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Evaluation Of Remediation Potential Of Cassava And Orange Peels On Polycyclic Aromatic Hydrocarbons And Total Petroleum Hydrocarbons Concentrations In Oil-Contaminated Soils

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Abstract

The application of cassava peel, orange peel, and their mixtures in the remediation of oil-contaminated soils from Rumuekpe in Emuoha Rivers State were assessed. Bioreactors that contain the oil-contaminated soil, the peels and their mixtures were set-up and monitored for 42 days. Standard methods recommended in APHA and HACH with GC-MS and GC-FID were used to determine the total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbons (PAH). The soils were collected from the top soil (0-30cm) and the results, showed that after 42 days of amendments, the maximum reduction of hydrocarbon contents of the treated soils was 65.02% for cassava peels (CP), 62.19% for orange peels (OP) and 72.39% for mixed peel (MP). For the maximum reduction in PAH content of the treated soils at 42 days of amendment application was 93.14% for cassava peel (CP), 89.53% for the orange peel (OP) and 95.31% for the mixed peel (MP). The ANOVA on the levels of PAH between the treatments and between the days showed significant difference where P<0.05. It was concluded that significant hydrocarbon reduction was achieved with the use of these organic wastes and this also proved that although the introduction of the organic wastes (CP and OP) treatment showed significant reduction in TPH and PAH, the mixture of these organic wastes (MP) showed a more significant reduction in TPH and PAH.

Keywords; *Remediation Potential, Cassava, Orange Peels, Soils, Rumuekpe, Rivers State*

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I. Introduction

The loss of soil function and quality is an increasing challenge to human existence. This loss of ecological functions arising from the release of petroleum hydrocarbons into the environment has been well documented. The presence of petroleum hydrocarbons in most of its structural forms leads to a distortion of the biochemical function of most organisms and hence linked to several negative biodiversity changes in environments challenged with hydrocarbon pollution.

Generally, there are different sources of energy available to man, with petroleum which is a product of the oil industry's lucrative industrial activities on earth being the main source of energy (Perez-Harnandez *et al.*, 2013). According to Namkoong *et al* (2002), with the hydrocarbon extraction activities on the increase in continental regions, it could lead to the degradation and erosion of huge land mass and this could create one of the world's most serious environmental issues (Ubelhor *et al.*, 2014).

Degradation of the soil is one of the most adverse aspects of petroleum extraction activities; it is as a result of the overall removal of plant cover as well as the layers of the top soil which takes place when drilling platforms are constructed along with the hydrocarbon contaminants, heavy metals and other chemical substances on soils which can be kept as by-products in mud as well as drilling cutting cells along with contaminated soil treatment instruments in the oil field installations (Willis *et al.*, 2005).

Hydrocarbon compounds such as aliphatics, alicyclics and polycyclic aromatic hydrocarbons (PAHs) make up crude oil. Amongst the compounds, PAHs are the most abundant in crude oil and many are toxic and can be carcinogenic to plants and animals (Maliszewska-Kordybach, 1999; CCME, 2010). Hence, crude oil according to Crude Oil (2011) is simply unprocessed oil found beneath the earth surface; it can range in colour from clear to black and can be found as a liquid or solid.

The commercial exploitation of the hydrocarbon resources available in Nigeria from the early 1930s to date is responsible for observable ecological perturbations in the predominant oil producing regions of the Niger Delta. The impact is not limited to just ecological effects that are observable in most oil producing communities but also social, economic and health of most local communities have been affected. The most significant impact of petroleum hydrocarbon presence in terrestrial ecosystems is the alteration in the structure of agricultural soils. Food cultivation has been adversely affected due to presence of crude oil contamination in agrarian community soils. Also, the presence of underground pipelines used in the transportation of crude oil across countries have led to more significant cases of crude oil contamination as a result of corrosion of oil pipelines and spillages. This contamination could lead to imbalance of the carbon to Nitrogen ratios. This could lead to nitrogen deficiency in plants (Yerima *et al*., 2011). Crude oil could also exhibit binding effects on soil particles which leads to the reduction of oxygen in the soil. Germination of seeds on such soil will be drastically affected.

