Determination and Remediation of Selected Polycyclic Aromatic Hydrocarbons in Petroleum Contaminated Water

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ABSTRACT: Determination and remediation of pollutants such as polycyclic aromatic hydrocarbons (PAHs) have not being fully regulated in Nigeria; hence contamination of surface water by such pollutant is a major concern. This study was designed to determine the level of selected PAHs in petroleum contaminated water using spectroscopic techniques and the efficacy of activated carbons made from *Bambusa vulgaris* and *Oxytenanthera vabyssinaca*. *Bambusa vulgaris* and *Oxytenanthera abyssinaca* were carbonized at 350°C and activated with Phosphoric acid (CBV350^{O}C H$_3$PO$_4$) and Potassium chloride (COA 350°C KCl) as dehydrating agent respectively. The adsorbents were then used to remediate PAHs in petroleum contaminated water. Liquid-Liquid extraction procedures were used for extracting selected PAHs from sampled solutions. The batch experiment was performed to study the adsorption capacity of adsorbents at 5hrs contact time. Analysis of PAHs concentration for each sampling day was determined by GC-MS. Total PAHs in simulated wastewater did not show a clear trend, contrary to the expectation that there should be a progressive increase with time due to photolysis or photodecomposition of compounds or PAHs. COA 350°C KCl showed a range of 6.2-19.3% removal efficiency of each selected PAH with a total percentage efficiency of 27.7-70.8 for all days. For CBV350^{O}C H$_3$PO$_4$ removal efficiency ranged from 10.26-19.30% for each selected PAH and a total efficiency of 50.8-100% for all selected PAHs for the 4 days intervals. The experimental result showed that adsorbent made from *Bambusa vulgaris* and *Oxytenanthera abyssinaca* and activated with H$_3$PO$_4$ and KCl as dehydrating agent respectively can efficiently adsorb the selected PAHs in contaminated water. The study also revealed that PAHs in contaminated water increases with time due to photodecomposition, thus necessitating their treatment on time.

Contamination of waterways and groundwater by petroleum substances has been a major issue of concern in the Niger Delta areas of Nigeria. The petroleum industry is a major life-wire of Nigeria's income and economic growth. According to reports, its operation started way back in 1958, and since then many researches have been conducted on the production of petroleum products, the causes and effects of petroleum pollution on the Nigerian environment (Ekundayo and Obuekwe, 1997; Ayotamuno *et al.,* 2002; Aroh *et al.*, 2010; Isehunwa and Onovae, 2011; Kadafa, 2012). Produced water and crude oil spills are the major sources of pollutants generated by the petroleum industry. Produced water is the largest by-product or wastewater attributed to the petroleum industry and consists of salt, organic and inorganic compounds. At times crude oil spills can be attributed to equipment failure during operation or damages that arise from production facilities by vandals (Kadafa, 2012). The attribute of water polluted with crude oil and that of produced water are similar because of their hydrocarbon content.

Among the organic constituent of crude oil is a group of hydrocarbons called polycyclic aromatic hydrocarbons, PAHs (Pampanine and Sydnes, 2013). These are large group of organic contaminants, which are characterized by the presence of at least two fused aromatic rings and are seen by the United State Environmental Agency (USEPA) as priority organic pollutants (USEP, 1994). Fluorene, Phenanthrene, Anthracences, Benz (e) acephenanthrylene and Benzo(e)pyrene are some of the prior PAHs contained in Nigeria petroleum. PAHs are highly lipophilic contaminants which are ubiquitously present in the environment (WHO, 1998). Because of their low biodegradation and bioaccumulation in the adipose tissues of organisms and biomagnifications through the food chain, they are considered as persistent organic pollutants, POPs (Haritash and Kaushik, 2009).

