {
        return mover;
    }
    public static void setMover(Mover crossCutterMover)
    {
        mover = (CrossCutter)crossCutterMover;
    }
}

```

```

public interface IMoverCrossCutterData extends ICrossCutterData
{
    int[] getPoints();
    IMoverCrossCutterData setPoints(int[] points);
}

```

```

public class MoveData implements IMoverCrossCutterData
{
    private int[] coords;

    public MoveData()
    {
    }

    public int[] getPoints()
    {
        return coords;
    }

    public IMoverCrossCutterData setPoints(int[] coords)
    {
        this.coords = coords;
        return this;
    }

    /** clones MoveData object */
    public Object Clone() throws CloneNotSupportedException
    {
        MoveData clone = new MoveData();
        int[] coords = new int[this.coords.length];
        for (int i = 0; i < coords.length; i++)
            coords[i] = this.coords[i];
        clone.setPoints(coords);
        return clone;
    }
}

```

```

public class Circle extends Shape
{
    private int x;
    private int y;
    private int xlen;
    private int ylen;
}

```

```

public Circle(int x, int y, int xlen, int ylen)
{
    this.x = x;
    this.y = y;
    this.xlen = xlen;
    this.ylen = ylen;
}

protected void paintComponent(Graphics g)
{
    super.paintComponent(g);
    g.setColor(Color.BLUE);
    g.drawOval(x, y, xlen, ylen);
}

public IMoverCrossCutterData getMoveData()
{
    int[] coords = new int[2];
    coords[0] = x;
    coords[1] = y;
    MoveData moveData = new MoveData();
    moveData.setPoints(coords);
    return moveData;
}

