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Remediation of crude oil polluted soil using ash made from oil palm empty fruit bunches (OEFB)

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ABSTRACT

Samples of garden topsoil (0 – 15cm) at atmospheric temperature and about 50% moisture content, with no previous history of pollution were spiked with 100mL Bonny light crude oil. The soil-oil mixture (250g of soil to 100mL of oil) was treated with ash made from oil palm empty fruit bunches and allowed to stand for two weeks, with the aim of elucidating the ability of the ash to degrade petroleum hydrocarbons present in the oil. Results obtained from the study reveals that two weeks after the treatment, there was complete removal of the saturated hydrocarbons (TPH) and a significant degradation of polycyclic aromatic hydrocarbons (PAHs). This degradation was affirmed by the reduction of the TPH of the treated sample from 9,743.0 mg/kg to zero and PAH concentration from 237,230.90mg/kg to 19,107.00mg/kg. The striking feature of this degradation pattern is the fact that though PAH water solubility, and thus bioavailability, decreases with an increase in molecular mass of oil. High molecular weight PAHs like indeno - (1,2,3 – c,d) pyrene and 1,1,2-Benzoperylene were completely degraded whereas lower molecular fractions like fluoranthene and pyrene were still available. This may be attributed to the treatment of soil-oil mixture with ash made from oil palm empty fruit bunches which has rich concentration of nutrients like phosphate, nitrate and the metal ions such a potassium. It may therefore be deduced from the above that ash made from oil palm empty fruit bunches can be used for bioremediation of crude oil contaminated soil.

KEYWORDS

Bioremediation;
Ash;
Crude oil;
Degradation;
TPH;
PAH;
Oil palm empty fruit bunches (OEFB).

INTRODUCTION

Contamination of soil environment by hydrocarbons (mostly petroleum hydrocarbons) is becoming prevalent across the globe. This is probably due to heavy dependence on petroleum as a major source of energy throughout the world, rapid industrialization, population growth and complete disregard for the environmental health. The amount of natural crude oil seepage was estimated to be 600,000 metric tons per year with a range of uncertainty of 200,000 metric tons per year. Release of hydrocarbons into the environment whether accidentally or due to human activities is a main cause of water and soil pollution[10]. These hydrocarbon pollutants usually caused disruptions of natural equilibrium between the living species and their natural environment. Hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutants[4].

Since oil pollution is a worldwide threat to the environment, hence the remediation of oil-contaminated soils, sediments and water is a major challenge for environmental research. Biological remediation, a process defined as the use of microorganisms or plants to detoxify or remove organic and inorganic xenobiotic compounds from the environment is a remediation option that offers a "green technology" solution to the problem of environmental degradation. This process relied upon microbial enzymatic activities to transform or degrade the contaminants from the environment. It offers a cost effective remediation technique, compared to other remediation methods, because it is a natural process and does not usually produce toxic by-products. It also provides a permanent solution as a result of complete mineralization of the contaminants in the environment. Advantages of biological remediation compared to other treatment methods include: i) destruction rather than transfer of the contaminants to another medium, ii) minimal exposure of workers to the contaminants, iii) longterm protection of public health and possible reduction in the duration of the remediation process[3,2].

Various studies such as those of Osuji et. al., 2006a, Osuji and Nwoye 2007, Ubochi et. al., 2006, Ebere et. al., 2011 and others has affirmed the effectiveness of organic fertilizers in bioremediation. The objectives of this research assesses the effectiveness of ash made from oil palm empty fruit bunches (OEFB) in bioremediation of garden topsoil spiked with bonny light crude oil, which is the most abundant crude oil in the Niger-Delta, Nigeria. The depletion of saturated hydrocarbons within the C6 – C40 range (aliphatic hydrocarbons) also referred to as Total petroleum Hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) were assessed within two weeks of treatment.

MATERIALS AND METHODS

Sample collection

Garden topsoil (0-15 cm) at atmospheric temperature and about 50% moisture content, with no previous history of crude oil contamination was collected from Abak Itenge in Abak Local government Area of Akwa Ibom State, Nigeria. The crude oil (Bonny light) was obtained from Technology Partners International Nigeria Limited, Port Harcourt. The Oil palm empty fruit bunches were obtained from a palm oil mill at Abak Itenge in Abak Local Government Area of Akwa Ibom State. These samples were sundried for one week before they were ashed in the oven at 100°C. The ash was stored in air tight containers at room temperature and portions were taken from there for analyses.