Most of the organic contaminants in water and wastewater associated with the petroleum industries are known to have adverse effect on surface waters,

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which in some case is source of livelihood. The rapid decrease in the level of water resources and increasing demand of water for consumption in our daily life has necessitated determination and remediation pollutants in industrial wastewater before disposal (Sangodoyin, 1993). Modern instrumental techniques developed for environmental concern are chromatographic separation and spectroscopic methods such as gas and liquid chromatography (GC and LC). These separating techniques are useful for identification and quantification of organic contaminants, metabolites and transformation products like PAHs (Noelia, 2011; Lindholm- Lehto *et al*, 2016). These pollutants cause severe environmental, ecological, and economic consequences in oil spill environments, hence the need effective decision to prevent the long-term effect impact on such geographical isolated locations (Raymond, et al; 2017: Arockiara, et al; 2019) Most of the oil and gas industries in the Delta region make use of conventional treatment methods such as the Induced Gas Flotation (IGF) or the Induced Air Flotation known as WEMCO and Enviro-cell. These are considered not adequate for remediation of dissolved hydrocarbons. Dissolved hydrocarbon in petroleum wastewater can best be removed by other fundamental mechanisms like absorption, adsorption, extraction, membrane filtration or oxidation (John et al, 2004; Jeffrey 2010). Meijer and Madin (2010) showed that techniques based on adsorption, like activated carbon or polymeric micro porous sorbents with big internal surfaces are certainly able to remove dissolved hydrocarbons. To ensure compliance with future discharge requirements, new technologies with granular activated carbon is envisaged as the next step in improvement of Petroleum wastewater treatment (Meijer and Madin, 2010). This study seek to determine the level of selected PAHs in petroleum contaminated water using spectroscopic technique and also examine the efficacy of carbonized *Bambusa vulgaris* and *Oxytenanthera abyssinaca* as adsorbents.

MATERIALS AND METHODS

Bambusa vulgaris and *Oxytenanthera abyssinaca* were carbonized at $350^{O}C$ and activated with Phosphoric acid (H_3PO_4) and Potassium chloride (KCl) as dehydrating agent respectively. These adsorbents were then used to remediate PAHs in petroleum contaminated water.

Formation of Petroleum contaminated water: In order to identify the quantity of Polycyclic Aromatic Hydrocarbon (PAHs) in petroleum wastewater as well as remediating it with produced adsorbent, crude oil sample was collected from petroleum industry in Nigeria. Adsorption behavior of PAHs in petroleum wastewater onto bamboo activated carbon was investigated by simulating petroleum wastewater with 2.5L of Bonny light crude oil and distilled water of 50L containing 3.5% NaCl salt. NaCl salt was used in the simulation in order to create an artificial aquatic environment according to Zubaidy, (2012). The simulated petroleum wastewater was then left to weather for 48 hrs. Sampling of simulated produced water was done within 4days at daily intervals. Analysis of PAHs concentration for each sampling day was determined by GC-MS. This was done in order to monitor the change in PAHs concentration as a result of change in days.

Adsorption Experiment: All experiments were carried out at ambient temperature. The batch experiment was performed to study the adsorption capacity of adsorbents. 200ml of simulated petroleum wastewater was sampled into different conical flasks of 250ml capacity. One gramme of *B. vulgaris* adsorbent and *O. abyssinaca* adsorbent was weighed into the conical flasks to form an adsorbent/solute solution. Solutions were agitated at a stirring speed of 160 rpm to ensure intimate contact of the adsorbent and solute in solution, while observing each solution in equilibrium for 5hrs contact time to attain dynamic equilibrium. After 5 hrs., solutions were filtered with 0.45μm paper and the filtrate of 150ml were poured into amber bottles with Teflon cap and kept at temperature of 4^0C for further analysis of extraction, clean up and GC-MS. The 5hrs contact time was chosen based on the experiment performed at the terminal station of the oil and gas industry. For accuracy, all experimental analysis was duplicated. The amount of selected PAHs (q_e) adsorbed by *B. vulgaris* adsorbent and *O. abyssinaca* adsorbent can be expressed mathematically as:

$$q_e = \frac{C_o - C_e}{M} \times v \quad \ldots\ldots\ldots\ldots\ldots..1$$

The percentage removal is evaluated using

$$\% \text{ Removal } = \frac{C_o - C_e}{C_o} \times 100 \quad ….2$$

Where: V is the volume of PAHs in solution (L); Co is initial concentrations of PAHs (mg/l); Ce is equilibrium concentrations of PAHs (mg/l); M is the mass of the adsorbent (g).