public void setMoveData(IMoverCrossCutterData data)
{
    int[] coords = data.getPoints();
    x = coords[0];
    y = coords[1];
}

```

Listing 1: Cross cutter pattern Implementation.

The Generic Cross Cutter Design Pattern

The shapes example provides a simple implementation of the design pattern. The figure 3 below, shows a generic UML diagram for the design pattern. The intent of the pattern is to encapsulate cross cutting concerns without the loss of locality, modularity and program understanding. The AbstractContext depicts the universe of discourse in the system while the ConcreteContextOne and so on, are the components of the AbstractContext. The AbstractContext depends on the data provided by the interface ICrossCutterData and the CrossCutterDaemon. The CrossCutterDaemon in turn depends on the interface ICrossCutter. The IVariegated Cross CutterData extends the ICrossCutterData. The ConcreteData implements the IVariegatedCrossCutterData class. Having demonstrated the pattern in a single threaded application, it is possible to scale up the application of the pattern to multi-threaded applications.

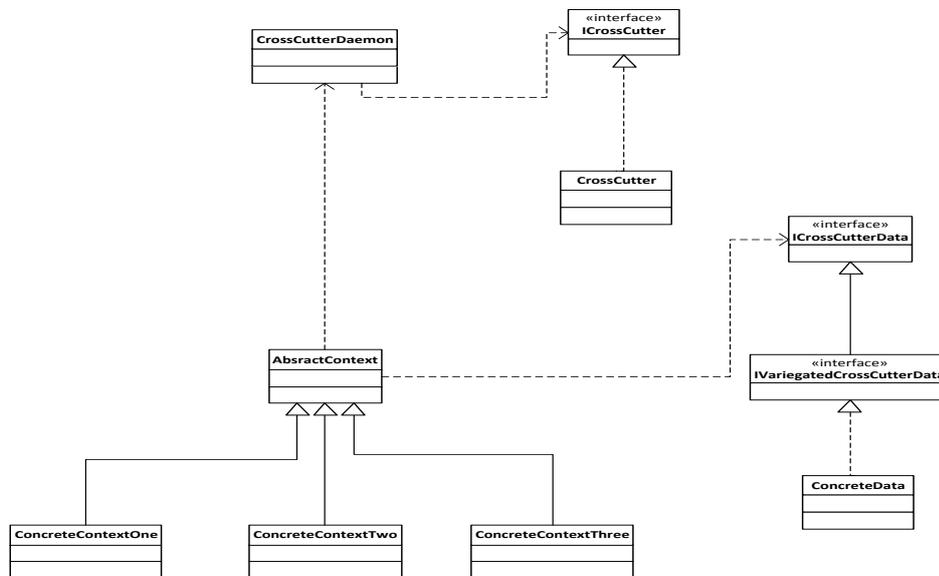


Figure 3 : The CrossCutter Design Pattern related works

Kuhlemann (2007) compared OOP, AOP and FOP (Feature Oriented Programming) in a quantitative case study of design pattern implementation. They subsequently evaluated OOP, AOP and FOP design pattern implementation with respect to modularity and showed that FOP performs best when compared to OOP and AOP.

In Hachani and Bardou (2002), the Visitor design pattern using Aspect-Oriented Programming technology was presented. They concluded that the implementation eased the trace of pattern application in programs and may improve the separate reuse of both pattern and main application code.

Steimann (2006) opined that much of aspect-oriented programming's success seems to be based on the fact that it improves modularity and the structure of code, while in actual fact; it works against the primary purposes of the two, which is independent development and program understandability. However, Steimann (2006) did not demonstrate the OOP structures that can stand for AOP implementation.

Schwanninger *et al.* (2004) described how design patterns can be evaluated for their suitability to solve problems caused by crosscutting concerns.

Hannamann and Kiczales (2002) considered the aspect implementation of the GoF design patterns. Improvement was observed in 17 of the 23 cases. These improvements are depicted in terms of better code locality, reusability, composability and pluggability. Also, the degree of improvement varies with the greatest improvement coming when the pattern solution structure involves crosscutting of some form, including one object playing multiple roles.

CONCLUSION

Several approaches had been presented in the separation of concerns in software systems. Our work investigated the use of OOP technology in separation concerns leading to the presentation of the Cross cutter design pattern. Our further work involves the application of the design pattern in network programming.

REFERENCES

- Ceccato, M. (2006). Migrating object-oriented code to aspect-oriented programming. *PhD Dissertation, University of Trento*.
- Gamma, E., Helm, R., Johnson R., Vlissides, J. (1995). Design Patterns: Elements of Reusable Object Oriented Software. Addison-Wesley. ISBN0-201-63361-2.
- Hachani, O., and Bardou, D.,(2002). Using Aspect-Oriented Programming for Design Pattern Implementation. In Proc. Workshop on Reuse in Object-Oriented Information Systems.
- Hannermann, J and Kiczales, G. (2002) Design Pattern Implementation in Java and AspectJ. In Proc. OOSPLA Seattle, U.S.A.
- Hitzler, P. and Scharfe, H. (2009). Concept structures in practice. Chapman and Hall/CRC studies in informatics series.
- Holub, A. (2004) Holub on Patterns.Learning Design Patterns by looking at Code.Apress U.S.A.
- Kuhlemann, M. (2007). Design Pattern Revisited. [Online] from <http://www.cs.uni-magdeburg.de> [Accessed 28th February, 2013]
- Kiczales, G., Lamping, J., Mendhekar, A., Maeda, C., Lopes, C.V., Loingtier, J. and Irwin, J. (1997). Aspect-oriented programming. Proc.European Conf. on Object-Oriented Programming (ECOOP), Finland, Springer-Verlag LNCS 1241.
- Kiczales, G., Hilsdale, E., Hugunin, J., Kersten, M., Palm, J., and Grisword, W. (2001). An overview of AspectJ._ In Knudsen, J.L. , editor, ECOOP 2001- Object-Oriented Programming 15th European Conference, Budapest Hungary, volume 2072 of Lecture Notes in Computer Science, pp.327-353. Springer-Verlag, Berlin.
- Snelting, G. (2006). Concept lattices in software analysis. Formal Concept Analysis, LNAI 3626, pp.272-287.
- Snelting, G. and Tip, F. (2000) Understanding Class Hierarchies Using Concept Analysis. ACM Transactions on Programming Language and Systems, Vol.22, No.3, pp.540-582.
- Steimann, F., (2006). “The Paradoxical Success of Aspect-Oriented Language.” *Proc .OOPSLA, U.S.A.*
- Schwanninger, C., Wuchner, E., Kircher, M. (2004) “Encapsulating Crosscutting Concerns” *Proc. Third AOSD Workshop, U.K.*
- Wormuth, B. and Becker, P. (2004) Introduction to formal concept analysis. Proc. Int. Conf. of FCA,Sydney.
- Tonella, P. and Ceccato, M. (2004). Aspect mining through the formal concept analysis of execution traces. Proc. 11th Working Conference on Reverse Engineering (WCRE '04) 1095-1350104.

CYTOGENETIC SCREENING OF MONOSODIUM GLUTAMATE (MSG), A FLAVOUR ENHANCER, USING THE *ALLIUM* TEST

¹Omoregie, Q. O., ¹Fasona, M. I. & ²Odeigah, P. G. C.

¹Department of Zoology, University of Lagos, Nigeria.

²Department of Cell Biology and Genetics, University of Lagos, Nigeria.

queenomoregie@yahoo.com

ABSTRACT

The cytogenotoxicity of Monosodium glutamate (MSG), Vedan seasoning, was investigated using the *Allium cepa* test. From the macroscopic and microscopic parameters considered, the EC₅₀ value of 8g/l was determined from the growth curve. Some root malformations noticed are crochet hooks, C-tumour and broken roots, and most of the roots at high concentration had translucent white roots. The mitotic index decreased with increase in concentration and positively correlated to the root length. No aberration was recorded in the chromosome of *A. cepa* exposed to the control. Chromosomal aberrations recorded are nuclear lesion; binucleate cells; chromosome bridge; spindle disturbance at prophase, early metaphase and spindle disturbance at prophase among others. Stickiness was noticed more in 0.5, 0.75 and 1g/l concentrations while multiple nuclei were more at higher concentrations. C-mitosis, bridges and multipolar anaphase did not follow a particular trend. The mitotic abnormalities in *Allium cepa* shown in the results of this study clearly suggests that MSG poses a genotoxic risk.

Keywords: *Monosodium glutamate (MSG), Vedan seasoning, Allium cepa test, cytogenotoxicity, genotoxic risk.*

INTRODUCTION

Monosodium glutamate (MSG) is a white crystalline, soluble and odourless sodium salt of amino acid glutamate. It is used as a flavour enhancer (Farombi and Onyema, 2006; Egbuonu *et al.*, 2009; Ashaolu *et al.*, 2011) and a popular condiment in West African dishes (Obaseiki-Ebor *et al.*, 2003) such as meats, soups and vegetables dishes. It is commonly used in restaurants, fast food joints and for bulk cooking. MSG, as flavour enhancers, reduce sodium intake (Yamaguchi and Takahashi, 1984) and according to Institute of Food Technologists' Expert Panel on Food Safety and Nutrition, (1987), improves the taste of the food it is added to.

Apart from the common flavour enhancers containing MSG like Ajinomoto, Vedan, A-one, all popularly called "white maggi" in Nigeria, other products that often contain MSG are Malt extract and flavouring, Soy sauce and extract, Worcestershire sauce, protein fortified, enzyme fortified, ultra-pasteurized, or fermented, Broth and Stock, Barley malt and so many more.

The use of MSG as a flavour enhancer could induce an increase in energy intake (Bergen *et al.*, 1998) which could lead to obesity (Mozes *et al.*, 2004) or alter the levels of carbohydrates, lipids and proteins (Diniz *et al.*, 2004) in the body. The intake of MSG in high doses and over time may be hepatotoxic (Egbuonu *et al.*, 2009), neurotoxic (Eweka and Adjene, 2007) and excitotoxic (Stegink *et al.*, 1987), which may damage the brain especially by oral intake without food (Walker and Lupien, 2000). The harmful side effects of MSG as reviewed in Truth In Labeling Campaign (TILC) (2004a; b) include brain damaging potentials, stunted skeletal development, behavioural aberration, neuroendocrine disorder, possible learning deficits, seizures (epileptic fits), learned taste aversion and hyperglycemia. Some symptoms of the effect of MSG could be manifested by migraine, diarrhoea, weakness, nausea/vomiting, stomach ache, tightness of the chest, flushing, sweating, sense of facial pressure or tightness, numbness,

tingling or burning in or around the mouth, rapid fluttering heartbeats (heart palpitations) and shortness of breath (Samuels, 1999).

Reputable International Organizations and nutritionists have continued to endorse MSG, reiterating that it has no adverse reactions in humans despite evidence of negative consumer response to MSG (Okwuraiwe, 1992). The Food and Drug Administration (FDA) of the United States reports that Monosodium glutamate is permitted as a safe food additive that needs no specified average, daily intake or an upper limit intake requirement. In Nigeria, the Directorate and Regulatory Affairs of Food and drug Administration and Control (FDA&C) now National Food and Drug Administration and Control (NAFDAC) agency, in 1992, also expressed the view that MSG is not injurious to health (Okwuraiwe, 1992). This makes The Truth In Labeling Campaign team ask that if truly MSG is not harmful, why is it hidden from the labels of most foods they are added to?

In Nigeria, some individuals use MSG as a bleaching agent for the removal of stains from clothes (Eweka *et al.*, 2010). There is a growing apprehension that its bleaching properties could be harmful or injurious to the body, or worse still, induce terminal diseases in consumers when ingested as a flavour enhancer in food.

The main objective of this study is to determine the genotoxic effects of a flavour enhancer, Vedan (Monosodium Glutamate [MSG]), using the *Allium* test.

METHODS

Vedan, a brand of MSG, marketed by Mac & Mei (Nigeria) was purchased from a regular foodstuff market, Ikotun Market, Lagos, South-west, Nigeria after a market survey, which placed it ahead of other brands based on sales volume and popularity among the customers.

The common purple onion, *Allium cepa* bulbs were also purchased from Ikotun Market, Lagos, Nigeria. Equal-sized bulbs were selected for this study. Just before use, the outer scales of the bulbs were carefully removed and the brownish bottom plates were scraped away without destroying the root primordia. The bulbs were then placed in tap water to protect the primordial cells from drying up.

Twelve replicate bulbs to be used for each concentration were grown in water to ensure proper root formation as described by Friskesjo (1987; 1995). After 72 hours, the best ten bulbs in terms of root growth were selected and exposed to the following test concentrations - Water only (control); 0.25g/l; 0.5g/l; 0.75g/l; 1g/l; 2g/l; 5g/l; 10g/l; 15g/l and 20g/l of the test samples (the high concentrations are to verify the safety of people who use MSG in large quantities especially for raw dishes like salads).

The experiments were maintained in stable conditions. The roots were protected from direct sunlight by planting them in test tubes in a carton in order to minimize fluctuation of the rate of cell division. The test solutions were replaced daily with fresh solutions throughout the experiment.

At the end of 48 hours, 2 root tips from 5 onion bulbs per concentration were harvested and fixed in ethanol:glacial acetic acid (3:1) for 24 hours. After which the root tips were processed for cytological study by the conventional aceto-orcein squash technique: the root tips were hydrolyzed in 1 normal hydrochloric acid (HCl) for five minutes to soften the tissue. Two root tips were then macerated on each slide and stained with aceto-orcein stain for 20 minutes. The macerated and stained root tips were covered carefully with cover slips to exclude air bubbles. The cover slips were then sealed on the slides with clear fingernail polish as suggested by Grant, (1982). This is to prevent drying out of the preparation by the heat of the microscope (Sharma, 1983).

Five slides with two root tips per slide were prepared for each concentration and analyzed for induction of chromosomal aberrations. A total of 1000 cells were scored per concentration and the mitotic activity, rate and kind of aberrations were scored using five replicates for each

concentration. The mitotic index (MI) was calculated as the number of dividing cells per 1000 observed cells. The frequency of aberrant cells (%) was calculated based on the number of aberrant cells per total cells scored at each concentration. The significance between the mean results and control was determined by t-test. Dose response relationships were determined from the correlation and regression coefficients and the corresponding regression lines for MI, abnormal cells and cells with other mitotic abnormalities.

The root length of onion bulbs from each concentration was measured on day 4 (96 hours) (Plate 1) of the experiment using a calibrated ruler. The mean root length of each concentration was calculated as a percentage of the control. EC₅₀ value (the Effective Concentration where root growth amounts to 50% of the controls), was determined from a plot of root length (% of control) against the sample concentrations using a Microsoft Excel computer programme. The effect of each concentration of MSG on the morphology of growing roots was also examined.

RESULTS

In the *Allium* test, parameters such as root shape and growth, frequencies of mitosis and abnormal cell division can be used to estimate the cytotoxicity, genotoxicity and mutagenicity of environmental pollutants and chemicals (Nielson and Rank, 1994).

Macroscopic parameters – root growth (length) and form were evaluated for general toxicity. The root length was directly proportional to concentration and so reduced as concentration increased as shown in Table 1. At 15g/l and 20 g/l, there was completed growth inhibition as the roots that had earlier sprouted wilted by day 2 of exposure. The root growth retardation is concentration dependent with an EC₅₀ value of 8g/l as shown in Figure 1.

Some root malformations were noticed as shown in Plate 2. Crochet hooks and broken roots were noticed at 0.75g/l, 2g/l and 10g/l concentrations respectively. Most of the roots at high concentration had translucent white roots.

The results of the microscopic effects are summarized in Table 1. The mitotic index decreased with increase in concentration and positively correlated to the root length, which followed the same trend. No aberration was recorded in the chromosome of *A. cepa* exposed to the control (water). MSG induced chromosomal aberrations recorded in the study as shown on Plate 3 A - H are nuclear lesion; binucleate cells; star metaphase sticky chromosome; chromosome bridge; spindle disturbance at prophase, early metaphase and spindle disturbance at prophase among others. Stickiness was noticed more in 0.5, 0.75 and 1g/l concentrations while multiple nuclei were more at higher concentrations. C-mitosis, bridges and multipolar anaphase did not follow a particular trend.

DISCUSSION

Inhibition in root growth was considered a toxicity indicator since it may result from a certain inhibition of cell division (Fiskesjö, 1995; Odeigah *et al.*, 1997a). Inhibition of root growth indicates retardation of growth and cytotoxicity, while root wilting suggests toxicity (Grant, 1982; Odeigah *et al.*, 1997b). This study provides evidence that MSG inhibited root growth and caused growth retardation as the root length was directly proportional to concentration and reduced as concentration increased. The roots that earlier sprouted wilted by day 2 of exposure to concentrations of 15g/l and 20 g/l. Nevertheless, both growth retardation and root wilting as seen in the 10g/l concentration was accompanied by suppression of mitotic activity and occurrence of chromosomal aberration.

The percentage aberrations were positively correlated with concentration which agrees with test results from Ashaolu *et al.*, (2011) and Eweka *et al.*, (2010), who assert that both dose and concentration produce significant effect on hematological and histological parameters of rats respectively. Results from Egbuonu *et al.*, (2009), prove that low concentrations of monosodium

glutamate could be hepatotoxic. These findings suggest that MSG, despite its flavouring functions in dishes, is detrimental to health.

Farombi and Onyema, (2006), worked on the modulatory role of vitamin C, vitamin E and quercetin and found that they were effective at ameliorating the effects of MSG. Ibrahim *et al.*, (2011) was also able to restore the MSG-induced hepatic histopathological alterations to near normal with the vitamin C treatment and so argues that MSG is safe for consumption.

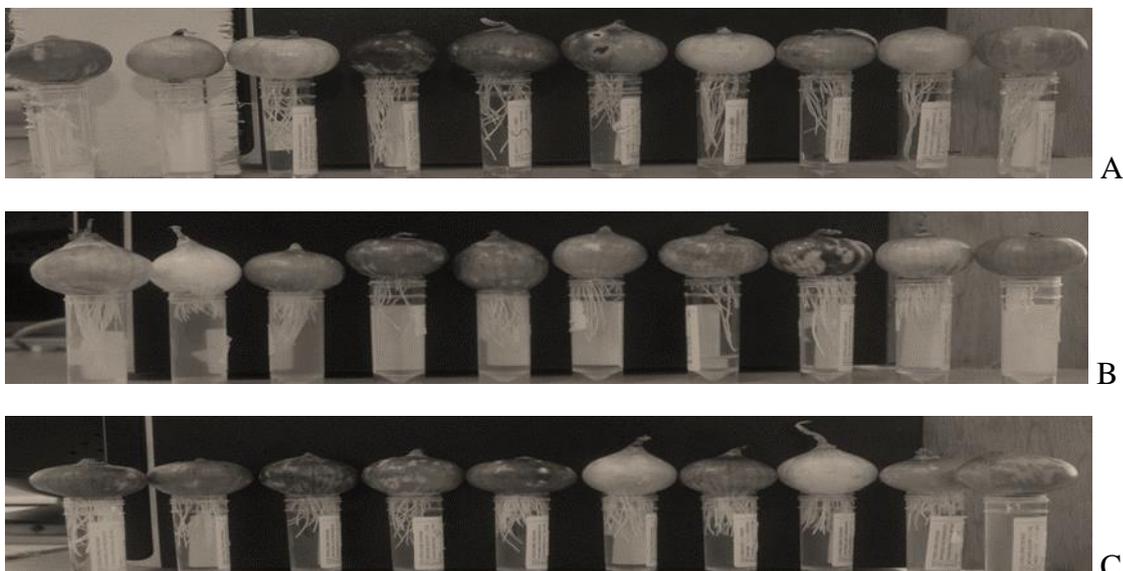
CONCLUSION

MSG induces mitotic abnormalities in *Allium cepa* as shown in the results of this study. This suggests that MSG poses a genotoxic risk. Further studies aimed at determining the quantity safe for human consumption is therefore highly recommended. It is also necessary to be careful in the use of MSGs as flavour enhancers as some earlier studies show some form of toxicity even at low concentrations. It is highly recommended that caution be taken in the use of any brand of MSGs especially in high concentrations and raw dishes.

REFERENCES

- Ashaolu, J. O., Ukwenya, V. O., Okonoboh, A. B., Ghazal, O. K. and Jimoh, A. A. G. (2011). Effect of monosodium glutamate on haematological parameters in Wistar rats. *International Journal of Medicine and Medical Sciences*. **3**(6): 219-222.
- Bergen, H. T., Mizuno, T. M. and Taylor, J. (1998). Hyperphagia and weight gain after gold-thioglucose and monosodium glutamate: relation to hypothalamic neuropeptide. *Y. Endocrin*. **139**: 4483-4488.
- Diniz, Y. S., Fernando, A. A., Campos, K. E., Mani, F., Ribas, B. D. and Novelli, E. L. (2004). Toxicity of hyper caloric diet and monosodium glutamate: oxidative stress and metabolic shifting in hepatic tissue. *Food Chemical Toxicology*. **42**: 319-325.
- Egbuonu, A. C. C., Obidoa, O., Ezeokonkwo, C. A., Ezeanyika, L. U. S. and Ejikeme, P. M. (2009). Hepatotoxic effects of low dose oral administration of monosodium glutamate in male albino rats. *African Journal of Biotechnology*. **8**(13): 3031-3035.
- Eweka, A. O. and Adjene, J. O. (2007). Histological studies of the effects of monosodium Glutamate on the medial geniculate body of adult Wistar rat. *Electronic Journal of Biomedics*. **22**: 9-13.
- Eweka, A. O., Eweka, A. and Om'Iniabohs, F. A. E. (2010). Histological studies of the effects of monosodium glutamate of the fallopian tubes of adult female Wistar rats. *North America Journal of Medical Science*. **2**: 146-149.
- Farombi, E. O. and Onyema, O. O. (2006). Monosodium glutamate-induced oxidative damage and genotoxicity in the rat: Modulatory role of vitamin C, vitamin E and quercetin. *Human and Experimental Toxicology*. **25**(5): 251-259.
- Friskesjo, G. (1987). The Allium test, an alternative in environmental studies; the relative toxicity of metal ions. *Mutation Research*. **197**: 243-280.