Sample preparation

250 g of garden topsoil samples were weighed into two perforated Aluminium containers. Each of the soil samples in the various containers were then spiked with 100 mL of Bonny light crude oil. The soil-crude oil mixture in each of the containers was stirred to achieve homogeneity. 50g of the ash was added to the sample in the first container (treated sample), stirred again and allowed to stand for two weeks. The two samples were exposed to natural environmental conditions of temperature, light and water, and stirred daily within the two weeks to enhance homogeneity and aeration. The sample without the ash (untreated sample) served as the control sample.

Oil extraction and gas chromatographic analyses

1g of each of the samples was weighed into well labeled clean and dry vials and 10mls of pentane was added to them. The samples weighed stirred using a magnetic stirrer for about 5 minutes before they were allowed to concentrate to 1ml. The extracts were fractionated into aliphatic fractions by adsorption liquid chromatography using a column of alumina and silica gel, while pentane was used as gradient solvent. The extracts were concentrated to 1ml and these were subjected to analysis[6].

The Total petroleum hydrocarbon (TPH) and Polycyclic aromatic hydrocarbon (PAH) of the samples were determined using a Hewlett Packard 6890 gas chromatograph made by Agilent (USA) with the following operational conditions; flow rate (H_2 30ml/min, air 300ml/min and N_2 30ml/min), injection temperature (50°C), detector temperature(320°C). For signals, the GC was interfaced to a Hewlett Packard (hp) computer.

RESULTS AND DISCUSSIONS

Total petroleum hydrocarbon (TPH)

Total petroleum hydrocarbons (TPH) is referred to as cumulative concentrations of petroleum hydrocarbons[12]. It is also a term used to describe a large family of several hundred chemical compounds present in crude oil[11]. The initial TPH of the untreated sample (TABLE 1) was 9,743.0 mg/kg whereas two weeks later, the TPH of the sample, 9491.9mg/kg (TABLE 1) revealed that the sample had undergone slight alteration. These results show that the samples had a concentration of *n*-alkanes within the $n\text{-}C_{12}$ to $n\text{-}C_{32}$ range with $n\text{-}C_{12}$ having the least concentration while $n\text{-}C_{14}$ had the highest concentration. The TPH of the treated sample which was obtained two weeks after the treatment (TABLE 1) show that the hydrocarbons within the $n\text{-}C_{12}$ to $n\text{-}C_{32}$ range had been completely degraded. This may be ascribed to the treatment of the later sample with ash made from oil palm empty fruit bunches (OEFB). The ability of the ash to cause degradation of hydrocarbons may be due to the fact that it has rich concentration of nutrients. Udoetok, 2012 reported that this ash contain metals such as Chromium, Zinc, Calcium, Potassium, Sodium, and Magnesium and anions such as Phosphate, Nitrate, Sulphate and Chloride. Nutrients such as Nitrate and Phosphate along with metal ion species like Potassium has been reported to enhance the degradation of Hydrocarbons by increasing the hydrocarbon degrading potentials of microorganisms which feed on hydrocarbons as their source of energy. Chorom et. al., 2010 showed that the hydrocarbon-degrading and heterotrophic bacteria count increased and heterotrophic bacteria population increased from 6×10^3 cfu/g soil to 1.4×10^8 cfu/g soil when soils were treated with NPK fertilizer. The studies of Ubochi et. al., 2006 also affirmed the enhancement of microbial utilization of hydrocarbons with the application of nutrients.

TABLE 1 : Total petroleum hydrocarbon of untreated and treated samples

Hydrocarbon Fraction	Amount (mg/kg)		
	Untreated Sample (Day 1)	**Untreated Sample (Two weeks later)**	**Treated Sample (Two weeks later)**
C6	-	-	-
C7	-	-	-
C8	-	-	-
C9	-	-	-
C10	-	-	-
C11	-	-	-
C12	255.2	220.2	-
C14	3,003.0	3,000.0	-
C16	947.1	905.1	-
C18	960.0	955.0	-
C20	1,280.1	1,260.7	-
C24	643.4	630.2	-
C28	456.9	420.4	-
C32	2,197.3	2,100.3	-
C36	-	-	-
C40	-	-	-
Total	9,743.0	9491.9	0

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that consist of two or more fused benzene rings and/or five-membered rings that are arranged in various structural configurations. They are highly recalcitrant molecules that can persist in the environment due to their hydrophobicity and low water solubility[1]. Some representative PAHs are shown in Figure 1 below.