Solvents and Chemicals used: All solvents and chemicals used are of analytical grade with 99.0% purity. A standard mixture of 16 priority PAHs of 2.0 mg/ml each was used to calibrate the GC-MS used for selected PAHs analysis. Dichloromethane and n-Hexane made by Loba(LO)chemice (India), Silica gel of 60-200 mesh size 500g for chromatography made

by Oxford laboratory(India) and Sodium Sulphate Anhydrous of 500g made by Qualikems (India) where all purchased from Labio Scientific Centre in Nigeria.

Extraction technique: Liquid-Liquid extraction procedures were used for extracting selected PAHs from sampled solutions. Mixture of dichloromethane (DCM) and n-Hexane in ratio 3:1 was used as extractant. The extraction processes were repeated twice for each sample. Cleanup of selected PAHs was carried out with 1cm of moderate packed cotton wool placed at the bottom of each 10mm ID 250mm loup chromatographic column used. Two grammes of activated silica gel and 10ml of 3:1 (DCM and hexane) was prepared and placed in the chromatographic column. To the top of the column was added 0.8cm of anhydrous sodium sulphate. The column was rinsed with additional 20ml mixture of 3:1 (DCM and Hexane) to pre-elute the column. Elute was allowed to flow though the column for about 2min or until the liquid in the column was just above the sulphate layer. Thereafter, 3ml of extracted samples was transferred into each prepared column. The extraction bottles were rinsed with 1ml of DCM (3) and Hexane (1)/eluent and added to the column as well. The stop cork of the column was opened and the aromatic extract collected into 10ml graduated cylinder each was allowed to concentrate and evaporate under oxygenated conditions and later kept at 4^0C before GC-MS analysis.

Determination of Selected PAHs in petroleum contaminated water by GC-MS: Quantification of PAHs was by an external standard method which relies on the reproducibility of the standard preparation. The linearity of external calibration was done by preparing different concentration of PAHs mix standards at dilution rate of 12.5,25,50,100 and

200ppm according to the specification given by the International Conference for Harmonization that requires a 5 point calibration curve serial dilution. The linearity was evaluated at different concentration using response factors and all showed good linearity with regression coefficients ranging from 0.972 to 1.000 for all PAHs. USEPA method 8270 was employed in GC-MS analysis. The gas chromatography that was used was Agilent Technologies 7890-A GC system G-3440-A A.01.14 series, coupled with Mass spectrometry detector (MS) Agilent Technologies 5975-C VL MS D series with Agilent Technologies 7683-B series injector powered with MSD chem-station G1701-EA E.02.10.1177 software to identify and quantify analytes in compounds. Selected hydrocarbon compounds were identified on the basis of their retention time and by comparing them to those of analytical standards. Matrix spikes, duplicates, solvent, and method blanks were also analyzed as quality control samples.

RESULTS AND DISCUSSION
Table 1 shows the physical properties of the crude oil sample that was simulated. The concentration of PAHs in the simulated petroleum wastewater on daily basis for 4 days and the initial concentration of PAHs in crude oil sample are detailed in Table 2.

Table 1 Characteristic of investigated crude oil sample

Physical Properties	Crude Oil
Appearance	Dark Brown
Water Content (% vol)	0.50
Specific Gravity at 15/15^{0}C	0.8966
Dry Specific Gravity at 15/15^{0}C	0.8961
API Gravity at 15/15^{0}C	26.4
Kinematic Viscosity at 400 ^{0}C (cst)	10.5

Table 2 Detected Selected PAHs in the sampled crude oil according to the calibrated standard