- Fiskesjo, G. (1995). Allium test. In: O'Hare, S. and Atterwill, C. K. (editors). Methods in Molecular Biology. Volume 43: *In Vitro Toxicity Testing Protocols*. Humana Press, Incorporated, Totowa, New Jersey. 119-124pp.
- Grant, W. F. (1982). Chromosome aberration assay in *Allium*. *Mutation Research*. **99**: 273 – 291.
- Ibrahim, M. A., Buhari, G. O., Aliyu, A. B., Yunusa, I. and Bisalla, M. (2011). Amelioration of Monosodium Glutamate- Induced Hepatotoxicity by Vitamin C. *European Journal of Scientific Research*. **60**(1): 159-165.
- Institute of Food Technologists' Expert Panel on Food Safety and Nutrition. (1987). Monosodium Glutamate. *Food Technologist*. **41**(5): 143-145.

- Mozes, S., Sefcikova, Z., Lenharde, L. and Raeek, L. (2004). Obesity and changes of alkaline phosphatase activity in the small intestine of 40-80-day old subjects to early postnatal overfeeding of monosodium glutamate. *Physiological Research*. **53**: 177-186.
- Nielson, M. H. and Rank, J. (1994). Screening of toxicity and genotoxicity in waste water by the use of *Allium* test. *Hereditas*. **121**: 249-254.
- Obaseiki-Ebor, E. E., McGhee, E. M. and Shankee, D. M. (2003). *Improved detection of the genotoxic and mutagenic potentials of a food condiment A-One (monosodium glutamate)*. Presented at the Fourth International Conference of the Pan-African Environmental Mutagen Society (PAEMS) in Dar El Diafa-Ain Shams University, Cairo Egypt. 2 - 4th March 2003: 63pp.
- Odeigah, P. G. C., Nurudeen, O. and Amund O. O. (1997a). Genotoxicity of oil field wastewater in Nigeria. *Hereditas*. **126**: 161-167.
- Odeigah, P. G. C., Makinwa, J., Lawal, B. and Oyeniya, R. (1997b). Genotoxicity screening of leachates from solid industrial waste evaluated *Allium* test. *ATLA*. **25**: 311-321.
- Okwuraiwe, P. E. (1992). The role of food and Drug Administration and control (FDA&C) in ensuring the safety of food and food ingredients: A symposium held at Sheraton Hotel, Lagos. 1st September, 1992. 6-15pp.
- Samuels, A. (1999). The Toxicity/Safety of MSG: A study in suppression of information. *Acceptability Research*. **6**(4): 259-310.
- Sharma, C. B. S. R. (1983). Plant meristems as monitors of genetic toxicity of environmental chemicals. *Current Science*. **52**: 1000-1002.
- Stegink, L. D., Filer, Jr. L. J. and Baker, G. L. (1987). Plasma amino acid concentrations in normal adults ingesting aspartame and monosodium L-glutamate as part of a soup/beverage meal. *Metabolism*. **36**(11): 1073-1079.
- Truth In Labeling Campaign (TILC) (2004a). Neuroendocrine disorders. <http://www.truthlabelling.org> Retrieved on 11 February, 2013.
- Truth In Labeling Campaign (TILC) (2004b). Learning and memory disorder. <http://www.truthlabelling.org> Retrieved on 12 February, 2013.
- Walker, R. and Lupien, J. R. (2000). The safety evaluation of monosodium glutamate. *Journal of Nutrition*. **130**(4S supplementary): 1049-1052.
- Yamaguchi, S. and Takahashi, C. (1984). Interactions of monosodium glutamate and sodium chloride on saltiness and palatability of a clear soup. *Journal of Food Science*. **49**(1): 82-85. [http://www.truthlabelling.org/III.What is MSG.html](http://www.truthlabelling.org/III.What%20is%20MSG.html). Retrieved on 11 February, 2013.



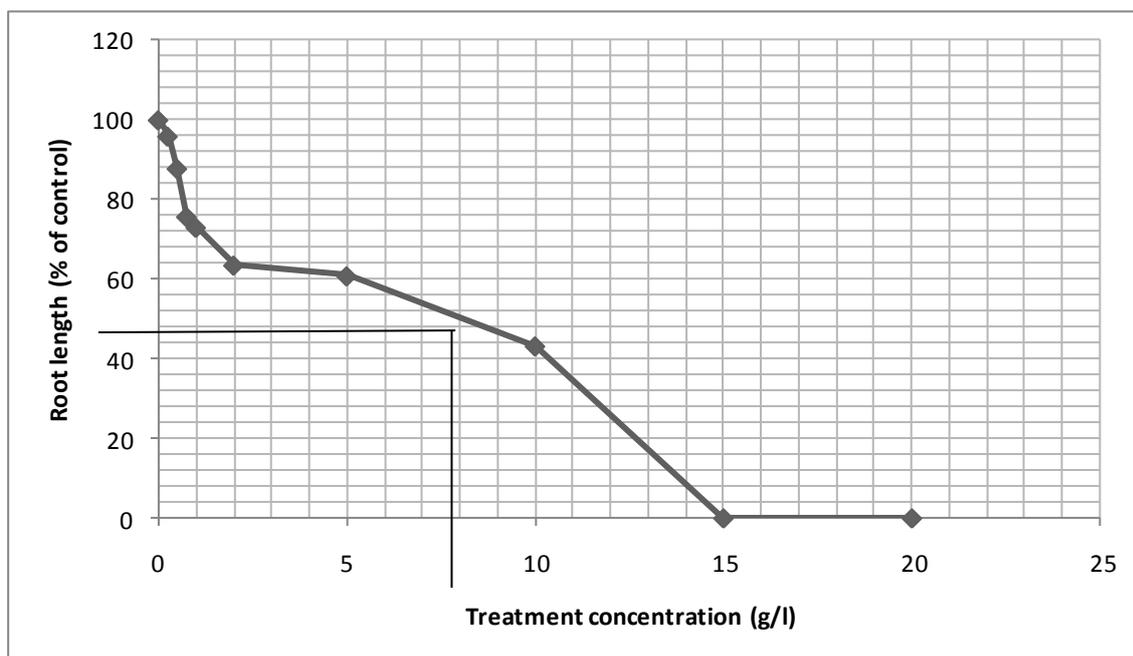
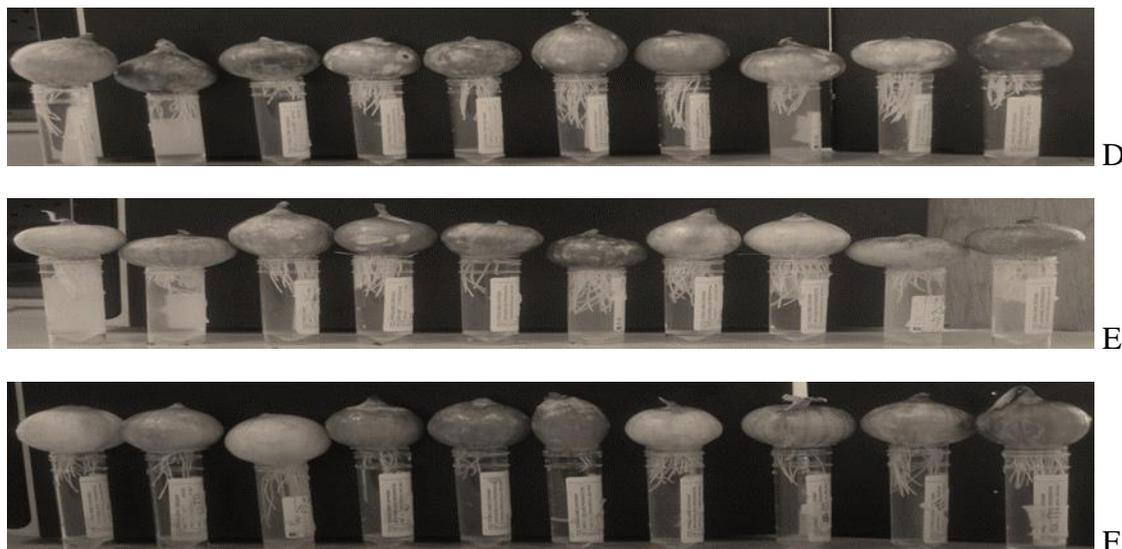


Figure 1: Growth response curve of *Allium cepa* roots in relation to control after exposure to varying concentrations of Vedan, a brand of monosodium glutamate. (EC₅₀ = 8 g/l).

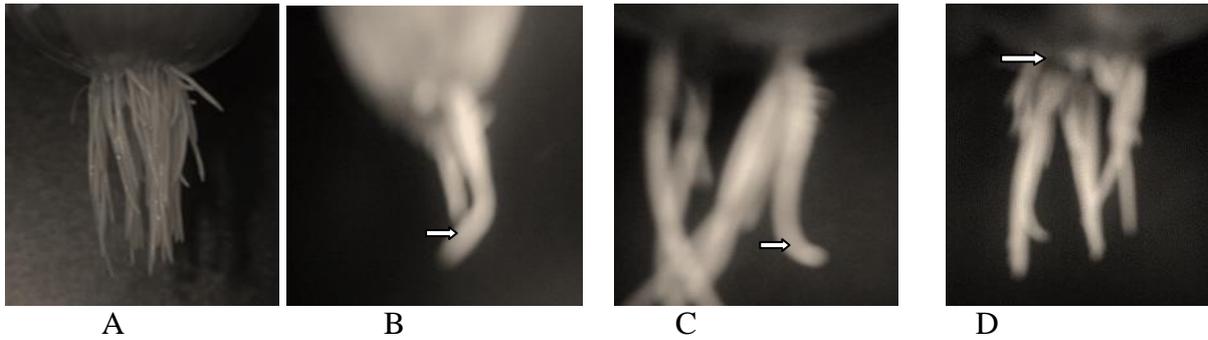


Plate 2 (A-D): Some macroscopic effects on *Allium cepa* roots exposed to various MSG concentrations.

(A) – Normal roots (from a control bulb); (B) – Crochet hooks (0.75g/l concentration); (C) – tumour (2g/l concentration) and (D) – Broken roots (10g/l concentration)

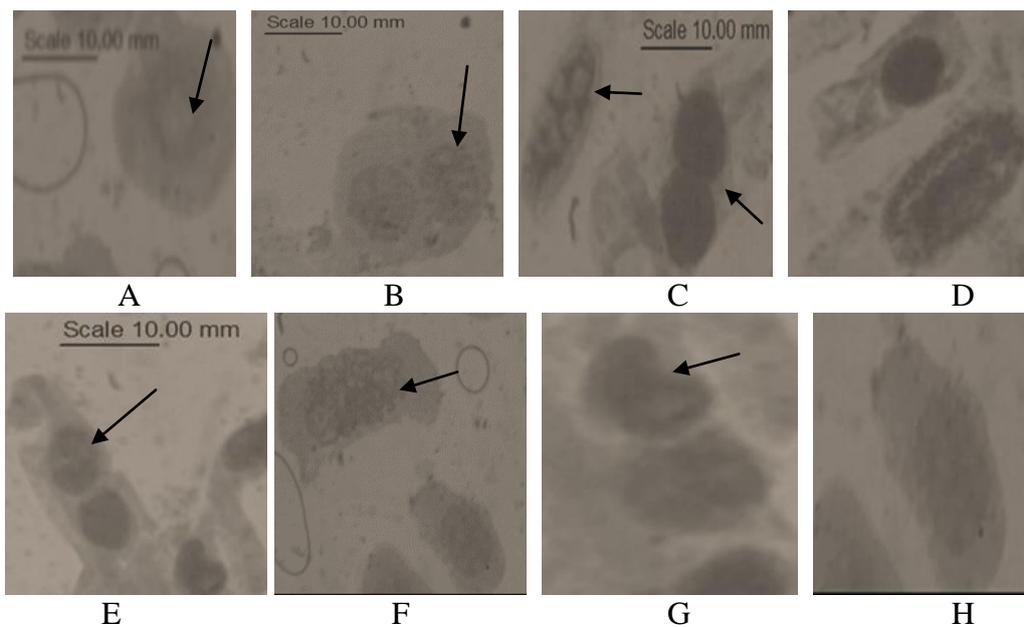


Plate 3 A - H: Chromosomal aberrations induced by Monosodium Glutamate (MSG) in root tip cells of *Allium cepa*.

(A) Nuclear lesion; (B) Binucleate cell; (C) Star metaphase and Binucleus; (D) Sticky chromosome; (E) Chromosome bridge; (F) Spindle disturbance at prophase, (G) Early metaphase and (H) Spindle disturbance at prophase.

Table 1: Effects of treatment with different concentrations of Vedan brand of Monosodium Glutamate (MSG)

Treatment Conc (g/l)	PHENOTYPIC INDICES			CHROMOSOME ABERRATIONS					
	Root length (% of control)	Mitotic index	No of cells	Stick -iness	C- mitosis	Multiple nucleus	Bridge frag- ments	Multi polar anaphase	% Aber- ration \pm SD
0 (Control)	100	57.6	500	0	0	0	0	0	0
0.25	95.9	48.8	500	8	0	5	3	2	4.0 \pm 0.2
0.5	87.8	46.3	458	12	0	3	5	0	4.1 \pm 0.4
0.75	75.7	46.1	424	15	1	5	0	1	5.1 \pm 0.6
1	73.0	35.0	412	10	0	8	6	4	7.8 \pm 0.6
2	63.5	33.5	383	8	2	10	4	0	6.7 \pm 1.1
5	60.8	25.3	379	7	2	10	4	1	6.3 \pm 0.1
10	43.2	14.2	312	8	0	18	7	0	10.4 \pm 0.7
15	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0

HAEMATOLOGY, BIOCHEMICAL PARAMETERS AND PROXIMATE COMPOSITION OF FARMED AND WILD NILE TILAPIA *OREOCHROMIS NILOTICUS*

Yusuff, Abayomi, Soyinka & Olufemi O.

Department of Marine Sciences, University of Lagos, Nigeria
soyinka.olufemi@gmail.com

ABSTRACT

The present study was carried out to determine the haematology, biochemical analysis and proximate composition of Nile Tilapia (*Oreochromis niloticus*) captured from the wild and those reared on a farm. Three (3) different sizes (small, 4.0-5.0cm; medium, 6.0-7.0cm and large, 9.0-10.0cm) of live *Oreochromis niloticus* were collected both from Remmy Fish Farm at Isolo, Lagos and another set from the wild in Lagos Lagoon. After two weeks of feeding in experimental tanks, blood samples were collected from both the live farmed specimens from the tanks and the wild. The carcasses were examined for proximate composition. The haematological parameters for farmed Nile tilapia had a higher level of erythrocytes ($6.98 \pm 8.28 \text{ gL}^{-1}$), haemoglobin ($10.52 \pm 3.09 \text{ gL}^{-1}$), haematocrit (31.85 ± 20.22) than those of the wild Nile tilapia. The biochemical parameters showed higher values in farmed tilapia than in the wild, however there were no significant differences ($p > 0.5$). The result of the proximate composition showed farmed tilapia having values of protein, fat, carbohydrate and energy higher than the wild stock. However, the wild tilapia had higher values of moisture, ash and crude fibre greater than the farmed tilapia. This suggested that farmed Nile tilapia is better in terms of nutrition and health than the wild Nile tilapia from Lagos Lagoon. The stress posed by anthropogenic activities on the biodiversity of a tropical lagoon as the Lagos Lagoon is further revealed.

Keywords: Nile tilapia, haematology, proximate analysis, parameters, farmed, wild

INTRODUCTION

In recent times, there have been increased decline in supply of fish as productions from capture fisheries no longer meet the current demand (Gabriel *et al.*, 2007). However, with this steady decline in capture fisheries, aquaculture is a readily veritable tool in the provision of fish to augment the protein need of people who depend a lot on supply from capture fisheries (Phillay and Kutty, 2005; Stickney, 2005).

Tilapias, alongside with the mud catfishes are excellent candidates for aquaculture. Although the catfish, *Clarias gariepinus* is more commonly cultured than tilapias in most farms in a country like Nigeria, yet there is need to begin to explore other candidate fishes due to certain demands by consumers. Many consumers prefer scaly and less fatty fish like the tilapias, rather than the scales and fatty catfishes (Personal observation). In aquaculture, tilapias show excellent growth rates on low protein diets. They tolerate wide ranges of environmental conditions; they also show little susceptibility to disease and are amenable to handling and captivity. They have a short generation time and breed in captivity. Most important of all, they enjoy wide acceptance as fish food because of their high palatability and history of use from inland fisheries (Usman *et al.*, 2013). According to Green (2006), the most commonly farmed tilapia is the Nile tilapia and its various hybrids. Over 80% of Nile tilapia is currently produced from Aquaculture (Ahmed, 2013).

The present study is to examine the haematology and proximate composition of the Nile tilapia, *Oreochromis niloticus* from the wild and those in a cultured condition, to ascertain the health status of the fish in the wild and the benefits from consuming the fish.

METHODS

Collection of Specimens

Three (3) different sizes (small, 4.0-5.0cm; medium, 6.0-7.0cm and large, 9.0-10.0cm) of live *Oreochromis niloticus* were collected both from Remmy Fish Farm at Isolo, Lagos and another set from the wild in Lagos Lagoon. The live specimens were transported in oxygen bags from point of collection and transferred into rectangular glass tanks at the Aquaculture unit, Marine Research Laboratory, University of Lagos.

Laboratory Procedures

Experimental Set-Up: The specimens were acclimatized in separate rectangular glass tanks 2/3 filled with clean freshwater for 5days at the Aquaculture unit. After acclimatization, the fishes from the farm were placed 10 per tank in five rectangular water tanks for the different sizes separately. The live specimens were fed coppens feed during the observations.

Length And Weight Measurement: The total length (TL) was measured for all specimen from the tip of the snout to the end of the caudal fin, while the fork length (FL) was measured from the tip of the snout to the forked end of the caudal fin. The length was measured to the nearest 0.1 centimeter with a meter rule. The total weight of the fish was taken on a 'sartorius' top loading balance (Model: 11062608053) to the nearest tenth of a gram.

Water Quality Parameter Determination: Physico-chemical parameters were determined. The temperature was measured using a simple mercury-in-glass thermometer. Dissolved oxygen of water samples was measured using Jenway DO meter (Model 4310). The pH value was determined using Jenway Hanna pH meter (Model, HI 991301).

Proximate Composition Analysis: At the termination of the study, large sized fish were taken from the farm and the wild tilapia stocks; were weighed and frozen for final body composition analysis. Proximate analysis of body water, protein, lipid and ash were performed according to standard AOAC (2012) methods. The proximate composition of the coppens feed used during the feeding is presented in Table 1.

Blood Sample Analysis: After two (2) weeks of experiment, samples of blood were taken from the large-sized stock of the Nile tilapia from the wild and farmed ones. They were not fed for 24 hours before the samples were collected and they were not anaesthetized so as to avoid it from impacting on the important chemical parameters of the blood sample. Haematological profile of culturable fish species have been studied with the aim of establishing normal value ranges with respect to sex, age, and physiological conditions (Gabriel *et al.*, 2007). The blood samples were used for determining erythrocyte count and haemoglobin count. Haematocrit values (Hct) were calculated according to formulae (Britton, 1963; Dacie and Lewis, 1984).

Blood from the caudal fin were collected using a 2ml syringe and an Ethylene diamine tetra-acetic (EDTA) bottle which has an anticoagulant effect on the blood. The two samples were taken to the Biochemistry Department of the Lagos State University Teaching Hospital (LUTH) for analysis.

RESULTS

Physico-Chemical Parameters

Water temperature ranged from 28.0°C to 29.5°C; pH ranged from 6.9 to 8.1, while the dissolved oxygen ranged from 7.0mg/l to 8.0mg/l

Proximate Composition

The result is shown in Table 2. It showed that body moisture, ash, protein, fat, carbohydrate, crude fibre and energy were not significantly affected ($P < 0.5$). Although protein content in the flesh of farmed tilapia was slightly higher, fat content and carbohydrate were relatively similar in both stocks. The wild tilapia had a higher crude fibre level, while the moisture and ash content were not significantly different. The flesh of the farmed Nile tilapia had higher energy content.

Haematological Parameter

In Table 3, it could be seen that Erythrocyte (RBC), Haemoglobin (Hb) and Haematocrit (Hct) levels in the blood sample collected from wild Nile tilapia were lesser than the values for the farmed tilapia. The blood indices calculated in the table showed that Mean Cell Volume (MCV), Mean Cell Haemoglobin (MCH) and Mean Cell Haemoglobin Concentration (MCHC) were higher in cultured Nile tilapia.

Biochemical Parameters

In this study the biochemical parameters (Table 3) such as the plasma glucose concentration showed higher value in farmed Nile tilapia (60.32 ± 20.20) than wild Nile tilapia from Lagos Lagoon (54.62 ± 15.32). There was no significant difference in plasma total protein for both set of fishes (3.06 ± 0.65 and 3.01 ± 0.57 respectively), while the total lipid was higher in cultured tilapia (6.53 ± 0.47) than wild Nile tilapia (5.29 ± 0.47).

DISCUSSION

The present study showed that the high protein concentration feed (Coppens starter feed) helped to improve the growth, haematological and biochemical parameters of cultured Nile tilapia as compared to the wild stock collected from Lagos Lagoon. The result showed that Nile tilapia reared on the farm benefited from the good water quality parameter and high protein feed to boost its growth, haematological and biochemical parameters. They were constantly aerated on the farm increasing the dissolved oxygen level, monitoring the water parameters (pH, and temperature) and constant changing of water, hence they showed a significant high growth rate, feed intake and conversion. This factor is the reason why they show better flesh composition and haematological parameters. Also fish from the wild are affected by the environmental conditions of salinity (Altinok and Grizzle, 2001) as experienced by the fish in the Lagos Lagoon. He suggested that the greater energy expended in maintaining the osmotic balance causes greater demand on the thyroid gland, resulting in insufficient hormone for growth. Thus the farmed stock had an advantage in this regard.

Also, Job (1969) showed that there existed optimal environmental conditions at which a high metabolic rate occurs and thus growth is possible. Water pollution has become a global problem in the world. Some essential trace elements for animal life such as copper are continuously increasing in water which may result in toxic effect on aquatic life, including fishes (Akan *et al*, 2012). Also, the influx of pollutants such as toxic wastes, into the Lagos Lagoon from industries and land based sources caused substantial level of tissue burden on wild Nile tilapia, which in turn causes reduction in food intake, increases metabolic cost and poor food intake (Chukwu, 2002)

The present study showed that fish reared on the farm showed higher RBC, H_b, H_{ct} than the wild. The decrease in these parameters in Nile tilapia from Lagos Lagoon might be due to the destruction of mature RBC and inhibition of erythrocyte production due to reduction of haem-synthesis that are affected by pollutants (Wintrobe, 1978). Also the decrease in RBCs count may be attributed to haemolytic crisis in most veritable including fish species exposed to different environmental pollutants (Khangrot and Tripathi 1991) or may be attributed to reduction of growth, and other food utilization process (James and Sampath, 1999). The calculated blood

indices MCH, MCV, MCHC have a particular importance in anemia diagnosis in most animals (Coles 1986). The perturbations in these blood indices may be attributed to defense against pollutant through the stimulation of erythropoiesis or may be related to the decrease in RBCs, H_b and H_{ct} due to the exaggerated disturbances that occurred both in metabolic and hemopoietic activities of fish exposed to pollutants (Moussa, 1999). The glucose level which was quite low compared to cultured Nile tilapia is a sensitive reliable indicator of environmental stress (Moussa, 1999).

The values of the proximate analysis of the flesh obtained from Nile tilapia reared on farm and captured from wild are in agreement with those described by Adam and Keji (2011). They both showed high level of body moisture, low level of ash, but farmed tilapia had a relatively high body protein which is attributed to the high protein concentrate fed they were cultivated with (Patrick *et al.*, 2006). The level of body fat though higher in culture Nile tilapia was not very significant ($p > 0.5$) as they both fell into the same range. Carbohydrate content of the flesh is quite similar but crude fibre was higher in wild Nile tilapia from Lagos Lagoon which may be attributed to the feed material present naturally or artificially in the Lagos lagoon. Energy content is quite similar. The result showed that culture Nile tilapia is probably more nutritious than the flesh of wild Nile tilapia from Lagos lagoon.

REFERENCES

- Adam Sulieman, H.M. and Keji James, G. 2011. A comparative study on the chemical and physical attributes of wild farmed Nile tilapia (*Oreochromis Niloticus*). *Online J. Anim. Feed Res.*, 1(6): 407-4011.
- Ahmed, N. 2013. On-farm feed management practices for Nile tilapia (*Oreochromis niloticus*) in Ghana. In M.R. Hasan and M.B. New, eds. *On-farm feeding and feed anagement in aquaculture*. FAO Fisheries and Aquaculture Technical Paper No. 583. Rome, FAO. pp. 191–211.
- Akan, J.C., Abbagambo, M.T. and Chellube, Z.M.. (2012). Assessment of pollutants in water and sediment in Lake Chad, Baga, North-Eastern Nigeria. *Journal of Environmental Protection*, 3 (11): 1428 – 1441.
- Altinok I. and, J. M. Grizzle (2001). Effects of brackish water on growth, feed conversion and energy absorption efficiency by juvenile euryhaline and freshwater stenohaline fishes. *Journal of Fish Biology*, 59 (5), 1142 – 1152
- AOAC (Association of Official Analytical Chemists) (2012). Official Methods of Analysis. 19th edition. Washington D.C.
- Britton, C. L. (1963). Disorders of the Blood. 9th ed. Achur-Chill. Ltd., London.
- Chukwu L.O (2002). Histophysiological indices of osmotic stress in euryhaline teleost *Elops larcerta*, adapted to different salinity regimes. *Journal of Science, Technology and Environment*. 2 (2):1-2
- Coles, E.H. (1986). Veterinary Clinical Pathology W.B. Saunder, Philadelphia, pp10 - 42.
- Dacie, J.V. and Lewis, S.M. (1984). Practical Hematology. 6th edition. Churchill
- Gabriel, U.U., Anyanwu, P.E. and Akinrotimi, A.O. (2007). Haematological profile of black-chinned tilapia (*Sarotherodon melanotheron*) from Buguma creek, Niger Delta, *Agricultural Journal* 2(3): 384 – 387.
- Green, B.W. 2006. Tilapia fingerling production systems. pp 181–210. In: C. Lim, C.Webster (Eds). *Tilapias: Biology, Culture, and Nutrition*. Food Products Press. Binghamton, NY.
- James, R. and Sampath, K. (1999). Effect of the ion exchanging agent, zeolite, on reduction of candium toxicity: an experimental study on growth and elemental uptake in heteropneustes fossils (Bolch). *J. Aqua. Trop*, 14(1)65-74.
- Job, S.V. (1969). The respiratory metabolism of *Tilapia mossambica* (Teleostei) II. The effect of size, temperature, salinity and partial pressure of oxygen *Marine Biology*, 3 (3): 22-226.

- Khangarot, B.S. and Tripathi, D.M. (1991): Changes in humoral and cells-mediated immune responses and in skin and respiratory surface of catfish *Saccobranchus fossilis*, following copper exposure. *Ecotoxicology and Environmental Safety*, **22**(3): 291-308.
- Moussa, M.A. (1999): Biological and physiological studies on the effect of the gramoxom and stomp herbicides on Nile tilapia (*Oreochromis niloticus*). Faculty of Science, Zoology Department Cairo University. 200pp.