Choosing a cost effective and environmentally friendly option to be employed in addressing the hydrocarbon pollution experienced by developing and developed countries is a serious problem challenging the world today. Though couples of physical and chemical concepts have been applied to cut down hydrocarbon pollution however, it has been established that they are not ecofriendly as well as time consuming. Hence, for an ecofriendly in addition to a cost-effective choice in the decrease of hydrocarbon pollution, the use of biological strategies is really a better option to be considered in the remediation of hydrocarbon contaminants as a substitute to environment harmful methods (Tharaka *et al.*, 2003). The activities of living organisms such as bacteria, fungi and yeast enzymatically attack most organic and inorganic chemicals. Crude oil and other society's environmental pollutants are among these chemicals. The actions of enzymes on these pollutants are together regarded as bioremediation. (Crawford & Crawford, 2005). Due to the presence of some metabolic mechanisms found in some of these micro-organisms like bacteria and fungi, they are able to use petroleum hydrocarbons for their carbon and energy sources (Tharaka *et al.,* 2003).

Hydrocarbon contaminants which find their way into the environment endangering public health usually as contaminants of the soil, water or sediments can be removed or detoxified through the productive use of biodegradative processes termed 'Bioremediation'. Being a desirable, developing, inexpensive as well as ecofriendly technology is dependent upon the use of micro-organisms to get rid of petroleum hydrocarbon contaminants from soil in addition to water (Bento *et al*., 2005; Wu *et al*., 2016). For instance, an estimated cost that ranges between $40 and $80 per cubic yard compared with $250 and $800 per cubic yard for bio treatment of biodegradable contaminants in soils and the use of incinerators respectively as published by Levin and Gealt (1993).

Studies have shown the remediation of soils contaminated with petroleum hydrocarbon which are primarily caused by the presence of some of its components like PAHs, which are toxic and carcinogenic threatening the environment and human health (Johnston & Leff 2015; Zeng *et al.,* 2016) and the overall clean-up of soils contaminated with petroleum hydrocarbon has been receiving interest, resulting in the development along with implementations of technological innovations (De Boer *et al.*, 2016).

Hydrocarbons in petroleum may serve as electron donors for sulphate reducing bacteria (SRB), which use sulphate as the terminal electron acceptor for respiration, resulting in sulphide production. As reported by Javaherdashti (2008), Little & Lee (2007), sulphate-reducing bacteria (SRB), iron and CO_2 reducing bacteria and iron and manganese oxidizing bacteria are the main types of bacteria associated with metals in pipeline systems. These microbiologically influenced corrosion (MIC) or bio-corrosion is a considerable problem for the oil and gas industry. Whenever corrosion is mentioned, attention goes to acid or aerobic corrosion (In the presence of moisture and air) but observations have shown that corrosion also occur in anaerobic environments like buried pipe lines. However, for the purpose of this research, the acid corrosion is considered.

Manihot esculenta also known as cassava is a woody shrub which is the most important food crops in the tropics which serves as a food security and income generation crop for millions of people in the developing countries (Adejo *et al.,* 2013). It is grown in many regions at the tropics including Nigeria where it serves as one of the basic food sources for about 200 to 300 million people (Umoren, 2009). For wider utilization, cassava products can be a catalyst for rural industrial development and raise the incomes of producers, processors and traders. It can also contribute to the food security status of its pursuing and consuming households (Obot *et al.,* 2009). Besides starch, the cassava tuber contains some soluble carbohydrates that are glucose and sugar. As reported by Annan, 1998, cassava peels are the major by-product of the cassava processing industry and these peels are largely underutilized as livestock feed. When fermented cassava products are processed, usually the roots are peeled to rid them off two outer coverings which are a thin brown outer covering, and a thicker leathery parenchymatous inner covering (Obadina *et al*., 2006). Such peels are considered wastes and are usually discarded and allowed to rot. With hand peeling, the peels will reflect 20 to 35 percent of the tuber's total weight (Odunfa, 1985). The wastes currently produced present a problem of disposal and will be even more difficult and challenging with growing manufacturing output of cassava products (Obadina *et al*,2006). In the cassava processing chain, cassava peels continue to constitute waste (Eustace and Dorothy, 2001). This is despite the possibility of using the byproduct as animal feed. There has been considerable evidence that the processed cassava peel could be used as an energy source for swine and poultry (Longe *et al*, 1983). The cassava peels generated through processing of garri are usually disposed as wastes and left to decompose in the open, leading to health hazards (Oboh, 2006).