Compounds	Retention Time (min)	Molecular Formula	Nominal Molecular Mass (m/2)	Mass Concentration (mg/cm³)	Mass Concentration (mg/l)	Responses Values
Fluorene	10.666	C13H10	166	2.2	0.044	2240
Phenanthrene	12.159	C14H10	178	17.93	0.359	36734
Anthracene	12.159	C14H10	178	14.09	0.282	36734
Flouranthene	14.786	C16H10	202	20.64	0.413	280
Pyrene	15.362	C16H10	202	21.90	0.438	182
Benz(e)acephenanthrylene	23.706	C22H12	252	56.98	1.140	161
Benzo(e)pyrene	24.948	C22H12	252	55.58	1.112	133
Total PAHS				189.32	3.788	

Mass Concentration in mg/l = Mass Concentration (mg/cm3) x (2/100); Amount of sample injected into the GC-MS instrument = 2; Amount of sample extracted = 100

Table 3 Comparison of Selected PAHs in Crude oil and Simulated Petroleum Wastewater at Daily Interval for 4day

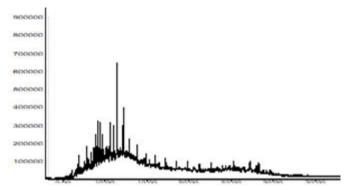| Compounds	Initial Mass Concentration (mg/l)	Mass Concentrations of PAHS (mg/l)			
		Day 1	Day 2	Day 3	Day 4
Fluorene	0.044	0.126	0.067	0.192	0.107
Phenanthrene	0.359	0.401	0.356	0.384	0.387
Anthracene	0.282	0.326	0.279	0.308	0.311
Benz(e)acephenanthrylene	1.140	1.163	1.140	1.141	1.151
Benzo(e)pyrene	1.112	1.112	1.112	1.112	1.112
Total PAHS	2.940	3.128	2.954	3.137	3.068

Fig 1: Spectra of Simulated Petroleum wastewater indicating PAHs, Frist day sampling.
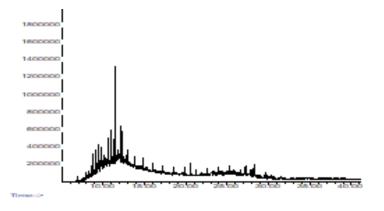

Fig 2: Spectra of Simulated Petroleum wastewater indicating PAHs, Second day sampling.
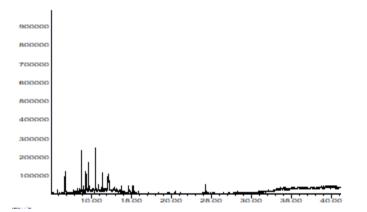

Fig 3: Spectra of Simulated Petroleum wastewater indicating PAHs, Third day sampling.

The parameters in Table 1 are important in classification of crude oil samples. According to API, (2011), crude oil sample with API gravity greater than 31 are classified as light crude oil, those between 22-31are medium crude, while those of 20 and below are referred to as heavy crude oil. The API gravity of crude oil increases as specific gravity decreases. API (2011) further stated that crude oils with lower densities and viscosities, and thus higher API gravities, usually contain higher levels of naphtha (gasoline-range hydrocarbons) with predominately volatile paraffinic hydrocarbons, which can be processed readily to produce gasoline and are considered "light" crude. Heavy crude oils are more viscous, have higher boiling ranges and higher densities, and thus have lower API gravities. Heavy crude oils are usually rich in aromatics and tend to contain more residual material, e.g. asphaltenes, and heterocyclics, which includes sulfur, nitrogen, oxygen-containing hydrocarbon analogs. This then expresses the fact that light or medium crude oil may contain minor to trace amount of larger polynuclear aromatic hydrocarbons (PAHs) and sulfur containing compounds as seen in Tables 2 and 3.This result are consistent with Walters, (2007) findings. Table 2 reveals that the PAHs in the crude oil sample that was simulated as petroleum wastewater, are Fluorene (FL), phenanthrene (Phe), anthracenes(Ant), benzo (e) acephenanthylene (BeA), benzo (e) pyrene (BeP), according to the standard used in calibrating. In Table 3, the mass concentration of Fluorene, phenanthrene, anthracenes, benzo (e) acephenanthylene, benzo (e) pyrene, are ranging from 0.044 to 1.5856mg/l thus buttressing the classification of the crude as medium light due to trace amount of PAHs.
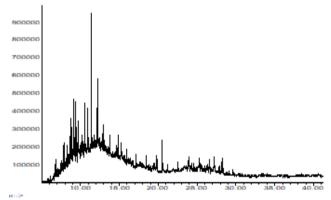
Fig 4: Spectra of Simulated Petroleum wastewater indicating PAHs, Fourth day