- Patrick, K., Xu, X., Neila, H., Jean, M. and Ibrahim, I.T. (2006). Effect of weaning age and diet on pikeperch larviculture. *Aquaculture* **264** (1-4): 197 – 204.
- Pillay TVR, Kutty MN (2005). Aquaculture, principles, and practices. 2nd Edn. Blackwell publishing. 624pp
- Pullin, R.S.V. and Lowe-McConnell, R.H. (1982). *The biology and Culture of Tilapias*. ICLARM 7th Conference Proceedings, Manila Philippines. 432pp
- Stickney RR (2005). Aquaculture: An introductory text. CABI, Texas: USA. 256pp.
- Usman, B.A., Agbebi, O.T., Bankole, O.R., Oguntade, O.R. and Popoola, M.O. (2013). Molecular characterisation of two cichlids populations (*Tilapia guineensis* and *Sarotherodon melanotheron*) from different water bodies in Lagos State, Nigeria. *International Journal for Biotechnology and Molecular Biology Research*, **4** (5): 71 – 77.
- Wintobe, M.M, (1978): In Clinical hematology. Henry Kimpton, London, pp. 448.

Table 1: Proximate composition of coppens starter fish feed

Components	Composition (%)
Protein	45- 56
Fat	10.4 – 15.5
Crude fibre	0.4 – 1.3
Ash	7.3 – 9.0
Total phosphorus	1.3 – 1.5
Vitamin A	22,500 IU/kg
Vitamin D ₃	2,500 IU/kg
Vitamin E	200mg/kg
Vitamin C (stable)	300mg/kg
Gross energy	20.5MJ – 4.9Mcal
Digestible energy	19.1 MJ – 4.6Mcal
Metabolisable energy	15.9MJ – 3.8Mcal
Calcium	0.7 – 18

Source: Patrick *et al*, (2006)

Table 2: Proximate analysis of farmed and wild Nile tilapia (*Oreochromis niloticus*).

Group	Moisture	Ash	Protein	Fat	CHO	C. Fibre	Energy
Farmed tilapia	23.80	2.20	32.26	6.80	33.45	1.50	324.02
Wild tilapia	23.90	2.30	31.22	6.32	33.42	1.87	323.52

Table 3: Mean haematological and biochemical parameters of wild and cultured Nile tilapia (*Oreochromis niloticus*).

Parameter	Cultured Nile Tilapia	Wild Nile Tilapia
Erythrocytes (RBCs) ($10^6/\text{mm}^3$)	6.98 ± 8.28	5.62 ± 9.34
Haemoglobin (HB) (g/dl)	10.52 ± 3.09	8.76 ± 8.05
Haematocrit (Hct) (%)	31.85 ± 8.45	30.02 ± 0.50
MCV	148.80 ± 153.19	101.04 ± 2.23
MCH	40.74 ± 34.19	36.40 ± 6.68
MCHC (%)	35.24 ± 14.92	24.02 ± 5.19
Glucose (mg/dl)	60.32 ± 20.22	54.62 ± 15.32
Total protein (g/dl)	3.06 ± 0.65	3.01 ± 0.57
Total lipid (g/dl)	6.53 ± 0.47	5.92 ± 0.57

SYNTHESIS AND ANTITUBERCULOSIS ACTIVITY OF COPPER (II) COMPLEXES CONTAINING 2-AMINOPYRIDINE SCHIFF BASE LIGANDS

C. U. Dueke-Eze¹, T. M. Fasina^{1*}, O.B. Familoni¹, C .C. Onubogu² & M. J. Mphahlele³

¹ Chemistry Department, University of Lagos, Akoka, Lagos State, Nigeria,

² Nigerian Institute of Medical Research (NIMR), Yaba, Lagos, Nigeria,

³ Department of Chemistry, College of Science, Engineering and Technology, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa.

tofefash@yahoo.ca, dueke4amaka@yahoo.co.uk

ABSTRACT

The *in-vitro* anti-tuberculosis activity of four novel copper(II) complexes (**CuL1–CuL4**) derived from Schiff base ligands obtained by condensation of 2-aminopyridine with substituted salicylaldehydes have been evaluated using the proportion method. These Schiff bases reacted as bidentate ligand to yield complexes of 1:1 (M:L). The compounds were characterized by elemental analysis, IR, ¹H and ¹³C NMR, electronic absorption spectroscopy and molar conductivity. All the complexes have square planar geometry owing to their spectra behaviour. The molar conductance measurements reveal the presence of non-electrolytic complexes. Incorporation of the copper (II) centre into Schiff base ligand scaffolds enhanced their efficacy against *Mycobacterium tuberculosis* H₃₇RV. When compared with first line drug isoniazid (INH), they can be considered as a good starting point to develop new lead compounds for the management of tuberculosis.

Keywords: 2-aminopyridine, Schiff bases, Copper (II) complexes, Antituberculosis, *Mycobacterial tuberculosis*.

INTRODUCTION

The high rate of mortality and co-morbidity of tuberculosis (TB) with HIV makes TB one of the greatest health problems in the world (Kwan and Ernst, 2011). Over the years, *Mycobacterium tuberculosis* (*M.TB*) the causative bacteria for TB has acquired resistance to nearly all the first-line anti-tuberculosis drugs such as isoniazid (INH), rifampicin, pyrazinamide, ethambutol etc., making it difficult to treat the infection clinically. This drug resistance led to renewed interest in the search for new classes of compounds active against *M.TB*. Since the discovery of Cisplatin, a metal-based anti-cancer drug, the development of metal-based therapeutic agents have been actively pursued (Jamieson and Lippard, 1999). This includes development of new anti-tuberculosis agents which is currently based on molecular modification of the existing compounds with anti-TB effect (Sriram *et al.*, 2009, Hearn *et al.*, 2009) and the screening of new classes of compounds active against *M. tuberculosis* (Tarallo *et al.*, 2010, Joseph *et al.*, 2012, Nandi and Sankar, 2012). The search of metal based compounds require the use of ligands or metal ions with inherent biological activity which may be further tried for the target activity required. Schiff bases, particularly those from salicylaldehyde are reported to show antibacterial (Bayrak *et al.*, 2009, Fasina and Dada, 2013), anticonvulsant (Pandey and Srivastava, 2009) and anti-tuberculosis (Utku *et al.*, 2011) activities. In addition, the compounds function as excellent chelating ligands with transition metals ion (Abd El-Halim *et al.*, 2011, Sakthilatha and Rajavel, 2013). Schiff base metal complexes have been investigated as models for antibacterial (Sheeja Lovely and Chridtudhas, 2013), antifungal (Singh and Dhakarey, 2009) and anti-tuberculosis (Joseph *et al.*, 2012) activity. Literature survey revealed the pyridine moiety as pharmacophore for the anti-tuberculosis activity (Lourenco *et al.*, 2007), this prompted our investigation of compounds containing 2-aminopyridine as potential leads in the search for new anti-tuberculosis drugs. In this paper, we report the anti-tuberculosis activity of copper complexes of Schiff bases of 2-aminopyridine and substituted salicylaldehyde derivatives.

METHODS

All chemicals and solvents used were obtained commercially from Aldrich Chemicals Ltd and used without further purification. Melting points were determined on a Stuart SMP3 melting point apparatus and are uncorrected. The Infrared (IR) spectra were recorded on an FTS 7000 series Digilab Win-IR Pro spectrometer equipped with a selenium ATR (attenuated total reflectance) accessory. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) were recorded on using deuterated chloroform (CDCl₃) as solvent with TMS as internal standard on a Varian Mercury 300 MHz spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. Electronic spectra were recorded at room temperature using freshly prepared solutions of the Schiff bases on a Cecil Super Aquarius 9000 series UV-Vis spectrophotometer with a 1 cm quartz cell. The quantitative determination of the metal ions was performed using Perkin-Elmer Atomic Absorption spectrometer. Antituberculosis screening was performed at the Nigeria Institute of Medical Research (NIMR), Yaba, Lagos, Nigeria.

Typical Synthesis of Schiff Bases

A solution of aldehyde (0.20 mmol) in ethanol (10 mL) was slowly added to a stirred solution of 2-aminopyridine (0.20 mmol) in ethanol (10 mL) with the addition of two drops of formic acid. The mixture was heated to reflux at 60 °C for 6 h and then allowed to cool to room temperature. The precipitate formed was collected by filtration, recrystallized from ethanol-hexane (1:1) and dried over silica gel in a desiccator to afford the desired Schiff base (Dueke-Eze, *et al.*, 2011).

Typical Synthesis of Schiff Base Copper(II) Complexes

A solution of copper (II) chloride (CuCl₂.2H₂O) (1.1 mmol.) in hot ethanol: water (5 ml, 1:1(v/v)) was added to a solution of the Schiff base (1.0 mmol.) in hot absolute ethanol (15 ml). The resulting mixture was stirred under reflux at 60 °C for 6h and allowed to cool to room temperature. The solid obtained was collected by filtration, washed severally with ethanol:water (1:1 v/v) and dried over silica gel in a dessicator

Anti-Tuberculosis Study

The anti-tuberculosis test activity was performed using the proportion method reported by Canetti *et al.*, 1963 and modified by Adeleye *et al.*, (2004). Lowenstein-Jensen (LJ) medium was prepared by blending freshly laid chicken eggs with mineral salt and 2% malachite green. A stock solution of the test compound in DMF (0.04 mg/ml) was prepared, filtered through 0.22 µg pore membrane and diluted with LJ medium to give solutions with concentrations 0.4, 0.2 and 0.1 µg/ml. Each solution (7-10 ml) was poured into a sterile universal container and inspissated at 85°C for 45 min (LJ slope). Control experiments were set up using a growth media without the test compound and with the solvent. The LJ slopes were inoculated with 10⁻² and 10⁻⁴ CFU/ml of *M.TB H_{37RV}* and incubated at 37°C for 28 days. The active compounds were further incubated for 14 days. INH was used as a reference compound.

RESULTS

Physical, Analytical and Spectroscopic Results of the Schiff Bases and the Corresponding Metal Complexes

The Schiff bases **L1-L4** were isolated in good yields from the condensation reaction of 2-aminopyridine with salicylaldehyde (**L1**), 5-nitrosalicylaldehyde (**L2**), 5-bromosalicylaldehyde (**L3**) and 5-methoxysalicylaldehyde (**L4**) (Scheme I). Treatment of ligands **L1-L4** with Cu(II) chloride gave complexes **CuL1-CuL4** with a metal:ligand ratio of 1:1. The confirmation of the synthesized compounds was demonstrated by physical, analytical and spectroscopic data summarized in Tables 1-3.

Anti-Tuberculosis Activity

The *in-vitro* anti-tuberculosis activity of the investigated compounds was evaluated against *M.TB* H37Rv at a concentration of 0.4-0.1 µg/ml on 10^{-2} and 10^{-4} CFU/ml of the standard strain using the modified proportion method (Adeleye *et al.*, 2004). The results are presented in Table 4. The unsubstituted ligand (L1) and its metal complex exhibited no activity at all concentrations used and on both 10^{-2} and 10^{-4} CFU/ml of *M.TB* H37Rv. However, the nitro containing compound (L2) exhibited activity at all the concentration used. In addition, and its metal complex showed significant activity at 0.05 µg/ml when compared to the reference compound (INH) which showed highest activity at 0.2 µg/ml. The bromo substituted (L3) ligand show the same level of activity as the metal complex. Compound L4, the methoxy containing ligand exhibited increased anti-tuberculosis activity in the presence of metal ion on 10^{-2} CFU/ml at 0.4 µg/ml and 10^{-4} CFU/ml at 0.2 µg/ml.

DISCUSSION

Spectroscopic Results of the Schiff Bases and the Corresponding Metal Complexes

The IR spectra of the ligands (Table 2) show important band in the region $1595-1608\text{ cm}^{-1}$ attributed to $\nu(\text{C}=\text{N})$ (azomethine) mode confirming the formation of the Schiff bases. This was further supported by a singlet observed at 9.34-9.53 ppm and 163.40 and 167.63 ppm in the ^1H and ^{13}C NMR spectra respectively. The metal complexes are soluble in common organic solvents such as DMF and DMSO. The low molar conductance values of the metal complexes reveal their non-electrolytic nature (Abou-Melha, 2008).

IR Spectra of the Metal Complexes

A study and comparison of the IR spectra of the ligands and the metal complexes suggest that the Schiff bases (**L1-L4**) act as bidentate ligands in nature with the azomethine nitrogen and phenolic oxygen as the two coordination sites. Diagnostic IR spectra bands of the ligands and their metal complexes are presented in Table 2. The characteristic absorption bands of the ligands occurred at $3331-3021\text{ cm}^{-1}$, $1595-1608\text{ cm}^{-1}$ and $1271-1286\text{ cm}^{-1}$ due to $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ vibrations respectively. The band due to phenolic OH group disappeared in the spectra of the complexes indicating the involvement of oxygen of the phenolic group in coordination. In addition, a considerable shift was observed in the $\nu(\text{C}-\text{O})$ frequency as a consequence of coordination of the phenolic oxygen of the ligands to the metal ion (Tantaru *et al.*, 2012). The band due to azomethine nitrogen atom of the Schiff bases shifted to either a lower or higher frequency at $1587-1614\text{ cm}^{-1}$ upon complexation indicating the involvement of the nitrogen of the azomethine group in coordination (Abdel-Latif *et al.*, 2007). In all the spectra of the metal complexes, new bands appeared at $482-521\text{ cm}^{-1}$ and $444-477\text{ cm}^{-1}$ assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations respectively. This confirms the nature of the metal:ligand (1:1) formed and based on the spectroscopic and analytical data, square planar geometry was proposed for all the metal complexes as shown in figure (A).

Antituberculosis Activity

A comparative study of the Schiff bases and their metal complexes revealed that some of the complexes exhibited anti-tuberculosis activity over the free ligand. The observed increased anti-tuberculosis of the some of the metal over the ligand and the reference compound (INH) is in agreement with most of the published work on biological assay of Schiff bases and their transition metal complexes (Tarallo *et al.*, 2010; Joseph *et al.*, 2012) and is based on increase in cell permeability. The lipid membrane which surrounds the *M.TB* cell favours passage of lipid soluble materials and metal complexes have high lipid character over the ligands (Siddappa and Sunilkumar, 2013).

In general, the most active compounds against *M.TB* H37Rv are the nitro containing compound and its copper complex (**L2** and **L2A**) which exhibited activity at lowest concentration 0.1

µg/ml and 0.05 µg/ml when compared with the reference compound which showed highest activity at 0.2 µg/ml. This result is in agreement with the findings of Solak and Rollas (2006) and Pandey *et al.* (2011), that the presence of a nitro group increased antimycobacterial activity of the Schiff base compounds.

CONCLUSION

The design and synthesis of new Schiff base Copper (II) complexes for antituberculosis study have been successfully demonstrated. The metal complexes showed enhanced inhibitory activity towards *Mycobacterium tuberculosis* strain compared to the free ligands. Compounds containing the nitro group (**L2**) and its metal complex (**L2A**) inhibited the growth of the organism at minimal concentrations compared to the reference compound (INH) and can be considered as a good starting point to develop new lead compounds for the management of tuberculosis.

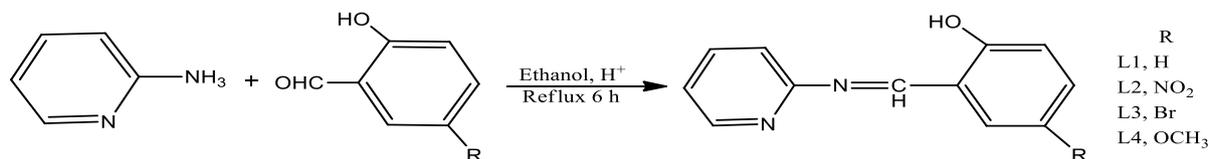
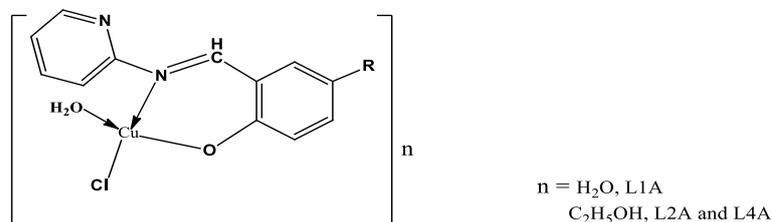
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REFERENCES

- 1 Abd El-Halim, H. F., Omar, M. M., Mohamed, G. G. and El-Ela Sayed, M. (2011). Spectroscopic and biological activity studies on tridentate Schiff base ligands and their Transition metal complexes. *Eur. J. Chem.*, 2(2): 178-188.
- 2 Abdel-Latif, S. A., Hassib, H. B., Issa, Y. M. (2007). Studies on some salicylaldehyde Schiff base derivatives and their complexes with Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II). *Spectrochim. Acta Part A*, 67: 950-957.
- 3 Abou-Melha, K. S. (2008). Transition metal complexes of isonicotinic acid (2-hydroxybenzylidene) hydrazide. *Spectrochim. Acta Part A*, 70: 162-170.
- 4 Adeleye, A. I., Ayolabi, C. I., Onubogu, C. C., Isawumi, A. O. and Nshioogu, M. E. (2004). Antimicrobial activity of crude extracts of twelve medicinal plants and Epa-ijebu (a wonder cure concoction) used in the South-West Nigeria on five common bacterial pathogens. *Handard Medicus*, 51: 1-8.
- 5 Bayrak, H., Demirbas, A., Karaoglu, S. A. and Demirbas, N. (2009). Synthesis of some new 1,2,4-triazoles, their Mannich and Schiff bases and evaluation of their antimicrobial activities *Eur. J. Med Chem.*, 44(3): 1057–1066.
- 6 Canetti, G., Froman, S., Grossett, J., Handiroy, P., Langerov'a, M. and Mahler, H. T. (1963). Mycobacteria: laboratory methods for testing drug susceptibility and resistance. *Bull world Health Organ.*, 29: 565-78.
- 7 Dueke-Eze, C. U., Fasina, T. M. and Idika, I. (2011). Synthesis, electronic spectra and inhibitory study of some salicylaldehyde Schiff bases of 2-aminopyridine. *Afri. J Pure and Appli. Chem.*, 5(2): 13-18.
- 8 Fasina, T. M. and Dada, R. O. (2013). Substituent effect on electronic absorption and biological properties of Schiff bases derived from aniline. *J. of Chem. and Pharma. Res.*, 5(10):177-181.
- 9 Hearn, M. J., Cyanamon, M. H., Chen, M. F., Coppins, R., Davis, J., Kang, HJ. –O., Noble, A.; Tu-Sekine, B.; Terrot, M. S.; Trombino, D.; Minh, T.; Webster, E. S. and Wilson, R. (2009). Preparation and antitubercular activities of *in-vitro* and *in-vivo* of novel Schiff bases of Isoniazid. *Eur. J. Med. Chem.*, 44:4169-4178.
- 10 Jameison, E. R, Lippard, S. J (1999). Structure, recognition and processing of cisplatin-DNA adducts. *Chem. Rev.*, 99: 2467-2498.

- 11 Joseph, J., Nagashri, K. and Janaki, G. B. (2012). Novel metal based antituberculosis agent: Synthesis, characterization, catalytic and pharmacological activities of Copper complexes. *Eur. J. Med. Chem.*, 49: 151-163.
- 12 Kwan CK, Ernst JD, HIV and tuberculosis: a deadly human syndemic. *Clin. Microbio. Rev.* 2011, 24(2): 351-376.
- 13 Lourenco, M. C. S., Souza, M. V. N., Pinheiro, A. C., Ferreira, M. L., Goncalves, R. S. B., Nogueira, T. C. M. and Peralta, M.A. (2007). Evaluation of antitubercular activity of nicotinic and isoniazid analogues. *Arkivoc.* 15: 181-187.
- 14 Nandi, J. and Sankar, V. K. (2012). Synthesis and docking studies of Schiff bases derived from 4-aminopyridine. *J. Pharm. Sci. Innov.*, 1(5): 9-11.
- 15 Pandey, A., Dewangan, D., Verma, S., Mishra, A. and Dubey, R. D. (2011). Synthesis of Schiff bases of 2-amino-5-aryl-1,3,4-thiodiazole and its analgesic, anti-inflammatory, antibacterial and antituberculosis activity. *Int. J. Chem. Tech. Res.*, 3(1): 178-184.
- 16 Pandey, S and Srivastava, R. S. (2009). Anticonvulsant Activity Of Some Schiff Bases Synthesized From 2- Aminopyridine, *Pharmacology*, 2,1048-1074.
- 17 Sakthilatha, D. and Rajavel, R. (2013). The template synthesis, spectral and antibacterial investigation of new N₂O₂ donor Schiff base (Cu(II), Ni(II), Co(II), Mn(II) and VO(IV) complexes derived from 2-hydroxyacetophenone with 4-chloro-2,6-diaminepyrimidine. *J. Chem. Pharm. Res.*, 5(1): 57-63.
- 18 Sheeja Lovely, K. L. P. and Christudhas, M. (2013). The DNA cleavage and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 4-pyridinecarboxaldehyde with 4-aminopyridine. *J. Appli. Chem.*, 4(3): 14-19.
- 19 Siddappa, K. and Sunilkumar, B. M. (2013). Pharmacological activity of (E) 3-2-(1-(1-hydroxynaphthalen-2-yl)methyleneamino)phenyl)-2-methylquinazole-4(3H)-one Schiff base and its transition metal complexes. *Int. J. Pharm. and Pharmaceut. Sci.*, 5(3): 725-732.
- 20 Singh, P. and Dhakarey, R. K. S. (2009). Synthesis, characterization and antimicrobial studies of metal complexes with schiff bases derived from 2-thienyl glyoxal. *Rasayan.* 2(4): 869-874.
- 21 Sriram, D., Yogeewari, P., Myneedu, N. S., Saraswat V. (2006). *Abacavir* prodrugs: microwave-assisted synthesis and their evaluation of anti-HIV activities. *Bioorg. Med. Chem. Lett.*, 16(8): 2127-2129.
- 22 Solak, N. and Rollas, S. (2006). Synthesis and antituberculosis activity of 2-(aryl/alkyl amino)-5-(4-aminophenyl)-1,3,4-thiadiazoles and their Schiff bases. *Arkivoc.* - XII: 173-181.
- 23 Tantar, G., Vieriu, M. and Poiata, A. (2012). Synthesis and antimicrobial evaluation of different Schiff bases and their metal complexes. *Natura Montenegrina, Podgor.* 9(3): 889-895.