The orange is the fruit of the citrus species, *citrus sinenesis* in the family Rutaceae, which is native to China. It is also called sweet orange to distinguish it from related *citrus aurantium*, referred to as bitter orange. The orange originated in China. Orange trees were found to be the most cultivated fruit tree in the world as at 1987 (Moj, 1987). For these sweet fruits, they are widely grown in tropical and subtropical climates. Orange tree fruit can be eaten fresh if processed for its juice or fragrant peel (Citrus seneasis, 2017). Nigeria produces 3% of fresh citrus in the World (FAO, 2004). The peels obtained from the pericarp of these fresh fruits are available in large quantities during the citrus season thereby constituting environmental problems since it is not being put into any productive use. The inability of the few and small capacity processing industries to convert the fruit juice and concentrate has led to the generation of wastes. Citrus byproduct waste has been traditionally valorized as molasses for animal feed (Bocco et al., 1998), fiber (pectin) production (Chou and Uang, 2003) and fuel production (Liorach et al.,2003).

II. Materials And Methods

Crude-oil Contaminated and Uncontaminated Soils

These soils were collected from the top surface soil (0 – 30cm) from Rumuekpe in Emuohua local government area of Rivers State.

Analytical Methods

Preparation of Peel Extracts

The fresh peels of cassava tuber and orange fruit were collected from farmers at Ubima town and orange sellers at Rumuola market in Ikwerre and Obio/Akpo Local Government Areas of River State respectively.

The peels were washed thoroughly with deionized water to remove sand and other impurities, sun-dried for 2 weeks and ground to powder using an electric blender. The powdered peels of each of the plants were extracted with the use of Soxhlet extractor. 5kg of each powdered sample was extracted with 1 liter of 99.8% methanol in the Soxhlet extractor. With the use of an oven at 40°C the resulting extracts were evaporated to near dryness to obtain a paste residue that is free of methanol. The extracts were then weighed and stored in sample bottles and stored in refrigerator.

Sample Collection

The crude contaminated and uncontaminated soils used for the study were collected from top soil (0 – 30 cm depth) at Rumuekpe in Emuohua Local Government Area of Rivers State. The soil 0 – 30cm depth was collected to cover the depth of penetration of the contaminant. The soil samples collected were placed into boxes of 40cm-by-40cm dimension made of wooden boards. The boards gave room for the control of the depth and exposed surface area of the soil and in turn, the temperature, nutrient concentration and oxygen availability. Cassava peels were collected from farmers in Ubima town in Ikwerre Local Government Area while orange peels were collected from fruit sellers at Rumuola area in Obio/Akpor Local Government Area, all in Rivers State.

Experimental Design

Exactly 2 kg of soil was introduced into each of eleven experimental boxes, built with wooden board, with the following treatment options:

Experimental Box V (1 box): Non contaminated soil to serve as Control 1

Experimental Box W (1 box): Contaminated soil without treatment to serve as Control 2

Experimental Box X (3 boxes): Contaminated soil with Cassava Peels Treatment (CPT) - Three boxes with different measurements of treatments- X_1- 100, X_2- 200, X_3- 300.

Experimental Box Y (3 boxes): Contaminated soil with Orange Peels Treatment (OPT)- Three boxes with different measurement of treatments- Y_1- 100, Y_2- 200, Y_3- 300.

Experimental Box Z (3 boxes): Contaminated soil with Mixed Peels Treatment (MPT)- Three boxes with different measurement of treatments- Z_1- 100, Z_2- 200, Z_3- 300.

These experimental boxes were moistened and properly homogenized before sampling the boxes at an interval of 14 days for a total duration of 42 days.

Analysis of TPH and PAH

Total Petroleum Hydrocarbon (TPH)

The method for the determination of TPH as recorded by Adesodun & Mbagwu (2008) was used. 5 grams of the crude contaminated soil sample was suspended in 25ml of hexane and with the use of mechanical shaker, it was shaken for 30 minutes. With the use of Whatman No.1 filter paper, the solution was filtered and the filtrate diluted by taking 1ml of the extract into 50ml of hexane. At a wavelength of 460 nm, the absorbance of the solution was read with the use of HACH DR/2010 Spectrophotometer using hexane as the blank. The actual TPH concentration (mg/kg) was calculated from the mathematical expression below:

$$\text{TPH} = \frac{\text{Instrument reading (conc. from calibration)} \times \text{Vol. of extract (ml)} \times \text{DF}}{\text{Weight of Sample (kg)}} \qquad (3.15)$$

Where TPH = Total Petroleum Hydrocarbon; DF = Dilution Factor; Conc. = Concentration

Polycyclic Aromatic Hydrocarbons (PAHs)

According to the method used by Edema *et al* (2011), 10g of the soil sample was weighed and then, 60ml of a mixture of acetone and dichloromethane (DCM) in the ratio 1:1 was added and the mixture was mixed and warmed at 30^{o}C for about 5minutes in a water bath. The extract was decanted into a clean dried round bottom flask and taken to the rotary evaporator to be concentrated to 30ml. With the use of 60ml DCM, the extract from the rotary evaporator was fractionated by a fractionating column of silica gel into aromatic portion. The DCM fractionates were transferred to a rotary evaporator and re-concentrated to 3ml and transferred to 3ml gas chromatographic vials and analyzed with a gas chromatography (6890 series).