The total PAHs in simulated wastewater does not show a clear trend, contrary to the expectation that there should be a progressive increase with time due to photolysis or photodecomposition of compounds or PAHs (Table 3). Day 2 shows a drop in total concentration of PAHs when compared to day one. Similarly, day 4 shows a drop in total concentration of PAHs when compared to day 3. This may have been due to many factors such as extraction processes, preservation methods and analytical procedures on GC-MS. Fig 1-4 shows Spectra of Simulated Petroleum wastewater indicating selected PAHs, during the four days of sampling.

Effectiveness of tested activated carbon in removal of selected PAHs from petroleum contaminated water: The rate at which selected PAHs were removed from petroleum contaminated water at daily interval for a period of 5hrs is shown in Tables 4-7.

It was observed that some of the selected PAHs were not detected after remediation while some were detected after remediation. It may be inferred that COA KCl and CBV H_3PO_4 were effective in removal of those PAHs that are not detected after remediation. It may also be as a result of lower resolution factors of the GC-MS employed in the analysis. The percentage removal efficiency for each selected PAHs analyzed was observed to be low. Table 4 revealed a range of 6.2-14.6% removal efficiency of each selected PAH with a total percentage efficiency of 27.7% for COA KCl. CBV H_3PO_4 produced 10.26-15.20% removal efficiency for each selected PAH with a total percentage efficiency of 50.8. Total percentage efficiency for each tested carbon used for remediation increased on the 2nd day with 41.3% for COA KCl and 63.4% for CBV H_3PO_4.

Table 4 Quantity of PAHs removed tested activated carbon (COA KCl and CBV H_3PO_4) at 5 hrs Contact time and 1st day sampling.

Compounds	Initial Mass Concentrations of PAHS (mg/l) Day1	Final concentrations of PAHS adsorbed by COA (KCl) mg/l	Percentage Removal Efficiency COA (KCl) %	Final concentrations of PAHS adsorbed by CBV (H_3PO_4) mg/l	Percentage Removal Efficiency CBV (H_3PO_4) %
Fluorene	0.126	0.114	10.02	ND	
Phenanthrene	0.401	0.349	13.11	0.345	14.11
Anthracene	0.325	0.278	14.61	0.276	15.20
Benz(e)acephenanthrylene	1.163	1.091	6.2	0.996	14.30
Benzo(e)pyrene	1.112	1.018	8.5	0.998	10.27
Total PAHS	3.127	2.850	27.7	2.619	50.8

ND: Not detected, COA KCl: Oxytenanthera abyssinaca activated with KCl; CBV H_3PO_4: Bambusa vulgaris activated with H_3PO_4

Table 5 Quantity of PAHs removed tested activated carbon (COA KCl, and CBV H_3PO_4) at 5 hrs Contact time and 2nd day sampling.

Compounds	Initial Mass Concentrations of PAHS (mg/l) Day2	Final concentrations of PAHS adsorbed by COA(KCl) mg/l	Percentage Removal Efficiency COA (KCl) %	Final concentrations of PAHS adsorbed by CBV (H_3PO_4) mg/l	Percentage Removal Efficiency CBV (H_3PO_4) %
Fluorene	0.067	ND		ND	
Phenanthrene	0.356	0.293	17.58	0.293	17.7
Anthracene	0.280	0.227	19.31	0.226	9.3
Benz(e)acephenanthrylene	1.14	1.023	10.23	1.024	10.2
Benzo(e)pyrene	1.112	0.999	10.12	ND	
Total PAHS	2.955	2.542	41.3	1.759	63.4

ND: Not detected, COA KCl: Oxytenanthera abyssinaca activated with KCl; CBV H_3PO_4: Bambusa vulgaris activated with H_3PO_4.