- 24 Tarallo, M. B., Urquiola, C., Monge, A., Costa, B. P., Ribeiro, R. R., Costa-Filho, A. J., Mercader, R. C., Pavan, F. R., Leite, C.Q-F., Torre, M. H. and Gambino, D. (2010). Design of novel iron compounds as potential therapeutic agents against tuberculosis. *J. Inorg. Biochem.* 104: 1164-1170.
- 25 Usharani, M., Akila, E. and Rajavel, R. (2012). Mixed ligand Schiff base complexes: synthesis, spectral characterization and antimicrobial activity. *J. Chem. Pharm. Res.*, 4:726-731.
- 26 Utku, S., Gokce, M., Aslan, G. M., Bayram, G., Ulger, M., Emekdas, G. and Fethisahin, M. (2011). Synthesis and *in vitro* antimycobacterial activities of novel 6-substituted-3(2H)-pyridazinone-2-acetyl-2-(substituted/non substituted acetophenone) hydrazone. *Tubitak.* 35: 331-339.

**Scheme I:** Reaction scheme for the synthesis of Schiff bases **L1-L4****Figure A:** Proposed structure for metal complexes.**Table 1:** Physical and analytical data of compounds **L1-CuL4**

Compound	Empirical formula (M.wt)	% (yield)	m.p (°C)	Microanalysis calcd (found)			
				C	H	N	Cu
L1	C ₁₂ H ₁₀ N ₂ O (198)	66	62-64	72.71 (72.33)	5.08 (5.03)	14.10 (14.00)	-
CuL1	C ₁₂ H ₁₅ ClCuN ₂ O ₄ (349)	54	164-166	41.15 (41.66)	4.32 (3.94)	8.00 (8.12)	18.14 (20.55)
L2	C ₁₂ H ₉ N ₃ O ₃ (243)	46	182-184	59.26 (59.14)	3.73 (3.56)	17.28 (16.96)	-
CuL2	C ₁₄ H ₁₆ ClCuN ₃ O ₅ (405)	57	249-256	41.49 (42.18)	3.98 (3.32)	10.37 (11.06)	15.68 (15.54)
L3	C ₁₂ H ₉ N ₂ OBr (277)	81	138-140	52.01 (51.96)	3.27 (3.21)	10.10 (9.88)	-
CuL3	C ₁₂ H ₁₀ ClBrCuN ₂ O ₂ (390)	62	289-295	36.66 (38.41)	2.56 (2.50)	7.13 (7.25)	16.16 (16.67)
L4	C ₁₃ H ₁₀ N ₂ O ₂ (228)	75	82-84	68.42 (68.32)	5.26 (5.28)	12.28 (12.14)	-
CuL4	C ₁₅ H ₁₉ ClCuN ₂ O ₄ (389)	53	208-209	46.16 (47.01)	4.91 (4.55)	7.18 (7.98)	16.28 (16.91)

M.wt = molecular weight (g/mol)

Table 2: Characteristic IR and NMR bands of compounds **L1-CuL4**.

Compound	IR bands (cm ⁻¹)						δ _{TMS} (ppm)	
	ν(OH)	ν(C=N)	ν(C-O)	ν(C=N)py	ν(M-O)	ν(M-N)	HC=N	
							δ _H	δ _C
L1	3058	1603	1276	-	-	-	9.41	161.84
CuL1	-	1595	1286	863	516	451	-	-
L2	3331	1595	1285	-	-	-	9.53	162.89
CuL2	3311	1605	1247	850	482	444	-	-
L3	-	1608	1276	-	-	-	9.34	160.87
CuL3	-	1587	1281	888	511	477	-	-
L4	3021	1598	1271	-	-	-	9.37	157.50
CuL4	-	1614	1278	886	521	467	-	-

Table 3: UV bands and molar conductance data of compounds **L1-CuL4**.

Compound	λ_{\max} (nm)				Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
	a	b	c	d	
L1	268	303	358	-	-
CuL1	-	292	356	410	5.20
L2	273	-	373	431	
CuL2		296	-	466	3.20
L3	-	305	358	-	-
CuL3	283		349	425	6.80
L4	-	305	365	-	-
CuL4	280	311	-	430	8.40

Table 4: *In-vitro* anti-tuberculosis activity of Schiff bases and their metal complexes on *M.TB* H37Rv.

Compound	0.4 y		0.2 y		0.1 y		0.05
	10^{-2} b	10^{-4}	10^{-2}	10^{-4}	10^{-2}	10^{-4}	10^{-4}
L1	20	2	35	3	62	7	-
CuL1	16	2	22	2	30	5	-
L2	0	0	0	0	0	0	-
CuL2	0	0	0	0	0	0	0
L3	10	0	12	0	30	6	-
CuL3	6	0	10	0	24	2	-
L4	24	0	33	6	41	10	-
CuL4	0	0	12	0	26	4	-
INH	0	0	0	0	12	8	-

Sensitivity values ≥ 1 = inactive, < 1 = active; y is concentration in $\mu\text{g/ml}$; b = CFU/ml

ETHNOMEDICAL SURVEY OF MEDICINAL PLANTS USED BY THREE INDIGENOUS TRIBES IN YOBE STATE, NIGERIA

Umar M. Umar & Ibrahim T. Babalola*

Department of Chemistry, Faculty of Natural Sciences, Yobe State University, Damaturu, Nigeria

Nigeria chemibrabal@gmail.com, drumumar@hotmail.co.uk

ABSTRACT

The use of plants in trado-medical systems of many cultures have been subject of investigation in recent times; with a view to preserve by documenting the indigenous knowledge of health-care system and to provide necessary clue for further scientific investigations. Ethnomedical survey was carried out amongst the Kanuri, Karekare and Hausa-Fulani tribes of Yobe State, Nigeria. The information were gathered through the use of questionnaires and direct interactions with some well established traditional healers, forest guards and community leaders (age-range:45-88years). The current report showed that fifty-one (51) plant species belonging to 32 families have been used commonly and continuously by these tribes in the treatment of wide spectrum of ailments in man, as well as animals. Most widely used amongst the plant families are leguminosae (*Acacia nilotica*, *Acacia sieberiana*, *Acacia senegalensis*, *Parkia clappertoniana*, *Pilostigma reticulatum*, *Pilostigma thoningi*, and *Tamarindus indica*), Combretaceae (*Combretum glutinosum*, *Guiera senegalensis*, *Terminalia avicenoides* and *Combretum dalzielli*), Curcubitaceae (*Mormodica charantia*, *Coccinia grandis*, *Cucumis sativus*, and *Cucumis melo*) in the treatment of fever, diabetes, as anti-emetics, anti-diarrhea, aphrodisiac, urethra and skin infections. The report highlights the individual tribal names and mode of preparation of the plants that are common to these people. The remedies mostly contain single plant material in form of decoction, maceration, infusion or ointment, or a mixture of two or more. This preliminary report provides evidence of an age-long and continuous ethnomedical practices amongst the Kanuri, Kare-kare and Hausa-Fulani tribes of the state. This is the first report on ethnomedicine of these indigenous tribal people.

Keywords: *Ethnomedicine, medicinal plants, indigenous knowledge, Kanuri, Kare-kare, Hausa –Fulani.*

INTRODUCTION

The study of indigenous health-care system is an essential phase in ethnomedical research. It is established that man had faced varying health challenges over the centuries and have had to explore his environment for ingredients in plants, animals, insects and minerals (Sofowora, 1982; Amrits, 2007). Remedies for different health conditions were developed overtime in different cultures of the world depending on their climatic, phyto-geographic and socio-cultural typologies. It is likely that the profound knowledge of herbal remedies in traditional cultures were developed through trial and passed from one generation to another (Rastogi and Dhawan, 1982; Gurib-Fakim, 2005). Traditional healers provide the basic cores of the health care delivery in 90 percent of African rural populations, and in consideration of this fact, WHO is pursuing a coordinated approach to promote and encourage recognition of traditional medicine on one side, and encouraging modern trained doctors and pharmacists to study the methodology and recipes offered by indigenous healers (WHO, 1993).

Nigeria's diverse flora offers a wide spectrum of unique medicinal plants (Dalziel, 1937). In Nigeria, medicinal plants are used in many parts of the country to treat diverse diseases including respiratory diseases.

Ethnomedical and ethnobotanical knowledge on some of these plants from different ethnic/tribal groups and cultures of the country have been reported (Gbile et al., 1991; Gill, 1992; Iwu, 1994, Obadoni and Ochuko, 2001; Tor-anyin, Shaato and Oluma, 2003, Mann, Gbate Nda-Umar, 2003; Igoli, Igwue and Igoli, 2003; Adamu et al., 2005; Igoli, Ogaji, Tor-Ayiin and Igoli, 2005). The use of medicinal plants and plant products in the treatment of diseases is highly revered and preferred by all the strata of the communities in Yobe. Herbal shops are found everywhere in the cities in addition to those hawking their products in trolleys, temporary tents and vehicles. Despite the wide acceptability of herbal medicine in treatment of disease conditions, no comprehensive record is available regarding the ethnomedicine of the indigenous people of Yobe, though there are few reports on similar plants from the neighboring communities such as Hausa-Fulani of Bauchi state and Kanuri tribe in Borno state. The objective of the present study is to document the ethnomedical practices amongst Kanuri, Kare-Kare and Hausa-Fulani people of Southern Yobe state.

METHODS

Study Area: Yobe state is one of the six states that form the North East geopolitical zone of Nigeria. It shares interstate boundaries with Borno state to the east, Gombe state to the South and Jigawa and Bauchi states to the west. Its northern border is shared with the Republic of Niger. The state consist of seventeen local governments and the main cities and towns in Yobe includes Damaturu (state capital), Potiskum, Gaidam, Buni yadi, Gujba, Gashua, and Nguru. Yobe state covers an area of 46,908.8 square kilometers and lies at latitude of 12⁰⁰ North and longitude of 11⁰³⁰ east. It has population of 2,321,339 (2006 census figures) and a population density of 31 person per square kilometer (Fig 1 &2). The major ethnic groups living in Yobe state are Kanuri, Hausa-Fulani, Kare-Kare, other ethnic group in the state includes Bade, Bolawa, Ngamo, Ngizim, Shuwa, Babur and Maga which are equally well represented in the state. There are six distinct modern languages that are indigenous to Yobe State-Duwai, Ngizim, Kanuri, Hausa, Fulfulde, Bade, Kare-kare, Bole and Ngamo (Schuh, 2003; 2004).

The survey was conducted between May 2013 and June 2014 at Damaturu, Gujba, and Kuka gadu area of Fika local government of Yobe state. Several visits were made to the selected traditional healers' home to enlighten them and to obtain their consent to work with the group, and much more importantly, to build their confidence in the project. The interviews were built on trust with a common aspiration to improve health-care situation in the country and to conserve the indigenous knowledge of health-care system of people of Yobe State. Traditional healers, forest guards, heads of households and adult members of the communities were interviewed. Interview of selected persons were conducted with the help of semi-structured questionnaire similar to the one described by Mann, Gbate and Nda-Umar (2003) and Igoli, Igwue and Igoli (2003). Information was also obtained from the healers, forest guards and other members of the community as to their age, gender, educational status, occupation, what they thought of diseases and their medical preference. The healers were interviewed on plants used, diseases treated, method of collection and preservation of plants, formulations, mode of administration, and any precautions which is needed to be followed during medication period. Essentially, traditional healers, forest guards and community leaders provided answers to the questionnaires and the information provided here were corroborated by the adult members of the community. They also provided guidance for the field-walk trips to the bush areas where they usually collect their medicines, pointed out the plants for collection and documentation, and discuss their various applications. The plants were duly authenticated by combined effort of technical staff of department of Biology (Botany Division) of Yobe State University and Directorate of Afforestation, Yobe State Ministry of Environment.



Fig. 1



Fig. 2



Fig. 3

Group picture at Baba Umar Tafida (Sarki Amale Jalam) compound, Kukar-gadu in Fika local govt of Yobe state.



Fig 4

The team in one of the forests with the traditional healers

Table 1. Compilation of Ethnomedical Information on Medicinal plants used by Kanuri, Kare-Kare and Hausa-Fulani People of Yobe State

	Botanical Family	Botanical Name	Local Names	Part Used	Therapeutic Indications	Ethnomedicinal Information
1	Amaranthaceae	<i>Afernanthera sessilis (Lin) DC</i>	Eng: Sessil joy weed	Root	Aphrodisiac	Powdered root of the plant plus the root of <i>Loudetia phragmitoids</i> , add root of 'Betobi' add to food and tea.
			Hau: Maikai dubu			
			Kan: Dubulitilo kəla miyaa			
			Kar:			
2	Anacardiaceae	<i>Mangifera Indica Lin.</i>	Eng: Mango	Leaves	Anti-Malarial & Typhoid, Liver diseases.	Decoction of the leaves with guava leaves, lemon leaves, banana leaves, Neem tree leaves and leaves of <i>Senna siamea</i> taken orally.
			Hau: Mangwaro			
			Kan: Mangulo			
			Kar: Mangoro			
3	Anacardiaceae	<i>Sclerocarya birrea (A. Rich) Hochst</i>	Eng: Marula tree	Stem/Bark	Treat dysentery	Maceration of the stem /bark (overnight) taken three times daily.
			Hau: Danya	Bark/Root	Diarrhoea	Decoction of the stem/bark plus bark of <i>Ficus platyphylla</i> taken orally.
			Kan: Malalea			
			Kar			
4	Asteraceae	<i>Vernonia perrottettii Schultz-Bip ex Walp.</i>	Eng:	Whole plant	Fever,	Decoction of the whole plant with <i>S.madagascariensis</i> and <i>P. thonningii</i> taken orally. Crushed leaves added to pomade, rub on the chest Decoction of the whole plants with potash taken orally. Maceration taken orally
			Hau: Burzu	Leaves,	Asthma.	
			Kan: Kaligi zərən	Root, leaves	Ex-viginalis	
			Kar: Mangwaro		Gunshot wound	
5	Bombacaceae	<i>Adonsonia digitata Lin.</i>	Eng: Baobab tree	Leaves	diarrhea	Powder of dry leaves taken orally to treat diarrhea. Chop into pieces and included in animal feed in fattening of animal Maceration taken for safe delivery.
			Hau: Kuka	Bark	Animal fattening	
			Kan: Kuka,kuwa			
6	Burseraceae	<i>Commiphora africana (A. Rich) Engl.</i>	Eng: African myrrh	Bark	Toothache	Decoction of the bark, gaggles regularly.
			Hau: Dashi, Biskiti	Seed	Fever Embrocation/ Rheumatism, body pain.	
			Kan: Kafi, Kafikafi	Root		Maceration of crushed leaves taken orally.
			Kar:			
7	Burseraceae	<i>Commiphora kerstingi Engl.</i>	Eng:	Stem/Bark	Vermifuge	Powdered and soaked in water to drink.
			Hau: Ararrabi, Bazara			
			Kan: Kafi Karagabe			
			Kar: Hararrabi			

8	Caesalpinaceae	<i>Cassia occidentalis</i> Lin.	Eng: Negro Coffee, Senna	Leaves	Anti inflammatory	Grind with red potash and rub at the inflamed part. Maceration of the whole plant taken orally.
			Hau: Majanfari, Tafasar, masar	Leaves, Whole plant with root	Malaria fever	
			Kan: Kōli, kainowa			
			Kar: Majanfari			
9	Caesalpinaceae	<i>Tamarindus Indica</i> Lin.	Eng: Tamarin tree	Root	Rehydration &diarrhea	Maceration of the root plus fruit of <i>Adasonia digitata</i> soaked and taken daily. Decoction of the fruit plus ginger/pepper taken orally.
			Hau: Tsamiya	Fruit	Rehydration (Hot season)	
			Kan: Tamsugu			
			Kar:			
10	Capparaceae	<i>Capparis tomentosa</i> Lam. <i>Capparis corymbifera</i> E. May ex Son.	Eng:	Whole plant	diarrhea in birds	Chop into pieces and soak in water to treat diarrhea in birds. powder and mix with cow butter and apply to the point of pain.
			Hau: Haujeri			
			Kan: Zaji, Fido	Root	Knee joint pain	
			Kar: Dikzaba			
11	Cochlospermaeae	<i>Cochlospermum tinctorium</i> Perr. ex A. Rich.	Eng: Zea maize	Root	Yellow fever	Root is soaked in water and taken twice daily. Grind the fresh leaves and wrap the affected finger in the treatment of witlow. As above.
			Hau: Rawaya, Balangade	Leaves	Whitlow	
			Kan: Masagwai	Root	Veneral diseases, Dysmenorrhoea, epilepsy.	
			Kar: Rawaya			
12	Combretaceae	<i>Combretum dalzielii</i> hutch or <i>C. fragrans</i> <i>Combretum adenogonium</i> Steud. Ex A. Rich.	Eng:	Leaves	Kwashioko	Dry leaves, powdered, add red potash to be taken in pap. Powdered leaves plus powder of 'Yaadia' (<i>Leptadenia hastata</i>) to treat emetic in pregnant women and for safe delivery. Maceration taken twice daily. As in above.
			Hau: Chiriri, Bakar T.	Leaves	Anti emetic/ Oxytocic	
			Kan: Zōndi			
			Kar: Jan zindi	Root	Yellow fever.	
13	Combretaceae	<i>Combretum glutinosum</i> Guill. Perr. ex DC	Eng:	Gum	Toothache	Apply to the point of pain Maceration of powder leaves, taken twice daily. As in above
			Hau: Kattagar, farar geza			
			Kan: Kadagar, kata'ar	Leaves and Bark Root	Leprosy, cough, deformation of limbs. Apetiser, Jaundice	
			Kar:			
14	Combretaceae	<i>Guiera Senegalensis</i> J. F. Gmel.	Eng:	Leaves	Fever	Powdered dry leaves and add to pap. Maceration of the leaves is given twice a day to newborn babies of lepers as prophylatic or preventive medication
			Hau: Sabara			
			Kan: Kasashi, kagashi	Leaves	Leprosy, diarrhoea and fever	
			Kar: Masasadi			
15	Combretaceae	<i>Terminalia avicennoi</i> Guill & Perr. Syn. <i>T.schimperina</i> Hochst	Eng:	Stem/Bark	Cough, diarrhoea, sore throat	Decoction of stem/bark plus the bark of <i>Lonchocarpus laxiflorus</i> with red potash taken orally. Decoction of the leaves taken trice daily, powder
			Hau: Baushe			
			Kan: Kōmanda	Leaves	Dysentry, wound dressing.	
			Kar: Baushe			

				Root	Induced abortion	leaves applied to wounds. Decoction is used as abortifacient.
16	Commelinaceae	<i>Commelina benghalensis</i> Lin.	Eng: Wondering jew Hau: Balasa Kan: Ngorgo chigube Kar:	Whole plant	Abdominal pain	Powdered and taken with water or pap
17	Commelinaceae	<i>Commelina diffusa</i> (Burm. F.)	Eng: Hau: Hanjin rago Kan: Guninguna Kar	Whole plant Leaves	Yellow fever, sores, Burns, Oedema Ophthalmia, yellow fever	Boiled in cow butter and drink and take juice of the leaves. Juiced or decocted.
18	Cucurbitaceae	<i>Coccinia grandis</i> (Lin.) Voigt. Syn. <i>Cucumis sativus</i> Lin.	Eng: Cucumber Hau: Gwanduwa Kan: Ngurli karagabe Kar: Ribsau	Fruit, leaves	Correction of bad sight	Eat raw fruit regularly and cook with the fresh leaves.
19	Cucurbitaceae	<i>Cucumis melo</i> (Lin.)	Eng: Musk melon Hau: Guna Kan: Guna Kar: Guna	Fruit	Chicken pox Pile, purgative	Chop into pieces, soaked in water and drink. Chop into pieces, dry and soak in water. Taken orally. Maceration of the leaves taken orally for treating constipation.
20	Cucurbitaceae	<i>Momordica charantia</i> Lin.	Eng: Balsam pear Hau: Daddagu, Garafini Kan: Daddago Kar: Randitabdo	Root Root, fruit & see	Itching Purgative, Aphrodisiac, Hypertension, laxatives vermifuge	Powdered add oil/cow butter and apply to the part. Decoction or maceration of powder taken.
21	Fabaceae	<i>Lonchocarpus laxiflorus</i> Guill & Perr. Syn. <i>Philenoptera* laxiflora</i> (Guill. & Perr.) Roberty	Eng: Hau: Halshen sa'a, Farin -sansamii, Fura bawa. Kan: Gombi Kar: Gombi	Fresh root	Anti-dote for snake venom	Chew the fresh root and swallow the juice after snake bite.
22	Fabaceae/Caesal-pinioideae	<i>Bauhinia rufescens</i> (Lam.) Syn. <i>Piliostigma rufescens</i> (lam), <i>Bauhinia adansoniana</i> Guill and Perrott.	Eng: Hau: Kargo, Na Allah Kan: Betobi, Sasa Kar: Jidben mandagai	Root	Aphrodisiac Astringent Febrifuge	Decoction of the powdered root of the plant with the root of <i>Loudetia phragmitoids</i> taken twice daily.
23	Fabaceae-Mimosoideae	<i>Dichrostachys glomerata</i> (Forsk) Chiov. Syn. <i>D. cinerea</i> (Lin) Wight et Arn.	Eng: Sicklebush, Bell mimosa Hau: Dundu Kan: Garwinna Kar: Bagayi	Leaves Bark Bark/Root	Anti-diarrhea, anti pyretic Syphilis, cough, Headache Stomachic, Vermifuge, Cure elephantiasis.	Maceration of the leaves plus cow milk and taken orally. Infusion of the root is used for treating cough Powdered and decocted or fresh plants parts decocted and taken twice daily.
24	Fabaceae-Mimosoideae	<i>Parkia biglobsa</i> (Jacq.) R. Br. ex G. Don. f.	Eng: West African locust bean Hau: Dorawa	Bark	Urethra infection/pain Treatment of	Powder and soaked in water taken orally. Powdered and apply in

			Kan: Runo, Ruwuno Kar: Runo		wounds.	wound dressing.
25	Leguminosae	<i>Acacia nilotica</i> (Lin.) Willd. ex Delile.	Eng: Nil Hau: Bagaruwa Kan: Kangar Kar: Gabaruwa	Seed/Fruit Leaves Bark	Diabetes, Tooth ache Anti-emetic Stomach ache	Powder of succulent adds to food to treat Diabetes. Dry, powdered and add to pap to treat nausea. Decoction of the bark taken orally to treat stomach disorder/diarrhoea
26	Leguminosae	<i>Piliostigma reticulatum</i> (DC) Hochst. Syn. <i>Bauhinia reticulatum</i> (DC), <i>P.thonningii</i> (Schum) Milne-Readhard	Eng: Monkey bread,Camel's foot tree Hau: Kargo Kan: Kalur, ka'al Kar: Kalar	Root Leaves, stem- bark	Greenish stool in birds. Rheumatism, Ulcers, Fever.	Maceration of the plant root plus the root of <i>Walteria indica</i> . Decoction of the leaves for treating fever, rheumatoids. Powdered leaves and stem bark for wound dressing.
27	Leguminosae	<i>Acacia Senegal</i> (Lin.) Willd.	Eng: Gum Arabic Hau: Dakwara,Dokora Kan: Kolkol, Gəḍər Kar: Kolkol			
