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Development of Analytical Techniques for the Determination and Remediation Of Anthropogenic Hydrocarbons in The Sediments Of The Lagos Lagoon System

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Concerns about the effect of organic pollutants on humans and the environment have existed for a long time. Polycyclic aromatic hydrocarbons (PAHs) present a danger due to their potential carcinogenic and mutagenic capabilities. PAHs are rapidly sorbed to particles and incorporated into aquatic sediments. Sediments therefore represent the most important reservoir of PAHs in the marine environment. About 80% of the industries in Nigeria are located in Lagos and they all discharge their effluents into the lagoon. Other sources of pollutants into the lagoon include domestic and municipal wastes. This study examined three trans-urban water bodies of the Lagos lagoon system; Odo Iya alaro, Ibeshe and Shasha creeks that receive domestic, municipal and industrial effluents, which are eventually emptied in to the Lagos lagoon.

Sediment samples were collected bimonthly from 21 sampling points for a period of one year for the analysis of PAHs, n-alkanes as well as organic carbon, pH and particle size distribution. Analytical methods for extraction such as Soxhlet, mechanical shaking and ultrasonication were investigated for the determination of the 16 USEPA priority PAHs pollutants in sediment samples. The clean-up and pre-concentration procedures were optimised by using both the conventional method (i.e. column packing with silica gel) as well as the solid phase extraction (SPE). Chromatographic conditions were optimised for the separation of PAHs using Gas Chromatography (GC) with mass spectrometric (MS) detection (GC-MS) and High Performance Liquid Chromatography (HPLC) using UV-DAD and fluorimetric detection with programmed excitation and emission wavelengths. The use of mathematical and statistical multivariate analytical tools for data analysis -'Chemometrics' on PAHs and n-alkanes from the Lagos lagoon and the adjoining creeks was employed. Remediation of the PAH contaminated sediments involving the use of Advanced Oxidation Process (AOP), Supercritical Fluid Extraction (SFE) and Superheated Water Extraction (SWE) were also investigated.

The optimised ultrasonic extraction procedure utilizing four 15-minutes extraction cycles at 50 ºC and SPE clean up with tetrahydrofuran: acetonitrile (1:1) and subsequent separation by gradient reversed phase HPLC with fluorimetric detection extracted the PAHs from the certified reference material CRM 131-100 with recoveries ranging from 64.9 % to 119.7 %. This was employed as the analytical method for the extraction, clean up, preconcentration and instrumental analysis of the PAHs in the surface sediments of the Lagos lagoon system. The distribution of the PAHs in the sediment samples had large variations among the sites investigated. The concentration of total PAHs (ΣPAHs) ranged from 10 to 6,449 µg/kg and showed a strong influence from anthropogenic inputs. In general, naphthalene, fluorene, phenanthrene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene and benzo (a) pyrene were the dominant PAHs found in the sediments. The concentrations of total aliphatic hydrocarbons (C9 – C38) in the sediment samples studied ranged from 15 to 148 µg/g dry weight and their distribution showed large spatial variations at various sampling points.

To determine the main source of PAHs to the sediments of the Lagos lagoon system, molecular indices of selected PAH isomeric pairs were used to distinguish between the PAHs of diverse origins in the samples. The calculations obtained from this study suggest that the distribution of PAHs in the surface sediments of the Lagos lagoon system is derived from both petrogenic and pyrolytic sources. This was found to be consistent with the distribution pattern of petrogenic n-alkanes found in the same sediment.

For the sediment remediation studies, the optimum ratio for the effective degradation of five selected PAHs (naphthalene, fluorene, anthracene, pyrene and chrysene) investigated was found to be 5:5:5 (acetic acid: hydrogen peroxide: water) for 24 hours using the advanced oxidation process (AOP). All the five PAHs were reduced by 60-100% of their original concentration. Supercritical Fluid Extraction (SFE) employing CO2 had the highest removal of PAHs at 90 ºC, pressure of 250 kg/cm2 and extraction time of 30 minutes.

Using superheated water extraction, the highest percentage removal of PAHs was found for the 2-and 3- ringed PAHs at an extraction temperature and time of 250 ºC and 40 minutes respectively. Generally, for the three remediation techniques studied the low molecular weight PAHs gave the highest removal from the sediment samples.

The concentrations of PAHs that was determined for the surface sediments in the Lagos lagoon system, were below the Effects Range Low (ERL) level of 4000 µg/kg, proposed as the

Sediment Quality Guidelines to marine ecosystems The contamination by hydrocarbons in the Lagos lagoon system sediments is relatively low at the present time, even though there are some localized areas of high hydrocarbon and PAHs concentrations. This thesis provides a necessary baseline for the assessment of hydrocarbon and PAH contamination in the sediments of the Lagos lagoon and the adjoining creeks as well as serving as a comparison for future studies in the study area.