III. Results And Discussion

The Baseline results of Total Petroleum Hydrocarbon (TPH) and Poly Aromatic Hydrocarbon (PAH) concentrations of the uncontaminated and contaminated soils are presented in Table 1. The TPH and PAH in the uncontaminated soil are 15.37mg/kg and <0.01mg/kg respectively while for the contaminated soil, the TPH and PAH results are 5752 mg/kg and 2.77 mg/kg respectively.

Total Petroleum Hydrocarbon (TPH) Concentration for the Organic Wastes Treated Soils

The analysis of the unpolluted soil in the area indicated a TPH value of 15.73 mg/kg as reported in Table 1. Before the application of the organic wastes on the contaminated soil, the TPH concentration in the soil was 5752mg/kg.

Table 1: Baseline Levels of PAHs and TPH

	PAH mg/kg	TPH mg/kg
Uncontaminated Soil (US)	<0.01	15.73
Contaminated Soil (CS)	2.77	5752
Cassava peels(CP)	0.00	NA
Orange peels (OP)	0.00	NA
Mixed peels (MP)	0.00	NA

US = Uncontaminated Soil, CS = Contaminated Soil, CP = Cassava peel, OP = Orange peel, MP = Mixed peels

Table 2: Levels of PAH and TPH in Contaminated Soils Amended with Organic Wastes

Treatment	Day 14		Day 28		Day 42	
	PAH mg/kg	TPH mg/kg	PAH mg/kg	TPH mg/kg	PAH mg/kg	TPH mg/kg
OP1	0.830	3463.00	0.50	2605.00	0.37	2326.00
OP2	0.660	3303.00	0.49	2518.00	0.33	2248.00
OP3	0.620	3139.00	0.47	2512.00	0.29	2175.00
CP1	0.610	3028.00	0.44	2494.00	0.28	2167.00
CP2	0.600	2971.00	0.41	2455.00	0.22	2086.00
CP3	0.590	2817.00	0.40	2400.00	0.19	2012.00
MP1	0.570	2738.00	0.39	2376.00	0.19	1996.00
MP2	0.550	2701.00	0.38	2371.00	0.13	1973.00
MP3	0.510	2643.00	0.37	2339.00	0.13	1588.00
Control	0.910	4250.00	0.89	4221.00	0.77	3937.00

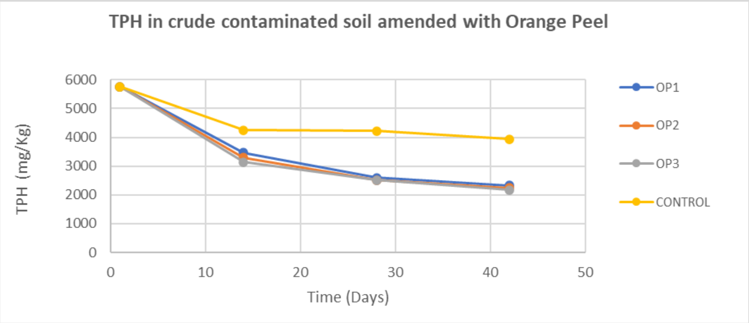
Table 3: Percentage Loss of TPH in Crude Oil Contaminated Soil Amended with Organic Wastes

Treatment	Time (Days)				% loss after 42 days	Net Loss
	1	14	28	42		
OP1	5752.00	3463.00	2605.00	2326.00	59.56	28.01
OP2	5752.00	3303.00	2518.00	2248.00	60.92	60.92
OP3	5752.00	3139.00	2512.00	2175.00	62.19	62.19
CP1	5752.00	3028.00	2494.00	2167.00	62.33	62.33
CP2	5752.00	2971.00	2455.00	2086.00	63.73	63.73
CP3	5752.00	2817.00	2400.00	2012.00	65.02	65.02
MP1	5752.00	2738.00	2376.00	1996.00	65.30	65.30
MP2	5752.00	2701.00	2371.00	1973.00	65.70	65.70
MP3	5752.00	2643.00	2339.00	1588.00	72.39	72.39
CONTROL	5752.00	4250.00	4221.00	3937.00	31.55	