28	Leguminosae	<i>Acacia sieberiana</i> DC	Eng: White thorne Hau: Farin-kaya Kan: Karamga Kar: Chancholi	Root Bark	Aphrodisiac Pile, General body pain.	Root soaked in water and drinks. Maceration of the bark taken to treat pile.
29	Leguminosae	<i>Tamarindus Indica</i> Lin.	Eng: Indian tamarin Hau: Tsamiya Kan: Tamsugu Kar: Dami	Leaves fruit Root	Skin infection Anti-poison, Laxative, antipyretic Eye infections	Decoction of the leaves is taken orally and bath several times daily for skin infections. Old fruit + "duban 'yeli" used to treat poison. Maceration or decoction is taken regularly.
30	Malvaceae	<i>Gossypium arboreum</i> Lin.	Eng: Tree cotton Hau: Shaashaaruwa Kan: kalətan, kəndər Kar: Shishi amu	Seed Leaves	Analgesic Blood purifier	Fried seed like groundnut and then grind, taken with food to relief pains. Soaked and pressed with water and drink.
31	Meliaceae	<i>Khaya Senegalensis</i> (Desr) A. Juss.	Eng: Dry zone mahogany Hau: Madaci Kan: Kagam, Ka'am Kar: Kagam,	Seed Bark	Eye and Ear infections. Gonorrhoea, fever, worm, stomach ache	Break shell, peel and fry, press to extract the oil. Soaked in cotton wool for the treatment of ear infection. Decoction of bark
32	Moraceae	<i>Ficus gnaphalocarpa</i> (Miq) A. Rich. <i>F. exasperate</i>	Eng: Sand paper tree Hau: Baure Kan: Tarmu Kar:	Root Bark	Cough Malaria (Kulongu)	Cut the root and collect the dropping water and drink. Boil with cow butter and

		<i>Vahl.</i>				garlic and drink
33	Moraceae	<i>Ficus polita Vahl.</i>	Eng: Nil	Seed and Leaves	Malaria fever	Seed and Leaves dried, powdered and add milk to treat malaria.
			Hau: Durumi			
			Kan: Lita			
			Kar: Durmi			
34	Moringaceae	<i>Moringa oleifera Lam.</i>	Eng: Horse radish	Root	Anaemia	Decoction of the root is taken orally to improve blood production Eat raw seed to treat diabetes or crushed leaves as tea. Decoction of the root.
			Hau: Zogale			
			Kan: Allam	Seed/leaves	Diabetes	
			Kar: Zogale			
35	Myrtaceae	<i>Psidium guajava Lin.</i>	Eng: Guava	Leaves	Anti Malaria & Typhoid	Decoction of the leaves with Mango leaves, lemon leaves, banana leaves, Neem tree leaves and Cassia siamea, taken trice daily.
			Hau: Goiba			
			Kan: Gofa			
			Kar: Gwaiba			
36	Olacaceae	<i>Ximenia Americana Lin.</i>	Eng: Sourplum	Leaves	Inflamed breast toothache Bladder infection Cystitis	Grind and rub the paste on the breast. Decoction or maceration.
			Hau: Tsada			
			Kan: Dadun	Root Bark		
			Kar: Datun			
37	Papilionaceae	<i>Indigofera pulchra Willd.</i>	Eng: Black bunu	Leaves	Whitlow	Fresh leaves, heated, powdered and add to cow butter. Insert the affected finger into the heated leaves at high temperature.
			Hau: Bakin bunu			
			Kan: Alin			
			Kar: Bakin bunu			
38	Poaceae	<i>Penisetum Pedicellatum Trin.</i> <i>Syn. P. polystachyon (Lin.) Schult.</i>	Eng:	Flower	Eye infection	Flower - when red, soak in small water and apply to infected eyes.
			Hau: Yan'swa			
			Kan: Fura	Leaves	Astringen/ antiseptic	
			Kar:			Fresh leaves are crushed to squeeze out juice, apply the juice to fresh wound and cuts.
39	Polygalaceae	<i>Securidaca longepedunculata Frer.</i>	Eng: Violet tree	Bark	Stomach ache	Chop the fresh bark into pieces and soak with bark of 'Marke' (<i>Anogeissus leocarpus</i>) 'gamafada' <i>Cassia arereh</i> in water taken orally. Decoction of dry or fresh root.
			Hau: Sanya			
			Kan: Gazawuro	Root	Menstrual disorders, cough, Rheumatism	
			Kar: Sanya			
40	Rhamnaceae	<i>Zizipus mauritiana Lam.</i>	Eng: Jujube	Leaves	Toothache Mouth sores, Wound healing, Blood tonic.	Chew/powder the leaves and apply to the affected area. Decoction is taken for blood.
			Hau: Magariya			
			Kan: Kusulu			
			Kar:			
41	Rhamnaceae	<i>Zizipus mucranata Willd.</i>	Eng: Bufalo thora	Seed/Fruit	Ringworm,	Red fruit/seed crushed fresh, apply to the affected part by ringworm
			Hau: Magaryar kura			
			Kan: Kusulu bultabe, Kusulu bina			
			Kar: Awuyo mzanje			
42	Rhamnaceae	<i>Zizipus spina christi (Lin.) Desf.</i>	Eng: Christ throne	Leaves	Ringworm	Grind the leaves with oil and apply to treat Ringworm.
			Hau: Kurna			
			Kan: Kurna			

			Kar: Kurna	Bark	Pile Slimmer	Powdered bark of the plant eating in food or drinks. As in above.
43	Rubiaceae	<i>Mitracarpus villosus (Sw) DC</i>	Eng:	Whole plant	Eczema, Leprosy and fungus growth in the throat	Juice of crushed plants is applied to the affected parts. Whole plant dried, powdered, add red potash, add cow butter, apply to the infected point. Powder and taken as tea or in food.
			Hau: Harwatsi, Gogamasu	Whole plant		
			Kan: Walwali, Arwali			
			Kar:			
44	Sapotaceae	<i>Butyrospermum Parkii (G. Don) Kotschy. Syn. Butyrospermum paradoxum, Vitellaria paradoxa* C. F. Gaertn.</i>	Eng: Shear butter tree	Bark	Body pain, Fever, Arthrites, Rheumatism, skin conditions	Powdered bark plus powder the bark of <i>Sterculia setigera</i> and bark of <i>Terminalia avicennoides</i> , mix with oil and rub for body pain. Shea butter is applied topically. It is also steamed to relief nasal congestion.
			Hau: Kadanya	Seed/Oil		
			Kan: Toso			
			Kar:			
45	Sterculiaceae	<i>Sterculia setigera Del.</i>	Eng: Karaya gum tree	Bark	Good health Anti hypertensive	For general health maintenance soak and take the extract. <i>Mimosa pigra</i> leaves plus leaves of <i>Sterculia setigera</i> soaked in water and taken twice daily to treat High blood pressure.
			Hau: kukkuki, kukoki	Leaves		
			Kan: Səgəwo			
			Kar: Sokobi			
46	Sterculiaceae	<i>Waltheria americana Lin.</i>	Eng:	Root	Aphrodisiac	Root plus bark of desert date 'aduwa'(<i>Balanite aegyptiacal</i>) and root of 'Gaude'(<i>Gardenia aqualla, syn.erubscens</i>), add potash; grind and sieve to be taken in food.
			Hau: Hankufa			
			Kan: kəlakəla bilu			
			Kar: Chaka'udau			
47	Ulmaceae	<i>Celtis integrifolia (syn-celtis zenkeri)</i>	Eng: Adolfi, Nettle tree	Gum	Cough Anti-emetic	Boiled and taken twice daily to relief cough Leaves soaked in water and drink to treat vomiting .
			Hau: Zuwo	Leaves		
			Kan: Nguzo			
			Kar: Gankilde			
48	Verbenaceae	<i>Vitex doniana Sweet.</i>	Eng: Black plum	Bark	Stomachache in Children Jaundice	Dried and powdered to be taken in soup. Boiled with potash, taken orally
			Hau: Dinya			
			Kan: Ngalibi			
			Kar:			
49	Vitaceae	<i>Ampelocissus granti (Baker) Planch. Syn. A. Africanus (Lour.) Merr.</i>	Eng:	Stem, Leaves	Weaning baby Joint pain, bone setting and healing ,menstrual cramp	Powdered and to add cow milk to prevent diarrhea.
			Hau: Dinya, Inabii, Roogon daaji			
			Kan: Mamman ngalibi			
			Kar:			

50	Vitaceae	<i>Cissus quadrangularis</i> <i>Lin.</i>	Eng: Devil's backbone, bone setter	Leaves	Analgesic	Decoction of the leaves and stem taken orally helps control soft bones in children and lack of calcium in pregnant women.
			Hau: Daddori, Daafaaraa			
			Kan: Diksama, Diksaba			
			Kar:			
51	Zygophyllaceae	<i>Balanites Egyptiaca</i> (<i>Lin.</i>) <i>Delile.</i>	Eng: Desert date	Bark	Aphrodisiac	Rub the leaves ground on the scorpion bite spot to relief pain.
			Hau: Aduwa			
			Kan: Chingo	Fruit	Laxative Vermifuge,	To the bark, add root of <i>Walteriicaa indica</i> , add root of <i>Gardenia erubiscens</i> , add potash; grind and sieve to be taken in food.
			Kar: Ajan			

Key: Eng-English; Hau-Hausa; Kan-Kanuri; Kar-Kare-kare

RESULTS

The present survey report shows that in the present study a total of fifty two (51) plant species belonging to thirty three families (32) were identified and collected with the respondents in Yobe state (Table1). It highlights the botanical and vernacular names of individual plants according to the three tribal dialects, the part(s) used, therapeutic indications, mode of preparation and administration. The family Leguminosae had the highest number of plants prescribed (5) followed by Combretaceae family (4), while Curbitaceae, Fabaceae and Rhamnaceae had three each. The report highlights a total of seventy nine (79) prescriptions for forty nine (49) different health conditions.

DISCUSSION

The unique value of ethnobotanical surveys of indigenous people of a community has been reported previously (Githens, 1949, Shellard, 1979, Sofowora, 1985). This study shows the existence of an age-long ethnomedical practices amongst indigenous people of Yobe, especially Kanuri, Kare-kare and Hausa-Fulani tribes. It also reveals the wide acceptability and continuous use of herbal medicine amongst these tribal people belonging to different strata of the society. Indeed, the majority of the people use these medications at one time or the other and this justifies the assumptions on the efficacy and safety of the plant materials used in the medicine. There are a number of reasons why people prefer plant medications, these includes ready availability, low cost, improved health after herbal treatment due to synergistic effect of complementary components, high cost and unavailability of synthetic drug in the rural areas. There are also cases of people who are already accustomed to and are comfortable only with traditional medications.

The report also revealed that some of the plants are commonly used for the same disease conditions by the tribes, while in some plants different usages were obtained. It also showed that there are significant similarities in the ethnomedical formulations of indigenous people of Yobe and those reported in some of the northern states of the country. The study also revealed that a number of plants are only known with their Hausa names by Kanuri and Kare-kare tribes suggesting close cultural similarities. The study also found that the understandings some of the traditional healers as regards some deadly and highly contagious diseases are vague and could be misleading, especially in conditions like tuberculosis, cancer, HIV/AIDS.

Although traditional medicines are still practiced both in the rural and urban cities in Nigeria, accurate information on the plant based ethnomedical practices remains largely with older

members of the communities as previously reported (Ene et al., 2010). Most of the elders interviewed have expressed concern that the indigenous knowledge of health care management is at the risk of extinction, this is because the younger generation are not keen about acquiring the knowledge owing to the parochial view that the practice is outdated.

It is essential therefore that the government and the people in academia to strive harder to document and preserve this indigenous knowledge, so that the future generation could benefit from its potentials. Documentation of indigenous knowledge will be beneficial in general healthcare, agriculture and drug discovery research. Traditional medicine should be incorporated in primary health care of the country as currently demonstrated by some developed nations.

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REFERENCES

- Adamu, H.M., Abayeh, O.J., Agbo, M.O., Abdullahi, A.L., Uba, A., Dukku, H.U., Wufem, B.M. (2005). An ethnobotanical survey of Bauchi State herbal plants and their antimicrobial activity. *J. Ethnopharmacol.*, 99: 1-4.
- Amrit, P.S.(2007). Ethics in Herbal Medicine. *Ethnobotanical leaflets*, 11:206-211. (<http://opensicuc.lib.siu.edu/cgi/viewcontent.cgi>).
- Dalziel, J.M. (1937). *The Useful Plants of West Tropical Africa*. Crown Agents for Oversea Government and Administration, pp.109.
- Ene, A.C., Atawodi, S.E., Ameh, D.A., Kwanashie, H.O., and Agomo, P.U. (2010) Locally used plants for malaria therapy amongst the Hausa, Yoruba and Ibo communities in Maiduguri, Institute, Lucknow (India). *Indian Journal of Medicinal Research* 1982, 76 (Suppl):27-45.
- Gill, L.S. (1992) *Ethnomedicinal uses of plants in Nigeria*. Uniben press, Benin City, Nigeria, p.276.
- Githens, T.S.(1949) *Drug Plants of Africa*. University of Pennsylvania Press, The University Museum, Philladepia. p125.
- Gurib-Fakim, A. (2006) *Medicinal Plants: Traditions of Yesterday and Drugs of Tomorrow. Molecular Aspect of Medicine*, pg. 4
- Igoli, J.O., Igwue, I.C.and Igoli, N.P. (2003). Traditional Medicinal Practices among the Igede People of Nigeria. *Journal of Herbs, Spices and Medicinal Plants*. 10: 1-10.
- Igoli, J.O., Ogaji, O.G., Tor-Anyiin, T.A. and Igoli, N.P. (2005). Traditional medicine practice amongst the Igede people of Nigeria, Part II. *African Journal of Traditional, Complementary and Alternative Medicines*. 2:134-152.
- Iwu, M.M. (1994). African Medicinal Plant in the Search for new drugs based on ethnobotanical leads. In: (D.J. Chadwick and J. Marsh, eds.) *Ethnobotany and the search for new drugs*. Ciba Foundation Symposium, Wiley, Chichester, 185: 116-129.
- Mann, A., Gbate, M. and Nda-Umar, A. (2003). *Medicinal and Economic Plants of Nupeland*. 1 Ed. Jube, Evans books and Publications, Bida, 279 pp.
- Schuh, R.G. (2003) The Linguistic influence of Kanuri on Bade and Ngizim. *Maiduguri journal of Linguistic and Literary studies (MAJOLLS)* 5:55-89.
- Schuh, R.G. (2004) Yobe State, Nigeria as a Linguistic Area. UCLA, Los Angeles (<http://www.humnet.ucla.edu/humnet/aflang/Yobe/>).
- Shellard, E.J.(1979). The significance of research into medicinal plants. In A Sofowora ed., *African Medicinal plants*. Proceedings of the Pan African conference on Research into medicinal plants held at the Univ. of Ife, Ile Ife in April 1974., University of Ife Press, Ile ife, Nigeria, pp 98-111.

- Sofowora, A. (1982). *Medicinal Plants and Traditional Medicine in Africa*. New York: John Wiley and Sons. Ltd, New York pp54.
- Sofowora, A. (1985). *Medicinal Plants and Traditional Medicine in Africa*. New York: John Wiley Sons Ltd, New York, pp.256.
- WHO (1993). Summar 9 WHO guidelines for the assesement of herbal medicines. *Herbal Grom* 28, 13-14.

DNA TYPING OF MICROBES ISOLATED FROM SOIL AND WATER SAMPLES

Dawodu O.G * & Olasusi O.O

Department of Science Laboratory Technology, Federal Polytechnic Ede, Osun State, Nigeria

*dawgrace@yahoo.com

ABSTRACT

This research was born with the passion of characterizing soil and water microbes according to their genetic information that can be found on the chromosomal DNA of the microbes. The soil and water sample were taken within the local community of Ede, very close to engineering village at conducive villa around Agbale Road Ede, Osun State. Both environmental samples were taken to the laboratory, and were made into serial dilutions. After this, inoculated into plates and covered with nutrient agar. It was then incubated, sub-cultured to give pure isolates. After these, their genomic DNA was extracted by alkaline lysis. It was then followed by the amplification of the extracted DNA. This was then subjected to gel electrophoretic analysis to determine their DNA banding pattern of which the photomicrographs of these patterns was taken, compared and analyzed genotypically to determine sequence of the DNA present. The result shows that the water and soil microbes responsible for these banding patterns were confirmed to be *Bacillus* species and *E. coli* which was then noted for the two environmental samples. This finding could be useful for the proper management and control of these microbes.

Keywords: DNA, genotyping, bacteria isolates, environmental samples, gel electrophoresis

INTRODUCTION

Genetic diversity of microbes can ultimately explain most phenotypic variability in bacteria, such as geographic distribution, host specificity, pathogenicity, antibiotic resistance, and virulence. As bacterial strains pose ever greater challenges to human health, including increased virulence and transmissibility, resistance to multiple antibiotics, expanding host spectra, and the possibility of genetic manipulation for bioterrorism, identifying bacteria at the strain level is increasingly important in modern microbiology. Fournier *et al.*, (2004).

DNA bands (fragments) can be generated by digestion of DNA with REs, DNA amplification, or by a combination of both. DNA amplification generates billions of copies of a genomic fragment and has many advantages, including sensitivity, speed, and applicability to a wide array of human specimens and environmental samples. Lo & Chan, (2006). REs precisely recognize and cut target DNA at a defined sequence, which makes enzymatic restriction an effective tool. Blakesley, (1987).

The aim of this study is to type soil and water microbial isolates based on their DNA banding pattern.

METHODS

MATERIALS FOR CULTURE

Petri dishes, Wire loop, Conical flask, Aluminum foil, Measuring cylinder, Weighing balance, Beaker, Bunsen burner, inoculums bottle, Spirit lamp, Screw cap test tubes, Inoculating chamber or Sterile bench, Bacteria enriched media(e.g. Nutrient Agar), Acetone/ alcohol, Cotton wool, Paper tape, Pipette, Autoclave, Incubator.

Bacterial DNA Extraction and Amplification

All needed reagents, pipettes, centrifuge, e-buffer, lysozyme solution, measuring cylinder, (10mg/ml in 10mM Tris HCl, pH8) Sucrose 5% triton x – 100, 50mM EDTA, 10mM tris HCl

(pH8.0) water bath stop clock sodium acetate volume of 100 μ L containing 50 ng of template DNA, 200 μ M of dNTP, 0.4 nM of each primer, buffer 1 (4mM $MgCl_2$, 0.4mM of each dNTPs) 1.5 mM of $MgCl_2$, and 2.5 U of Taq DNA polymerase.

PROCEDURE

Microbial (Bacteria) Isolation

The methods of Natakus., 2007 & Saman., 2010 was adapted for this study.

DNA Extraction Procedure

The method of Jones & Bartlet., 2008 was adapted for this study

For chromosomal bacterial DNA isolation the method of Hassan *et al.*, 2012 was used in this study.

Bacteria DNA Amplification Method

For bacterial DNA amplification, the method of Wejun Li *et al.*, (2009)

The summary of the methodology is illustrated in the flow chart below.

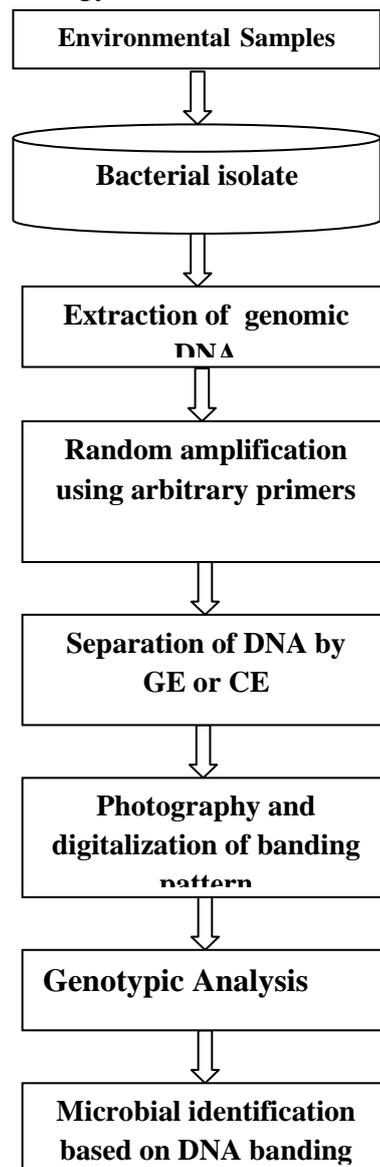


Fig 1. Flowchart for DNA isolation, extraction purification and amplification (Wenjun Li. *et al.*, 2009) GE- gel electrophoresis, CE- capillary gel electrophoresis

RESULTS

DNA Purification Result

Protein expression was kept under tight control to prevent it from interfering with the result.

Absorbance: 260nm /280nm

Sample amount:20µg/ml

Genotypic Analysis Result

Electrophoresis of the DNA, blaCTX-M and RAPD PCR products was carried out on 0.8 % and 1.5% agarose gel at 100 V for 1 h respectively. Bands were viewed under ultraviolet light for photo-documentation. DNA bands were sized by extrapolation using 1kb and 100 bp DNA molecular weight markers.

DISCUSSION

Microbial Growth Report

After incubation it was observed that the growth was much on soil culture plate compared to that of water. This is due to the fact that soil contains a lot of organic matter which act as a facilitating medium for the growth and sustenance of different microbes. Therefore soil is more susceptible to the breeding of more microbes than water which have little or no organic matter dissolved in it. Jussen *et al*, (2002).

In the process of isolation it was also been observed that some isolate growth inhibits the growth of the other due to the production of various metabolite which are inform of antibiotic in nature. This automatically leads to reduction in microbial growth causing few organisms to be isolated. Due to the antibiotic nature of the various metabolites, it tends to wipe out some microbes that are less resistant to their effect in and around the particular colony producing it. For example, many different antibiotics are produced by *Streptomyces* species isolated from soil.

Appearance: The growth on both environmental samples appeared to be creamy and mouldy. Some were seen to be concave in shape with light edges, while some were seen to be cocci in shape in which it follows a regular pattern.

Gram Reaction: They were all seen to be gram positive, some were suspected to be bacillus while others are between *Staphylococcus aureus* and *E.coli* sp.