Table 6 Quantity of PAHs removed tested activated carbon (COA KCl and CBV H₃PO₄) at 5hrs Contact time and 3rd day sampling.

Compounds	Initial Mass Concentrations of PAHS (mg/l) Day3	Final concentrations of PAHS adsorbed by COA (KCl)mg/l	Percentage Removal Efficiency COA (KCl) %	Final concentrations of PAHS adsorbed by CBV (H₃PO₄)mg/l	Percentage Removal Efficiency CVB (H₃PO₄) %
Fluorene	0.192	ND	100	ND	100
Phenanthrene	0.384	ND	100	ND	100
Anthracene	0.308	ND	100	ND	100
Benz(e)acephenanthrylene	1.141	1.024	10.25	ND	100
Benzo(e)pyrene	1.112	ND	100	ND	100
Total PAHS	3.137	1.024	67.4	ND	100

ND: Not detected, COA KCl: Oxytenanthera abyssinaca activated with KCl; CBV H3PO4: Bambusa vulgaris activated with H3PO4.

Table 7 Quantity of PAHs removed tested activated carbon (COA KCl and CBV H₃PO₄) at 5 hrs Contact time and 4th day sampling

Compounds	Initial Mass Concentrations of PAHS (mg/l) Day4	Final concentrations of PAHS adsorbed by COA (KCl)mg/l	Percentage Removal Efficiency COA (KCl) %	Final concentrations of PAHS adsorbed by CBV (H₃PO₄) mg/l	Percentage Removal Efficiency CBV (H₃PO₄) %
Fluorene	0.107	ND	100	ND	100
Phenanthrene	0.387	ND	100	ND	100
Anthracene	0.311	ND	100	ND	100
Benz(e)acephenanthrylene	1.151	0.895	22.28	ND	100
Benzo(e)pyrene	1.112	ND	100	ND	100
Total PAHS	3.068	0.895	70.8	ND	100

ND: Not detected, COA KCl: Oxytenanthera abyssinaca activated with KCl; CBV H3PO4: Bambusa vulgaris activated with H3PO4.

For each PAH selected, the removal efficiency remained at a range of 10.11-19.3% for COA KCl and 10.15-19.3% for CBV H₃PO₄ (Table 5). There were further increases in Table 6 with an appreciable removal percentage of 67.5% for COA KCl, while there was no detection of parameters with CBV H₃PO₄ adsorbent. Table 7 shows that reduction in total PAHs has little difference when compared to day 3, for COA KCl and no detection for CBA H₃PO₄. Comparing the efficiency of tested adsorbent used for remediation of different concentration of PAHs per day for duration of 4 days, it can be inferred that CBV H₃PO₄ showed greater removal efficiency with percentage range of 50.8-100, while COA KCl showed a lower removal efficiency of 27.7-70.8%.

These may have resulted from chemical interaction between the adsorbent and adsorbate due to their surface contact. The acid activated adsorbent (CBA H₃PO₄) is negatively charged while COA KCl is positively charged. It can then be deduced that an adsorbent with positively charged surface will attract anions while those of negatively charged will attract cations. This indicates that selected PAHs in petroleum contaminated water are positively charged and are easily attracted to negatively charged adsorbent

Conclusion: This study shows that adsorbens made from *Bambusa vulgaris* and *Oxytenanthera abyssinaca* and activated with Phosphoric acid (H₃PO₄) and Potassium chloride (KCl) as dehydrating agent respectively, efficiently adsorbed selected PAHs in petroleum wastewater, hence are good adsorbents that can be adopted in the petroleum industries for remediation operations. Since PAHs in contaminated water increases with time due to photodecomposition thus early treatment should be considered when there are spillages on waterways.

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