Results obtained from this study (TABLE 2) show that there was abundance of PAHs in the untreated sample on the first day of the study and two weeks later. It revealed a total PAH concentration of 237,230.90mg/kg on the first and 237,088.50mg/kg two weeks later for the untreated sample. It also shows that Pyrene, a four-membered ring PAH was the most abundant. These results show that the hydrocarbons were only slightly degraded two weeks after. However, the result obtained for the treated sample shows that two weeks after the treatment of the oil-contaminated soil with ash made from oil palm empty fruit bunches, the hydrocarbons had been severely degraded as depicted by the reduction the PAH concentration from 237,230.90mg/kg to 19,107.00mg/kg. The striking feature of this degradation pattern is the fact that though several studies like that of Wilson and Jones, 1993 has reported that PAH water solubility and thus bioavailability decreases with an increase in molecular mass, high molecular weight PAHs like indeno-(1,2,3 – c,d) pyrene and 1,1,2-Benzoperylene were completely degraded whereas lower molecular fractions like fluoranthene and pyrene (Figure 1) were still available. This may be attributed to the rich concentration of nutrients like phosphate, nitrate and the metal Potassium in the ash[12]. The presence of these nutrients may have enhanced the degradation ability of the microorganisms in the soil such that they were able to attack the polycyclic rings of the hydrocarbons thus being able to completely utilize them as their source of energy.

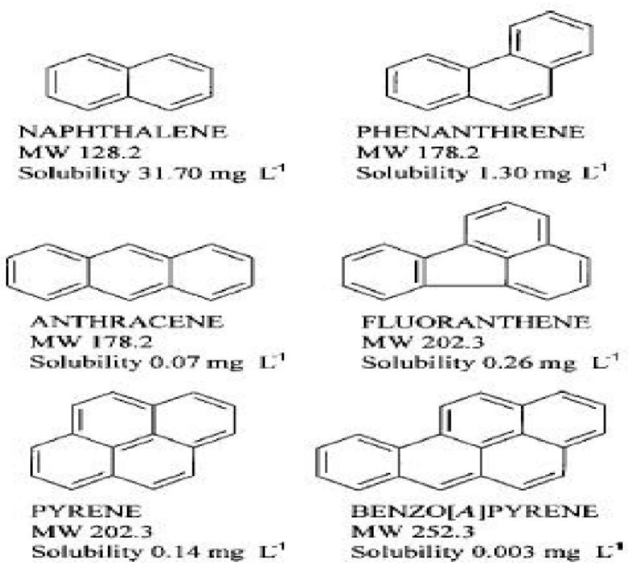

Figure 1 : Representative of PAHs (adapted from Bamforth and Singleton, I. 2005).

Mechanism of degradation

Studies on characterization the ash used in this remediation as reported by Udoetok, 2012 reveals that the ash has a rich concentration of nutrients while the suspension produced by adding water to the ash is alkaline (has a pH of 10.9). He also said that the filtrate obtained from the above suspension has the ability of emulsifying palm oil. This therefore points to the fact the degradation of the hydrocarbons may have followed one or both of the following mechanisms proposed below:

TABLE 2 : Polycyclic aromatic hydrocarbon of untreated and treated samples

Hydrocarbon Fraction	Amount (mg/kg)		
	Untreated Sample (Day 1)	Untreated Sample (Two weeks later)	Treated Sample (Two weeks later)
Naphthalene	-	-	-
Acenaphtylene	-	-	-
Acenaphthene	-	-	-
Fluorene	-	-	-
Phenanthrene	1,449.4	1,440.4	-
Anthracene	3,356.9	3,342.6	-
Fluoranthene	30,784.1	30,748.3	1,481.0
Pyrene	64,347.9	64,327.2	1,412.3
1, 2 DiBenzanthracene	14,925.5	14,900.5	10,452.2
Benzo (b) Fluoranthene	18,695.0	18,687.0	5,761.5
Benzo (k) Fluoranthene	10,813.2	10,802.8	-
Benzo (a) Pyrene	33,590.2	33,580.6	-
Indeno-(1,2,3 -c,d) Pyrene	15,502.6	15,498.6	-
1,2,5,6 DiBenzanthracene	17,000.6	17,000.0	-
1,1,2-Benzoperylene	26,765.5	26,760.5	-
Total	237,230.90	237,088.50	19,107.00