In this study, isolation, purification and genomic profiling of microbial life present in the two environmental samples (soil and water) were specifically carried out to determine the type of microbes present in these samples.

The result starting with the DNA purification was gotten and recorded as tabulated in fig.2.0 above. It was done to give the purity of DNA of each isolates together with their yields in nanomicro (nµ) yield.

Purity is measurement of absorbance, although it could be argued that fluorescence measurement is easier, absorbance measurement is simple and requires commonly available laboratory equipment. All that is needed for the absorbance is a spectrophotometer with UV lamp, UV transparent cuvettes (depending on the instrument) a solution of purified DNA. Wilfinger *et al*, (1997).

Absorbance readings were performed at 260nm (A260) where DNA absorbs light most strongly, and the number generated gives room for the estimation of the DNA concentration in the sample solution. To ensure that a useful figure was gotten at each stage, A260 was done within the instrument linear range (generally 0.1-2.0) DNA concentration was estimated by measuring the absorbance at 260nm, adjusting the A260 measurement for turbidity (measuring absorbance at

320nm), multiplying by the dilution factor and using the relationship that an A260 of 1.0 = 50µg/ml pure ds DNA.

Concentration (µg/ml) = (A260reading-A320readings) × dilution factor50µg/ml. This equation of concentration is as derived from Beer's Law.

Total yield is obtained by multiplying the DNA concentration by the final total purified sample volume.

DNA yield (µg) = DNA conc. × total sample volume (ml).

However, DNA is not the only molecule that can absorb UV light at 260nm. Since RNA also has a great absorbance at 260nm, and the aromatic amino acid present in protein absorb at 280nm. Both contaminants, if present in the DNA solution, will contribute to the total measurement at 260nm. In the light of this both contaminants were kept under tight control to ensure an accurate result.

Good-quality DNA will have an A260/A280 ratio of 1.7-2.0 as can be observed from the purification result in fig.4.0 of this noble research. A reading of 1.6 does according to Wilfinger, does not render the DNA unsuitable for any application, but lower ratios indicate more contaminants are present. The ratio can be calculated after correcting for turbidity (absorbance at 320nm).

DNA purity (A260/A280) = (A260reading-A320reading) ÷ (A280reading-A320reading)

Strong absorbance around 230nm can indicate that organic compounds or chaotropic salts are present in the purified DNA. A ratio of 260nm to 320nm can help evaluate the level of salt carryover in the purified DNA. The lower the ratio, the greater the amount of thiocyanate salt is present, for example as a guideline, the A260/A320 is best if greater than 1.5.

A reading at 320nm will indicate if there is turbidity in the solution, Another indication of possible contamination.

Therefore, taking a spectrum of reading from 230nm to 320nm is most informative. Wilfinger et al., (1997).

It can be observed from table 1 that despite the variation in isolates purity, some samples e.g. sample 15 and 6, 12 and 10, 9 and 3 are having more or less the same purity value.

Also looking through the table some degree of closeness can be observed in the isolates DNA purification yield which was written in nanomicro yield (nµ)

It can also be observed that the degree of DNA purity can be grouped into basically two broad categories in which 1.40-1.99 forms the major purity range while 1.27, 2.01 and 2.02 forms the minority range.

It was observed that the number of yield also varied from 98 to 3175 nanomicro yield.

Sample 17 can be seen to have moderate purity and at the same time produce the lowest yield in the table, while sample 16 can be seen to have the lowest value for purity and also have the highest value of yield.

RAPD Profiling was used in this research to help distinguish between bacteria isolates by DNA fingerprinting. These isolates were primarily environmental and an indispensable means of livelihood for the biotic (living) community. Myers *et al.*, (1993)

Result in fig.2 A and B shows that the intensity of several bands varies according to the DNA bands of the recovered species. It can be observed that bacillus species was recovered as seen from the A part of the banding pattern while E.coli was seen to come into expression in the B part of the banding pattern. This pattern was observed to remain essentially unchanged at even 100-fold template dilution.

In accordance with the banding pattern result, we can see a number of base pair (bp) that shows the presence of both the Bacillus and E.coli in the sample.

Also the result shows that sample 2, 4, 7, 8, 11 with base pair 200, 100 and 50 are *Bacillus* sp., while sample 9, 10, 12 with base pair 250, 100 and 50 respectively are *E. coli*.

Results presented here demonstrate that introduction of RAPD profiling in the genomic analysis of microbes can significantly simplify the process of screening large numbers of isolated microbes. However, the specific banding pattern that generate the unique DNA profile can easily be found in figure 2 (A) and (B). The research can therefore lead to the identification of different species that are present in a sample showing that it is the most informative banding pattern that can be used.

CONCLUSION

It can be clearly seen from this research that *Bacillus* sp and *E. coli* was confirmed to be present in this two indispensable environmental samples [Water and soil]. This particular act of tracing is known to be genotypic analysis. Then this kind of analysis can give rise to phylogenetic analysis through the method of gene sequencing and it is done by merely comparing their gene sequence result of genotypic analysis with an existing data based software, which allow for easy classification and grouping of each organism into different strata and substrata in accordance with their genetic evolutionary trend. The group or strata can then be arranged to form a tree-like structure. This particular arrangement is known as phylogenetic tree.

Finally going through all these, it can be deduced that this research is informative enough to ensure proper identification, management and control of both water and soil microbes. This research is also vital for various medical and pharmaceutical diagnoses in terms of microbial strain generated by the soil and water microbes.

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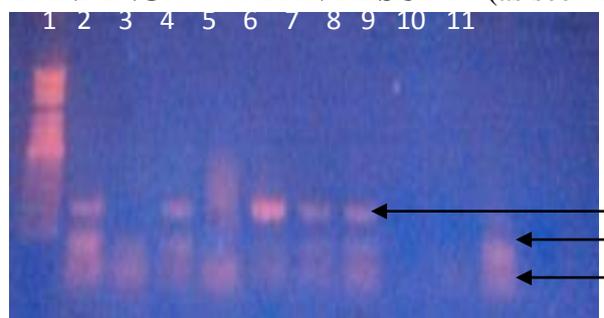
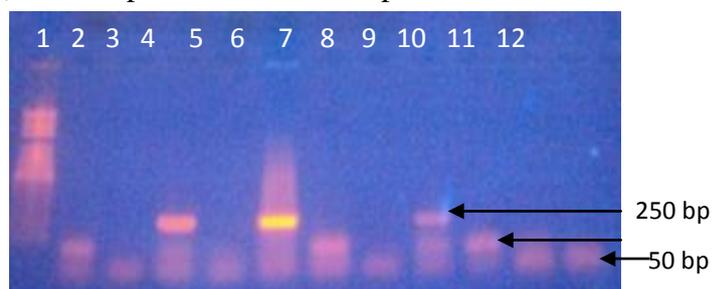
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REFERENCES

- Blakesley RW (1987) Restriction endonuclease: *cleavage*, ligation, and sensitivity. *Gene Amplif Anal* 5: 51–102. *PubMed, CAS*
- Fournier PE, Zhu Y, Ogata H & Raoult D (2004) Use of highly variable intergenic spacer sequences for multispacer typing of *Rickettsia conorii* strains. *J ClinMicrobiol* 42: 5757-5766. *Cross Ref, PubMed, CAS, Web of Science® Times Cited: 26*
- Hassan A.M.EL Dermerdash (2012) A Simple and Inexpensive Procedure for Chromosomal DNA Extraction from Bacteria *MolBiol*226: 15–20. *PubMed,CAS*
- Jones & Bartlet (2008). *Experimental Techniques in Bacteria Genetics* 245:6623:28-29
- Jussen P.H *et al.*, (2002). "Improve Culturability of Soil Bacterial and Isolation in pure culture of novel Member of the Divisions Acido Bacterial and verruco microbial Appl environ microbial 68:2391-2396.
- Lo YM & Chan KC (2006) Introduction to the polymerase chain reaction. *Method MolBiol*336: 1–10. *PubMed,CAS*
- Myers, L.E., S.V. Silva, J.D. Procnier, and P.B. Little. (1993). Genomic fingerprinting of "Haemophilus somnus" isolates by using a random-amplified polymorphic DNA assay. *J. Clin. Microbiol.* 31: 512-517.
- Natatsu C.H (2007) Soil Microbial Community Analysis using Denaturing gradient Gel Electrophoresis. *Soil scisoc am J* 71:562-571.
- Saman S. Saman and Patty S. (2010) Isolation Discription and Novel Species *Bacillus Samanii* sp. Nov. from snow Accepted with revision *Microbiology insight*.
- Wilfinger, karol Mackey and Piotr Chomeczynski (1997). Effect of pH and ionic strength on the spectrophotometric assessment of Nucleic Acid Purity: *BioTechniques* 22:474-481.

Table 1: Amount of purified DNA in NanoMicro yield (nμ)

S/N	PURITY	YIELD (nμ)
Sample 1	1.60	98.3
Sample 2	1.99	233.2
Sample 3	2.02	268
Sample 4	1.66	346.1
Sample 5	1.50	224
Sample 6	1.61	290.7
Sample 7	1.40	147.5
Sample 8	1.73	305
Sample 9	2.01	131.7
Sample 10	1.88	159.3
Sample 11	1.90	149
Sample 12	1.88	344
Sample 13	1.54	194.7
Sample 14	1.4	105
Sample 15	1.61	330
Sample 16	1.2	3175.7
Sample 17	1.51	98.2
Sample 18	1.95	306

RAPD BANDING PATTERN RESULT –(as seen from gel electrophoresis)**Fig 2 (A):** RAPD profile of *Bacillus* species recovered from the environmental samples**Fig 2 (B):** RAPD profile of *E. coli* isolates recovered from the environmental samples

TENSILE PROPERTIES OF PRE-HEATED BITUMEN QUENCHED DUAL PHASE MEDIUM CARBON STEEL

M.O.H. Amuda^{*}, T. A. Olaniyan and L. O. Osoba

Materials Development and Processing Research Group (MADEPREG)

Department of Metallurgical and Materials Engineering

University of Lagos, Lagos, Nigeria 101017

mamuda@unilag.edu.ng

ABSTRACT

The tensile properties of Dual Phase Steel (DPS)-duplex structure-produced by quenching in pre-heated bitumen have been investigated. Medium carbon steels intercritically heated at different temperatures and holding times were quenched in hot bitumen. Optical and scanning electron microscopy characterisation of the duplex structure revealed extensive network of fibrous martensite in a ferritic matrix with occasional presence of polygonal martensite. The duplex phase structure exhibited continuous yielding dynamics improving the tensile and hardness values by about 42 and 35%, respectively relative to the normalised structure. But, the elongation decreased by about 42 when compared to the normalised structure. These values are similar to those obtained in duplex structure produced using conventional oil quenching. These findings suggest that pre-heated bitumen can be exploited for the production of DPSs.

Keywords: *Duplex structure, fibrous martensite, intercritical annealing, tensile fractured surface*

INTRODUCTION

In the last three and half decades, stringent energy/service economics and environmental considerations have necessitated the drive for the development of advanced steel materials with potential for lower carbon footprint discharge without sacrificing on the performance of conventional ferrite-pearlitic steels (Hall, 2011; WorldAutoSteel, 2011; Granbom, 2010; Tsipouridis, 2006). There are several grades of such better steels that have been developed and commercially available in the market ranging from transformation induced plasticity (TRIP) steels, high strength low alloy (HSLA) steels to dual phase (DP) steels all belonging to a class of steels called *Advanced High Strength Steels (AHSSs)*(Hall, 2011).

Recently, however, advancement in these steels has focused mainly on the DPS because this grade of steel exhibits superior strength and plasticity relative to other high strength low alloy steels (Mazinani and Poole, 2007; Sun and Pugh, 2002; Xu et al., 2008). This is a new class of high- strength low-alloy steel having a microstructure consisting strong martensite and/or bainite colonies dispersed in a soft matrix of ferrite (Ghosh et al., 1991). Instances of the additional presence of retained austenite in the ferrite matrix have also been reported but this has not been shown to have significant influence on the improved properties of the material (Tayanc et al., 2007; Bayram et al., 1999; Rashid, 1981). The martensite content in the steel which usually range between 15-25% coupled with its morphology influences the mechanical properties of the steel. But, irrespective of the distribution and forms of the martensite, the DPS is reported to exhibit continuous yielding with no yield point, lower yield strength/tensile strength ratio, higher initial strain hardening rate, uniform elongation and higher strain rate sensitivity with better fatigue resistance relative to conventional ferrite-pearlite plain carbon steel (Mazinani and Pool, 2007; Bello, 2007; Bhattacharyya et al., 1993). These combinations of strengths and formability have made DPS very attractive to industries, particularly, the automobile sector; and there is

indication that this could equally be extended to many other areas particularly those related to structural applications (Khamedi et al., 2009; ThyssenKrupp Steel Europe, 2008). The duplex structure in DPS offers the potential for combining the strength of conventional high strength low alloy steels with a formability approximating that of plain carbon steel.

A major variable in the metallurgy and properties of DPS is the quenching medium through which the steel is produced (MacKenzie, 2011). This is majorly influenced by the viscosity of the medium. For instance oil (be it vegetative or synthetic) has a higher viscosity than water and as such, usually produce a DPS with better microstructural features and properties than water. Oil quenching therefore represents a more attractive process for producing DPS with improved properties than water quenching.

But there are issues of environmental sustenance and bio-degradability associated with conventional synthetic oil quenchant which has motivated the drive for organic oils. While much success has not been reported with organic oil quenchant, there is still the need to develop alternative to the conventional synthetic oil quenchant. It is in the light of this that bitumen in the pre-heated state is investigated as a possible quenchant for the production of DPS from medium carbon steel.

METHODS

Preliminary Treatment

The dark supercooled bitumen shown in Figure 1 was heated and melted in a stainless pot fired by a fossil fuel chamber to boiling point. Small quantity of about 20 ml was poured into a PENSKEY MARTENS close-cup flash point tester with facility for temperature reading. The temperature at the point the orifice in the tester released a flash of fire was noted as 310⁰C and recorded as the flash point. This value is both lower than the boiling point (350⁰C) and flash point (378⁰C) values available in literature for bitumen obtained from fractional distillation of crude oil (Speight, 1992).

Hot rolled carbon steel supplied as cylindrical rods of Ø12 mm x 1000 mm specification was cut-into coupon size of Ø 12 mm x 80 mm long. The composition of the steel, as provided by the manufacturer and validated via *in-house* spectroscopy, presented in Table 1 in comparison with published data (Alaneme, 2010; American Iron and Steel Institute, 1995) show that the material belongs to the medium carbon steel grade. The normalizing treatment was conducted at 870⁰C for 45 minutes in a muffle furnace followed by air cooling.

Intercritical Annealing Treatment

The intercritical (A₁ and A₃) annealing temperatures for the coupons were estimated from the chemical composition using the empirical relationship provided by Gorni (2006), Leslie (1981) and represented by Khamedi et al. (2009). The lower and upper critical temperatures calculated using those empirical relationship were found to be 722.4 and 804.2⁰C, respectively. Therefore, the lower and upper temperature values of 730 and 810⁰C and their mid-point were used for the intercritical treatments at soaking times of 30 and 60 minutes.

The coupons were subsequently intercritically treated at the various combinations of temperature and holding time listed in Table 2 and then rapidly quenched in hot bitumen maintained at a preheated temperature of 280⁰C. The surface of the quenched pieces was then cleaned off and then minimally ground to remove oxidised surface scales before metallographic preparation.

Microstructural and Mechanical Characterisation

The treated coupons were prepared for microstructural evaluation by grinding successively in a series of emery papers while final polishing was done with 0.05 µm alpha agglomerated alumina suspension. Etching was conducted with 2% Nital solution for 5-10 seconds just before microscopic examination.

Macrohardness of the coupons were evaluated using a Brinell hardness tester. Polished surface of the samples were indented with a load of 500gf until a permanent indentation was achieved. The diameter of the indentation was measured with a Brinell reading microscope and the corresponding hardness number was obtained from the conversion table. This test was repeated thrice and the average was taken as representative value.

Tensile testing repeated thrice was conducted at room temperature on appropriately machined sample in an Instron machine rated 100 KN at a strain rate of $2 \times 10^{-3} \text{s}^{-1}$ in accordance with ASTM E8M standards (2013). The specifications of the tensile samples are a gauge diameter of 4 mm, gauge length 10 mm and specimen length 40 mm. Morphological characterisation and fractography of the tensile fractured surface were conducted using scanning electron microscope in the secondary electron imaging mode at an applied voltage of 15 KV.

RESULTS AND DISCUSSION

Microstructural Analysis

The microstructure of the normalised sample from optical microscope shown in Figure 2 indicates a matrix of ferrite with grain boundary iron carbides and small islands of pearlite. The network of grain boundary iron carbide is very wide. Rashid (1981) reported similar microstructural features in normalised medium carbon steel whereas most published works have only reported on the existence of ferrite-pearlite microstructure in such normalised steels.

Figure 3 shows the microstructure of samples intercritically treated at 730⁰C for 30, 45 and 60 minutes, respectively. The microstructures at these conditions consist of ferrite matrix networked by polygonal martensite. The distribution of martensite estimated using graduated eye piece show increasing volume fraction of martensite with increasing soaking time. It is presumed that the low distribution of martensite at lower soaking time of 30 minutes is caused by the short heating times resulting in a non-homogeneous austenite. This inhibits complete diffusion of carbon into the austenite phase and a concentration gradient exists. With increasing soaking time, however, carbon diffusion is enhanced and a more homogeneous austenite evolves resulting in higher martensite distribution. The morphology of the martensite phase transits from polygonal to fibrous martensite at maximum soaking time of 60 minutes but with apparent increase in grain morphology.

Figures 4 and 5 are the micrographs obtained at intercritical treatments of 770 and 810⁰C for holding times of 30 and 60 minutes, respectively. The phase distribution in these micrographs is similar to those obtained at 730⁰C intercritical treatment; except that the morphology of the martensite is more fibrous at these higher intercritical temperatures than the polygonal obtained at 730⁰C.

Previous works reported the additional presence of retained austenite in ferrite-martensite dual phase structure produced through intercritical treatment (Giodarno et al., 1991) but such retained austenite is only observed in samples treated at 730⁰C for all soaking times but this is not seen in other treatment conditions (see Figures 3-5). Therefore, there is a need for more extensive study in this regard with diffraction technique; because if this is validated, it presents an innovative

strategy for improving the deformation behaviour of such dual phase structure resulting in improved formability of the steel.

The optical micrographs at the various intercritical treatment conditions were reinforced with scanning electron microscopy for detailed morphological analysis. These electron micrographs shown in Figure 6 revealed fibrous martensite whose morphology become coarser with increasing intercritical temperature and holding time with those treated at 810⁰C providing the more fibrous network of martensite in a ferritic matrix than the other treatment conditions.

Analysis of Mechanical Properties

The mechanical properties of the normalised sample presented in Table 3 show a bulk hardness of 95 HBN, tensile strength of almost 487 MPa and percent elongation of 17%.

Figure 7 shows the change in bulk hardness of bitumen quenched samples at different intercritical treatment temperatures. The bulk hardness increases with increasing holding time across all treatment temperatures with those held for 60 minutes exhibiting the highest hardness value. The hardness between 730 and 810⁰C range between 100 and 120 HBN for holding time of 30 minutes; and for 60 minutes, it range between 120 and 180 HBN. The hardness values from the quenched samples are higher than that of the normalised sample by about 16-90% across all the treatment conditions. The higher values in the quenched samples is predicated on the microstructure in the samples, wherein, the normalised samples consist of ferrite and iron carbide phases the quenched samples consist of dual phase structure of ferrite and martensite. The enhanced hardness is primarily due to martensite distribution in the ferritic matrix (Rashid, 1981). Increasing intercritical temperature and holding time increases the distribution of austenite in the two phase structure which eventually transforms to martensite on quenching in the preheated bitumen.

Figure 8 provides the trend of tensile strength in the quenched samples. The strength increases with increase in intercritical temperature up to a temperature of 770⁰C and subsequently reduces afterwards. The reduction is rapid at holding time of 30 minutes but gradual at holding time of 60 minutes. The minimum tensile strength value range between 501 and 566 MPa in the treatment temperature range 730-810⁰C for 30 minutes holding time. The range is 535-626 MPa for the same condition of temperature and 60 minutes holding time. These strength values are greater than the 487 MPa obtained in the normalised sample. The reduction in tensile strength at treatment temperature beyond 770⁰C can be predicated on the development of coarse martensite observed in Figure 5 and 8 as a result of high temperature treatment. Odusote et al. (2012) and Ekrami and Bahrehbarpoor (2005) reported similar findings of drastic decrease in tensile property. But Alaneme et al. (2010) reported continuous increase in the tensile strength of oil quenched dual phase steel up to intercritical temperature of 780⁰C. This contrasting information might be due to the chemistry of the steel samples since the samples investigated in the reported works were not of the same composition. In general, increase in hardness with increase in soaking time of treatment are accompanied with increase in strength, however, the formation of coarse martensite at intercritical temperature could alter the trend as observed in the current study.

The plastic flow trend in the dual phase structure with changes in intercritical temperature and holding time characterised in term of the percent elongation is shown in Figure 9. It emerged from the figure that the percent elongation decreases with increase in intercritical temperature but the influence of the holding time were generally inconsistent.

Intercritical treatment at 730⁰C for 30 minutes exhibited the highest percent elongation of 24% whilst that at 810⁰C is just about 19% for the same holding time. Similar trend is observed across the intercritical temperatures at holding time 60 minutes. The percent elongation in the quenched dual phase steel is greater than that of the normalised samples except for the value at 810⁰C for a holding time of 60 minutes. In this instance, the percent elongation is marginally lower by about 3 units.

It is believed that higher intercritical temperature promotes the transformation of ferrite to austenite and this increases the distribution of martensite in the final dual phase structure. Thus, with increased martensite distribution in the matrix the plastic flow decreases and the percent elongation is consequently reduced.

Tensile Surface Fractograph

The fractograph shown in Figure 10 revealed different fracture mode ranging from purely cleavage fracture to mixed mode of cleavage-dimple fracture. The cleavage mode is predominant at the intercritical temperature of 730⁰C while the mixed mode is prevalent in intercritical temperature 810⁰C. The fracture mode at 730⁰C temperature is presumed to be due to the presence of polygonal martensite while the mixed mode is influenced transition of the polygonal martensite to fibrous martensite. Such fibrous martensite has been reported to facilitate continuous yielding in DPSs (Alaneme et al., 2010).

CONCLUSIONS

The mechanical properties of medium carbon DPS produced via quenching in pre-heated bitumen have been investigated. The followings emerged from the investigation:

- i. The martensite morphology in the DPS is mainly a function of intercritical temperature rather than holding times. The morphology is essentially fibrous at higher temperature with sparse distribution of polygonal martensite at temperature around and below 750⁰C.
- ii. The tensile strength and hardness of the DPS are about 42 and 35% higher than that of the normalised samples but the percent elongation and impact energy are lower by about 42 and 50 percent, respectively. This contrasting finding is due to the increased transformation of ferrite to austenite which eventually yield hard but brittle martensite in the dual phase structure.
- iii. The tensile fractured surface revealed transition between a predominantly cleavage mode in the lower annealing temperature to a mixed mode in the upper bound of the annealing temperature.
- iv. These findings suggest that pre-heated bitumen can be exploited as an alternative to more expensive oil quenchant for the production of DPSs.

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REFERENCES

- Alaneme K.K., Ranganathan S. and Mojisola T. (2010). Mechanical behaviour of duplex phase structures in a medium carbon low alloy steel, *Journal of Minerals and Materials Characterization and Engineering*, Vol. 9, No.7, pp.621-633.
- American Iron and Steel Institute (1995). AISI-SAE Classification of steels: SAE Standard J403f. Accessed from <http://www.blueshield.ca/en/docs/pdf/techinfo/databook/e-fsection218to228.pdf> on Friday, August 22, 2014.

- ASTM E8/E8M (2013). Standard Test Methods for Tension Testing of Metallic Materials. ASTM International, *Pennsylvania, USA*.
- Bayram A., Uguz A. and Ula M. (1999). Effects of Mechanical properties of Dual – Phase Steels, *Materials Characterization*, Vol.9, pp 259 – 269.
- Bello K.A. (2007). Effect of Intercritical and Tempering Heat Treatment on the Microstructure and Mechanical Properties of a High Martensite Dual Phase Steel, M.Sc. Dissertation, Metallurgical Engineering Department, Ahmadu Bello University Zaria, Nigeria.
- Bhattacharyya A., Sakaki T. and Weng G. J. (1993). Influence of Martensite Shape, Concentration, and Phase Transformation Strain on the Deformation Behaviour of Stable Dual – Phase Steels, *Metallurgical and Materials Transactions A*, Vol. 24, No.2, pp 301 – 314.
- Ekrami A. and Bharehbapoor M (2005). High temperature behaviour of dual-phase steel.
- Ghosh, P. K., Gupta, P. C., Ramavtar and Jha, B. K. (1991). Weldability of intercritical annealed dual phase steel with resistance spot welding process. *Welding Journal*, Vol. 70, No. 1, pp 7s-14s.
- Giodarno, L., Matteazzi, P., Tiziani, A. and Zambon, A. (1991). Retained austenite variation in dual phase steel after mechanical stressing and heat treatment. *Materials Science and Engineering A*, Vol. 131, No. 2, pp 215-219.
- Gorni, A. A. (2006). *Steel Forming and Heat Treating Handbook*. Vol. 2, pp 4. Sao Vacente, Brazil.
- Granbom, Y. (2010). Structure and mechanical properties of dual phase steels – An experimental and theoretical analysis. Doctoral Thesis, Royal Institute of Technology. Sweden.
- Hall, J. N. (2011). Evolution of advanced high strength steels in automotive applications; Power Point Presentation in Great Design in Steel Seminar, pp 1-27. Accessed from <http://www.autosteel.org>. Accessed on Friday, August 22, 2014.
- Khamedi, R., Fallahi, A. and Zoghi, H. (2009). The influence of morphology and volume fraction of martensite on AE signals during tensile-loading of dual phase steels. *International Journal of Recent Trends in Engineering*, Vol. 1, No 5, pp 30-34.
- Leslie, W. C. (1981). *The Physical Metallurgy of Steel*. Pp 257. McGraw-Hill Series in Materials Science and Engineering, Hemisphere Publishing Corp. Washington DC.
- MacKenzie, D. S. (2011). Heat Treating: Selecting the right quenching oil. Accessed from <http://www.slideshare.net/HoughtonInternational/> on Friday August 22, 2014.
- Mazinani M. and Poole W. (2007). Deformation Behaviour of Martensite in a Low-Carbon Dual – Phase Steel, *Advanced Materials Research*, Vols. 15 – 17, pp 774 – 779.
- Oduote J. K., Ajiboye T. K. and Rabiou A. B. (2012). Evaluation of mechanical properties of medium carbon steel quenched in water and oil. Assumption University, *Journal of Technology* Vol. 15, No. 4, pp 218-224.
- Rashid, M. S. (1981). Dual phase steels. *Annual Review of Materials Science*, Vol. 11, pp 245-266. DOI: 10.1146/annurev.ms.11.080181.001333
- Speight J. G. (1992). Asphalt in – Kirk Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 3, pp 689 – 724, John Wiley and Sons, New York..
- Sun S. and Pugh M. (2002). Properties of Thermomechanically processed Dual – Phase Steels containing fibrous Martensite. *Materials Science and Engineering A*, Vol. 335, Issues 1 –2, pp 298 – 308.
- Tayanc, M., Aytac, A. and Bayram, A. (2007). The effect of carbon on the fatigue strength of dual phase steels. *Materials and Design*, Vol. 28, No. 6, pp 1827-1835.
- ThyssenKrupp Steel Europe (2008). DP-W[®] and DP-K[®] dual phase steels for the manufacture of complex high-strength structural elements. Accessed from [http:// www.thyssenkrupp-steel-europe.com/upload/.../Dual_phase_steels.pdf](http://www.thyssenkrupp-steel-europe.com/upload/.../Dual_phase_steels.pdf) on Tuesday, August 26, 2014.

Tsipouridis, P. (2006). Mechanical properties of dual phase steels. Doctoral Thesis, Technical University Munchen, Germany.

WorldAutoSteel (2011). Future steel vehicle: overview report, pp 1-78. Accessed from <http://www.autosteel.org>. Accessed on Friday, August 22, 2014.

Xu U., Yang W. and Sun Z. (2008). Mechanical properties of fine-grained dual phase low – carbon steels based on dynamic transformation, Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Materials, Vol. 15, Issue 5 pp 556 –560.



Figure 1: Dark supercooled bitumen before melting

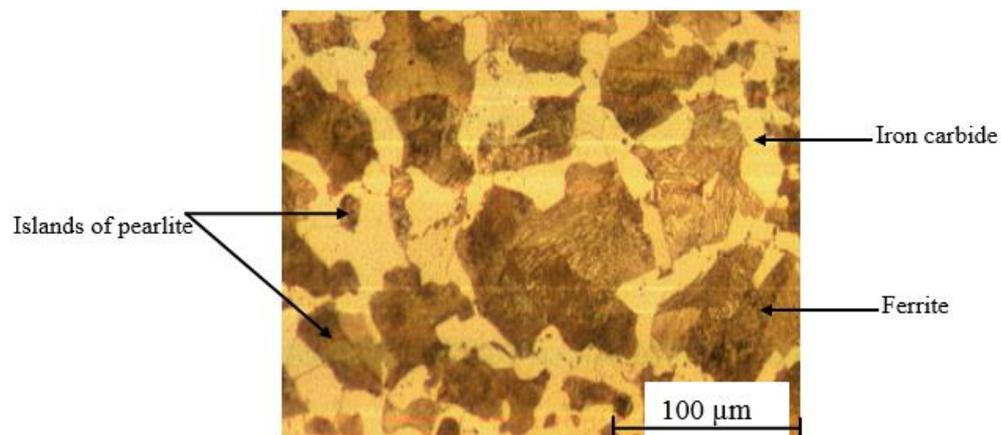


Figure 2 Microstructure of normalised sample before intercritical treatment

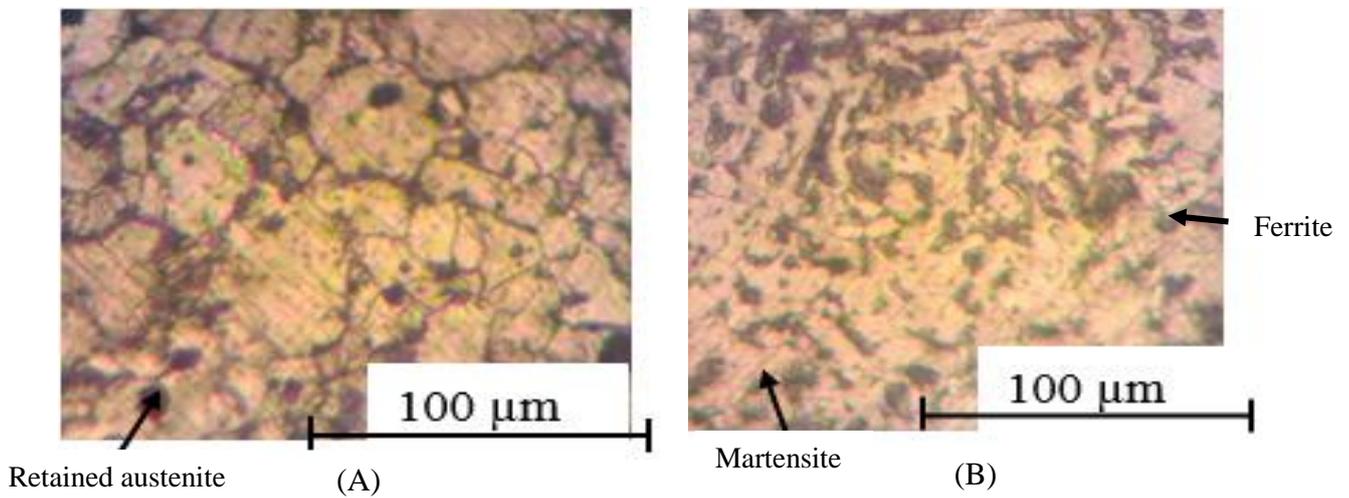


Figure 3 Microstructures of samples treated at 730⁰C at different holding times: (A) 30 and (B) 60 minutes

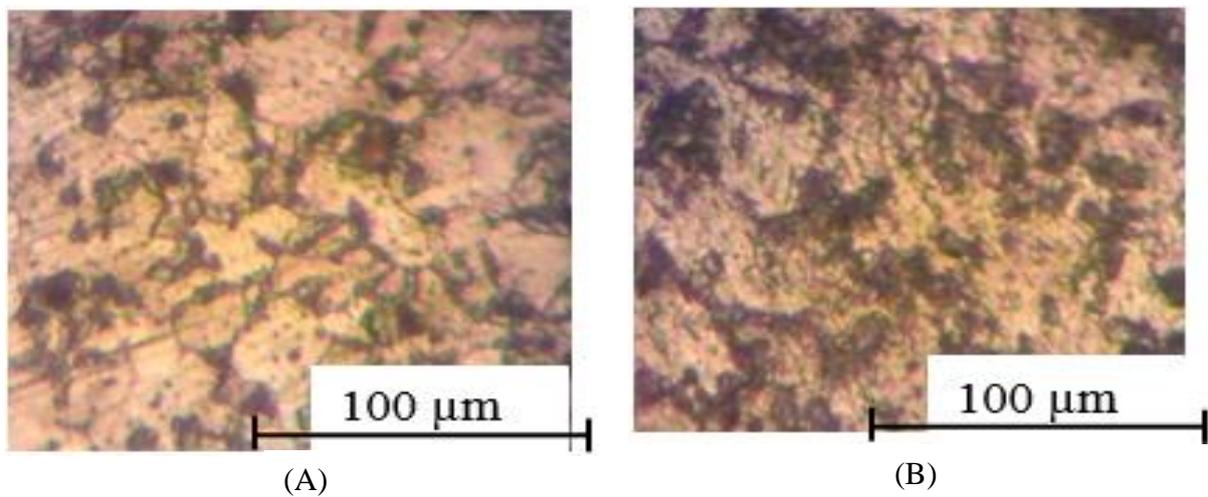


Figure 4 Microstructures of samples treated at 770⁰C at different holding times: (A) 30 and (B) 60 minutes

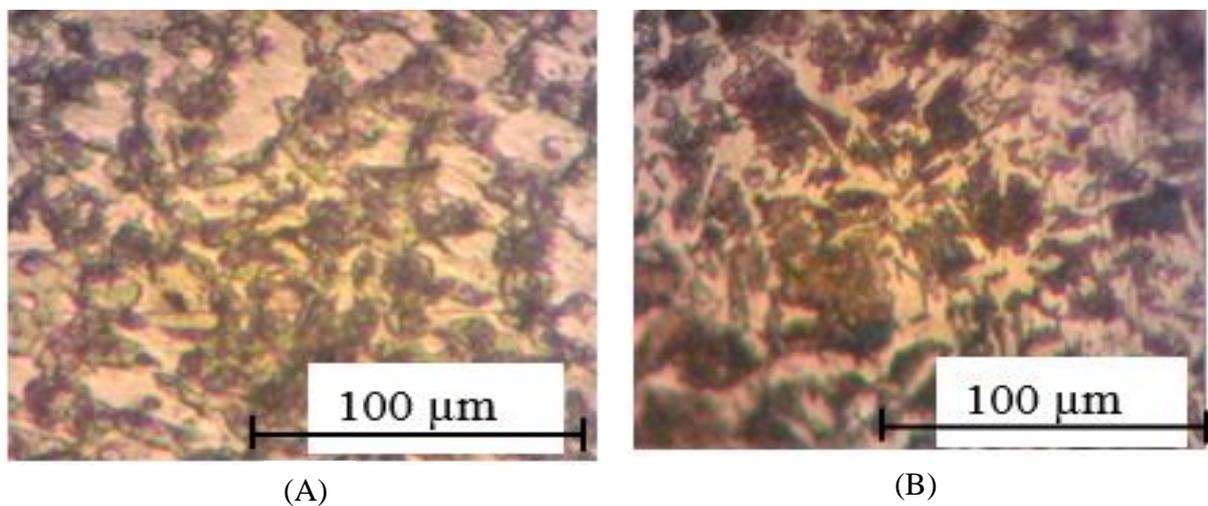


Figure 5 Microstructures of samples treated at 810⁰C at different holding times: (A) 30 and (B) 60 minutes

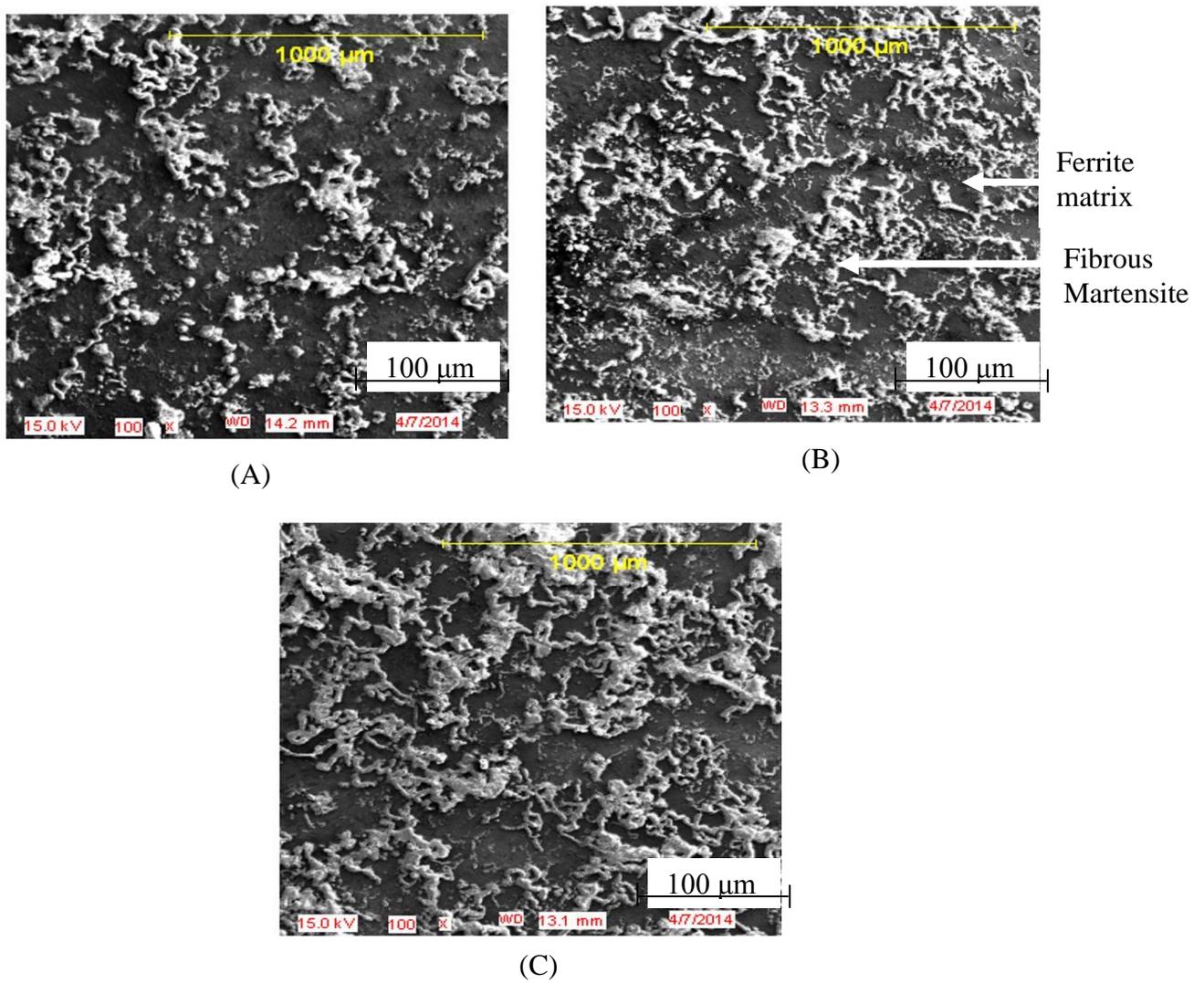


Figure 6 SEM morphology of samples intercritically treated at different temperatures at a holding time of 60 minutes: (A) 730, (B) 770 and (C) 810^oC

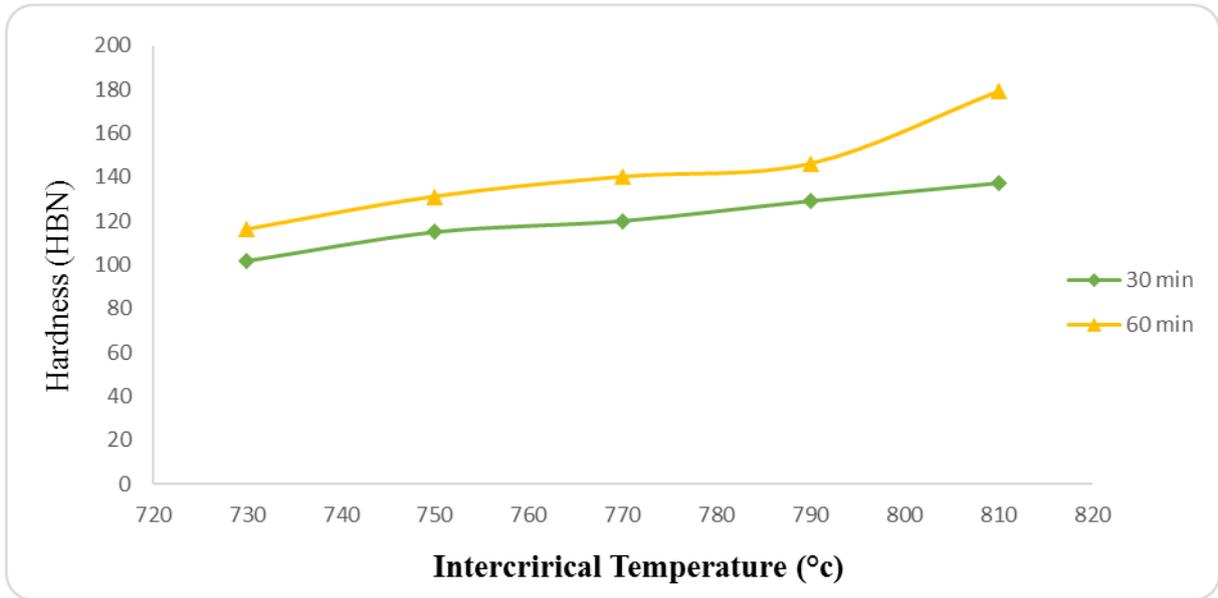


Figure 7 Hardness variations with intercritical treatment conditions

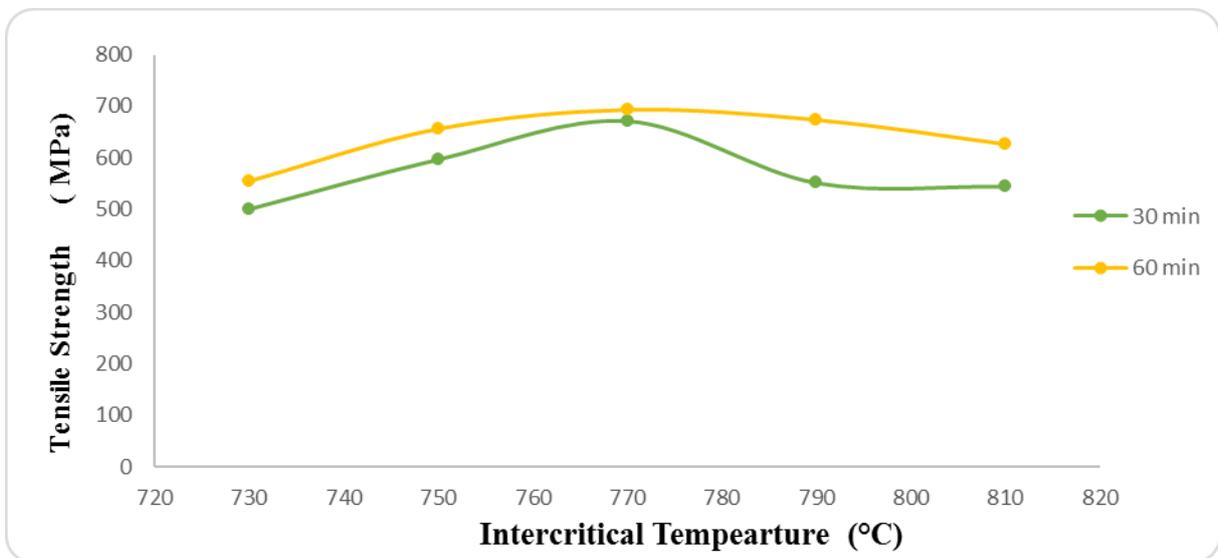


Figure 8 Tensile strength of dual phase steel at different intercritical temperatures and holding times

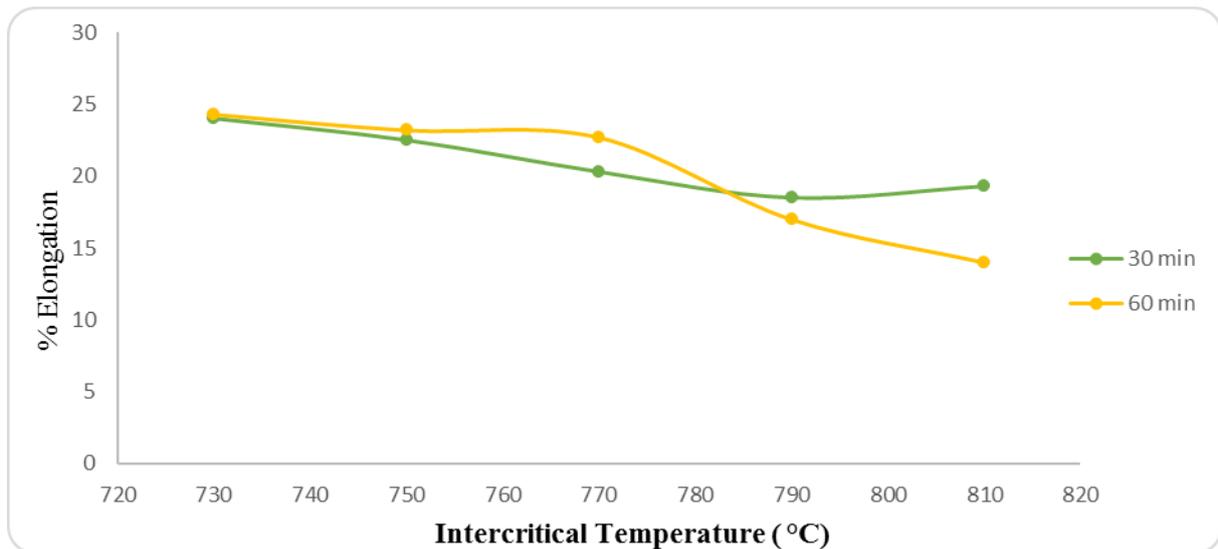


Figure 9 Percent elongation of dual phase steel at different intercritical temperatures and holding times

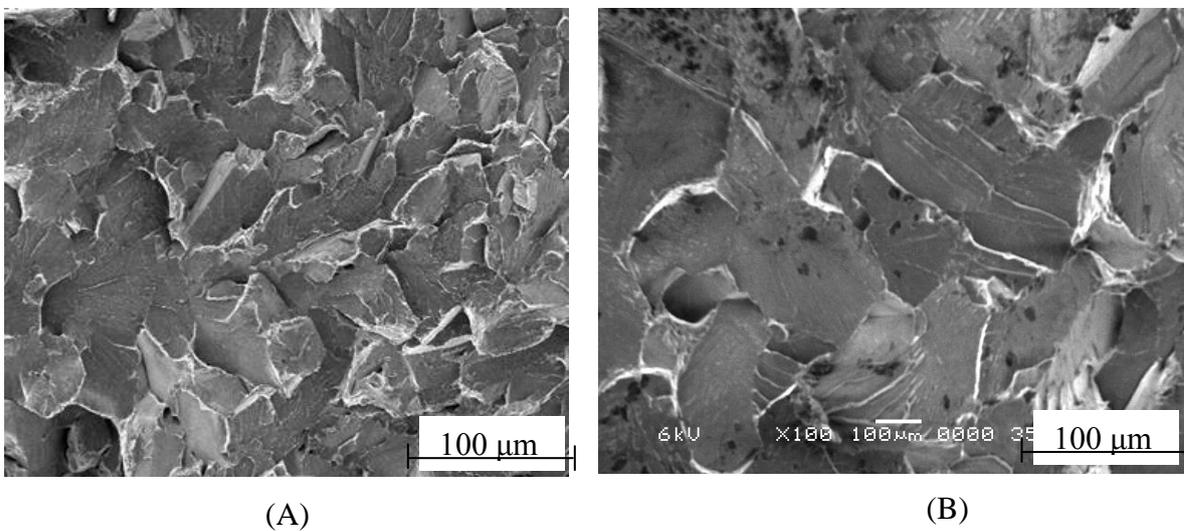


Figure 10 Tensile surface fractograph in dual phase steel intercritically treated at: (A) 730 and (B) 810^oC at holding time of 60 minutes

Table 1 Chemical composition of the hot rolled steel

Material Specification	Composition (wt. %)						
	C	Si	Mn	P	S	Fe	Trace Elements
Medium Carbon Steel	0.327	0.231	0.73	0.036	0.033	96.3	Balance

Table 2 Combination of temperature and holding time for intercritical annealing

Treatment Temp (^o C)	Holding Time (min)	
	30	60
730	X	X
770	X	X
810	X	X

Table 3 Mechanical properties normalised medium carbon steel

Sample Designation	Tensile Strength (MPa)	Elongation (%)	Hardness (HBN)
Normalised Sample	486.90	17.06	95

NUMERICAL SOLUTION OF THE BURGER'S EQUATION USING BACKWARD TIME CENTERED SPACE ALGORITHM VIA A HIGHER ORDER SEMI-DISCRETIZATION APPROXIMANT

Ehigie J. O.¹, Okunuga S. A. and Aderibigbe L. Y.
Department of Mathematics, Univeristy of Lagos, Akoka

ABSTRACT

In this paper, the Burger's equation is transformed to a system of nonlinear Ordinary Differential Equations (ODE) by some newly introduced approximations to the derivative terms using semi-discretization. The nonlinear ODE is consequently transformed to a system of nonlinear equations by the Backward Time Centered Space (BTCS) algorithm. These resulting nonlinear equations are finally solved by Newton's formula to obtain numerical solutions to the Burger's equation. The results obtained are very interesting and revealing.

INTRODUCTION

The Burgers' equation is a one-dimensional analogue of the Navier-stokes equations, a nonlinear model of the incompressible momentum equations. This Equation due to Burger [2] first appeared in the paper of Bateman [1], who gave two steady solutions. The Equation is used to model head conduction, gas dynamics, shock waves, longitudinal elastic waves and other physical processes in fluid mechanics and engineering.

The one-dimensional time dependent Burger's equation is given as

$$\frac{\partial u}{\partial t} = \mu \frac{\partial^2 u}{\partial x^2} - \frac{1}{2} \frac{\partial(u^2)}{\partial x}$$

where $\mu > 0$ is the coefficient of kinematic viscosity. The initial and boundary conditions are

$$\begin{aligned} u(x,0) &= f(x), & 0 \leq x \leq 1 \\ u(0,t) &= \beta_1, \quad u(1,t) = \beta_2, & t \geq 0 \end{aligned}$$

The exact solutions of the equation easily obtained for large values of viscosity constants but when viscosity is low, stiffness is experienced and special numerical methods required to tackle such cases. This paper explores the finite difference method as utilized by [6], but by a modified higher order semi-discretization technique.

Theoretical Procedure

The Burgers equation is rewritten in conservative form as

$$\frac{\partial u}{\partial t} = \mu \frac{\partial^2 u}{\partial x^2} - u \cdot \frac{\partial u}{\partial x} \tag{1}$$

The solution space involving a rectangular grid with sides parallel to the x -axes and t -axes, and with good spacing Δx and Δt , when $m\Delta x = 1$ is considered. A mesh ratio $r = \frac{\Delta t}{(\Delta x)^2}$ is

specified, denoting $u(i\Delta x, t)$ by $u_i(t)$, $i = 1, 2, \dots, M-1$, the partial derivatives $\frac{\partial u}{\partial x}$ and $\frac{\partial^2 u}{\partial x^2}$ are approximated by the semi discreticaton formulas

$$\frac{\partial u(i\Delta x, t)}{\partial x} = \frac{u_{i+1}(t) - u_{i-1}(t)}{2\Delta x} \tag{2}$$

¹Corresponding Authour +2348028490310

and

$$\frac{\partial^2 u(i\Delta x, t)}{\partial x^2} = \frac{[u_{i+1}(t) - 2u_i(t) + u_{i-1}(t)]}{(\Delta x)^2} + O((\Delta x)^2) \quad (3)$$

respectively in [6]. But in this paper, these partial derivatives are replaced by some higher order semi-discretization schemes derived from numerical differentiation formulas given by

$$\frac{\partial u(i\Delta x, t)}{\partial x} \cong \frac{-u_{i+2}(t) + 8u_{i+1}(t) - 8u_{i-1}(t) + u_{i-2}(t)}{(\Delta x)^2} \quad (4)$$

and

$$\frac{\partial^2 u(i\Delta x, t)}{\partial x^2} \cong \frac{-u_{i+2}(t) - 16u_{i+1}(t) - 30u_i(t) + 16u_{i-1}(t) - u_{i-2}(t)}{12(\Delta x)^2} \quad (5)$$

respectively. So by spatial-discretization (1) becomes

$$\begin{aligned} \frac{du_i(t)}{dt} = \mu \cdot & \frac{-u_{i+2}(t) + 16u_{i+1}(t) - 30u_i(t) + 16u_{i-1}(t) - u_{i-2}(t)}{0.12} \\ & - u_i(t) \cdot \left(\frac{-u_{i+2}(t) + 8u_{i+1}(t) - 8u_{i-1}(t) + u_{i-2}(t)}{0.01} \right) \end{aligned} \quad (6)$$

$i = 1, 2, 3, \dots, M - 1$

A systems of nonlinear ODE involving 9 first ordinary differential equations for $\Delta x = 0.1$.

Numerical Experiment

We explore the higher order semi-discretization approximant on the one dimensional time-dependent Burgers equation

$$\frac{\partial u}{\partial t} = \mu \frac{\partial^2 u}{\partial x^2} - \frac{1}{2} \frac{\partial(u^2)}{\partial x} \quad (7)$$

where $0 \leq x \leq 1$ and $0 \leq t \leq 1$. The exact solution is given by

$$u(x, t) = \frac{1}{e^{\frac{0.5x - 0.25t}{\mu}}} \quad (8)$$

From which the corresponding initial conditions $u(x, 0)$ and boundary conditions $u(0, t), u(1, t)$ are obtained.

Geometry of Solution Space.

$j = \Delta t$

$i = \Delta x$

With Δx and Δt , when $m\Delta x = 1$ and $\mu = 1$, the BTCS algorithm

$$u^{j+1} = u^j + h \cdot u^{j+1} \quad (9)$$

is applied to transform (7) to a system of nine nonlinear equations given by

$$u_i^{j+1} = u_i^j + \Delta t \cdot \left[\frac{-u_{i+2}^{j+1} + 16u_{i+1}^{j+1} - 30u_i^{j+1} + 16u_{i-1}^{j+1} - u_{i-2}^{j+1}}{\Delta x^2} - u_i^{n+1} \cdot \left(\frac{-u_{i+2}^{j+1} + 8u_{i+1}^{j+1} - 8u_{i-1}^{j+1} + u_{i-2}^{j+1}}{\Delta x} \right) \right]$$

$$i = 1, 2, 3, \dots, 9. \quad (10)$$

To obtain the numerical solution for grid points $u_i^j \equiv u(i\Delta x, j\Delta t)$, $i = 1, 2, \dots, 9$, $j = 1, 2, \dots, \frac{1}{\Delta t}$, which denotes the solution at grid (i, j) , the Newton's formula for solving nonlinear equations is applied to

$$F(u) = u_i^{j+1} - u_i^j - \Delta t \cdot \left[\frac{-u_{i+2}^{j+1} + 16u_{i+1}^{j+1} - 30u_i^{j+1} + 16u_{i-1}^{j+1} - u_{i-2}^{j+1}}{\Delta x^2} - u_i^{n+1} \cdot \left(\frac{-u_{i+2}^{j+1} + 8u_{i+1}^{j+1} - 8u_{i-1}^{j+1} + u_{i-2}^{j+1}}{\Delta x} \right) \right] = 0$$

$$i = 1, 2, 3, \dots, 9.$$

Hence the solution is obtained from

$$(u_i^{j+1})^{s+1} = (u_i^{j+1})^s - [J^{-1}(F(u)) \cdot F(u)]^s$$

Where $J^{-1}(F(u))$ is the Jacobian matrix of $F(u)$ and s is the number of iteration until convergence in the Newton's algorithm. Figure 1 presents numerical result for various t values.

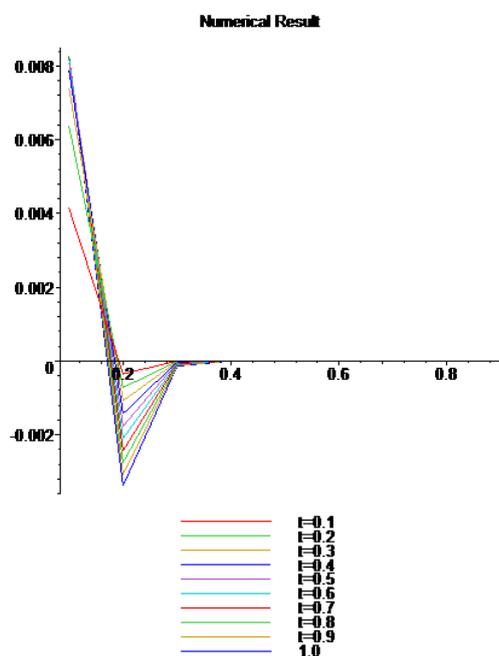


Fig 1. Graphical Result for the One-Dimensional Time-Dependent Burgers Equation for t values

REFERENCES

1. H. Bateman. Some recent researches on the motion of fluids. Monthly Weather Review. 43, 163 -170.
2. J. M. Burgers. A Mathematical example illustrating the theory of turbulence. Advances in Applied Mechanics. Academic Press. New York 1, (1948) 171 - 199
3. J. R. Cash. Two new finite difference schemes for parabolic equations. SIAM Journal of Numerical Analysis. 21, (1984) 433 - 446.

4. M. T. Diamantakis. The NUMOL solution of time-dependent PDEs using DESI Runge-Kutta formulae. *Applied Numerical Mathematics*, 17, (1995) 235 – 249
5. J. D. Lambert. *Computational methods in Ordinary Differential Equations*, John Wiley and sons, New York. (1973).
6. H. Ramos and J. Vigo-Aguiar. An almost L-stable BDF-type methods for the numerical solution of stiff ODEs arising from the method of lines. *Wiley Interscience*. (2006) 1110 - 1121
7. L. F. Shampine. ODE solvers and the method of lines. *Numerical Methods for Partial Differential Equations*. 10, (1994) 739 – 755