Degradation through emulsification

An emulsion is a mixture of two or more liquids that are normally immiscible (non-mixable or unblendable). The ability of the filtrate obtained from the suspension of this ash to emulsify palm oil suggests that this solution can also emulsify crude oil, though the two types of oils, may exhibit differences. Since the oil-contaminated soil was exposed to natural environmental conditions of temperature light and water, it may be deduced that rainwater may have been in contact with the oil-contaminated soil/ash mixture, leading to the creation of favourable conditions for the emulsification of the oil in the mixture.

Degradation by microorganisms

Several studies such as the one of Osuji et. al., 2006 has shown that microorganisms are able to utilize hydrocarbons as the sole source of their energy. They reported the attenuation of petroleum hydrocarbons by microorganisms within two seasonal variations of two and six months respectively. This observation indicates that the degradation of petroleum hydrocarbons in this study may have been due to the enhancement of their hydrocarbon degrading ability by the treatment of the sample with the nutrient-rich ash. The nutrients in the ash may have boosted the hydrocarbon degrading potential of the microbes thus resulting in the complete disappearance of saturates and a significant alteration of the PAH profile of the oil.

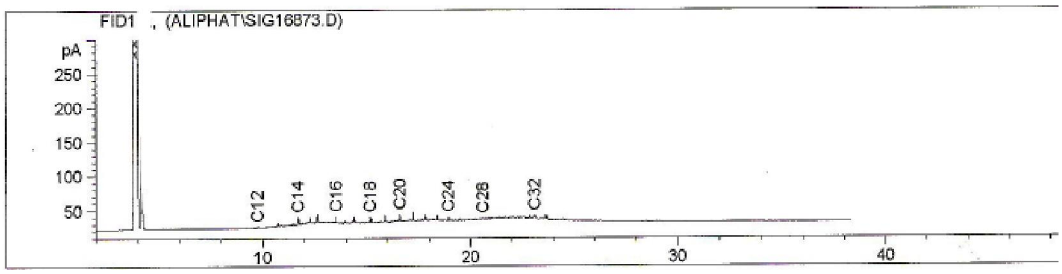

Figure 2 : Fingerprint showing TPH of the samples before treatment.

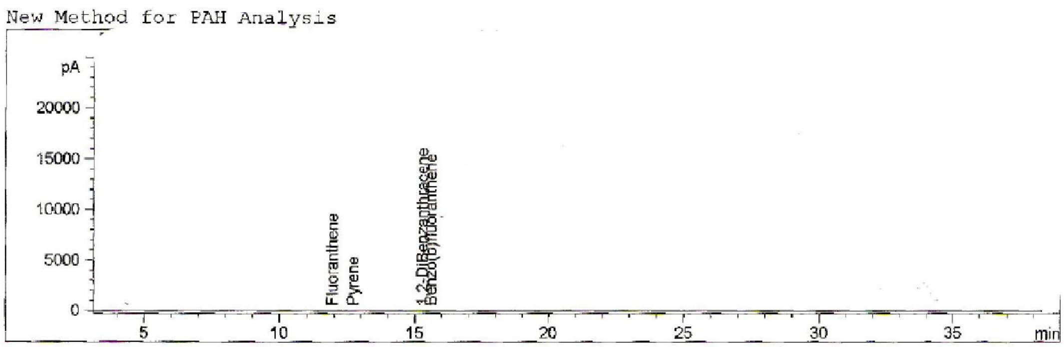

Figure 3 : Fingerprint showing PAH profile of the sample after treatment

CONCLUSIONS

The treatment of crude oil contaminated soil with ash made from oil palm empty fruit bunches revealed that after two weeks of treatment, there was complete disappearance of the saturated hydrocarbons while the polycyclic aromatic hydrocarbon profile of the oil was significantly altered. This shows that this ash which has been confirmed to possess rich concentration of nutrients and potassium ions species can contribute to bioremediation. This study has also proposed the mechanism of degradation of the hydrocarbons which may be through degradation by microorganisms and/or degradation through emulsification. There is need for further studies on this subject so as to elucidate the actual mechanism of degradation that took place in this study.

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