The total petroleum hydrocarbon (TPH) concentrations from days 14 to 42 in soils amended with the organic wastes as recorded in Table 2 showed a decrease in concentration from 3463 to 3139mg/kg for soil amended with 100g of orange peel (OP1) to 300g of orange peel (OP3) and 3028 to 2817mg/kg for contaminated soil amended with 100g of cassava peel (CP1) to 300g of cassava peel (CP3) while for the soil amended with 100g of mixed peel (MP1) to 300g of mixed peel (MP3), there was also a decrease in the concentration from 2738 to 2643mg/kg for the day 14 trend. While on day 28 as shown in the table, the TPH values for the orange peel amended soils decreased from 2605 to 2512mg/kg for OP1 to OP3. The trend was similar for the cassava peel amended soil with the TPH values of 2400mg/kg recorded for CP3 and the values for CP2 and CP1 was 2455mg/kg and 2494mg/kg respectively. This was similar for the mixed peel amended soil where the TPH ranged from 2376 to 2339mg/kg with MP1 to MP3 amended soil. Finally, for the 42 day treatment, the TPH values for contaminated soils amended with orange peel organic waste recorded values in the range of 2326mg/kg to 2175mg/kg as OP1 recorded the highest value of 2326mg/kg while OP2 and OP3 recorded 2248mg/kg and 2175mg/kg respectively. Similarly, the soils amended with cassava peel organic waste recorded the following values of 2012, 2086 and 2167mg/kg for CP3, CP2 and CP1 respectively. While the soils amended with mixed peel organic wastes recorded the following results ranging from 1588 to 1996mg/kg for MP3 to MP1 with MP3 recording the least value of 1588mg/kg. The TPH values for the control were 4250mg/kg, 4221mg/kg and 3937mg/kg for days 14, 28 and 42 respectively.

After 42 days of amendments, the results revealed that the rate of hydrocarbon degradation in the soil amended with the natural organic wastes (MP, CP and OP) were more when compared to the unamended control soil. The soil amended with MP3 reported the highest rate of biodegradation and then followed by CP3 and then OP3 amended soils. There was actually a significant difference on day 42 between percentage hydrocarbon reduction in MP3 amended soil and that of OP3 amended soil while the hydrocarbon reduction profile in the CP3 and OP3 were close. It is therefore evident that the crude oil contaminated soil amended with organic wastes has greater oil biodegradability compared to the unamended control soil. Within days 14 to 42, the hydrocarbon degradation caused by biostimulation exhibited a substantial difference between the organic wastes amended soil and the unamended control soil as shown in Appendix 8 and 9. This could be owing to the bacteria's activity which was greatly aided by the addition of the peels from the organic wastes. The increase in the population of the hydrocarbon utilizing bacteria after the addition of the peels from the organic wastes could be another factor that could lead to the biodegradation of the hydrocarbon.

According to Crecchio *et al*, (2001), studies conducted in both microcosms and field tests revealed that organic treatments not only improve soil structure and serve as a source of nutrients, but they can also significantly boost microbial activity. As a result, by amending contaminated systems with nutrients, pollutants degradation rates can be improved. According to Yan *et al*, (2006), this results in a rise in the population of indigenous microbes and knowing the growth fluxes can provide insight into the effectiveness of the treatments. Other scholars (Ideriah *et al*, 2017; Ibne *et al*, 2011 & Stephen *et al*, 2013), all reported the effectiveness of nutrient sources in the degradation of TPH in crude contaminated soil amended with organic wastes. To arrive at the effectiveness of each organic wastes amendment, the percentage loss of crude oil in the contaminated soil was calculated as reported in Table 3. From the results in Table 3, 300g of the mixed peel amendment proved to enhance its biodegradability strength more than the other organic wastes amendments. The nitrogen and phosphorous content of these organic wastes which enhances the stimulation of the indigenous microorganisms could be the reason behind this when compared to the other amendments. Similar results by other scholars (Abioye *et al*, 2009 & Agbor *et al*, 2012) found that high nitrogen content was identified in brewery spent grain/melon shell and cocoa pod/plantain peel respectively, as one of the most necessary nutrients for efficient bioremediation to take effect. As seen in Table 3, after 42 days of treatment, MP3 amended soil reported the highest percentage oil loss of 72.40% while CP3 reported 65.02% and OP3 recorded the lowest at 62.19%. There was also oil degradation seen in the unamended control soil which was at 31.55%, showing that there was also a natural biodegradation in the control soil. This shows that the indigenous microorganisms recorded biodegradation without the addition of the nutrients from the treatment (MP, CP and OP).



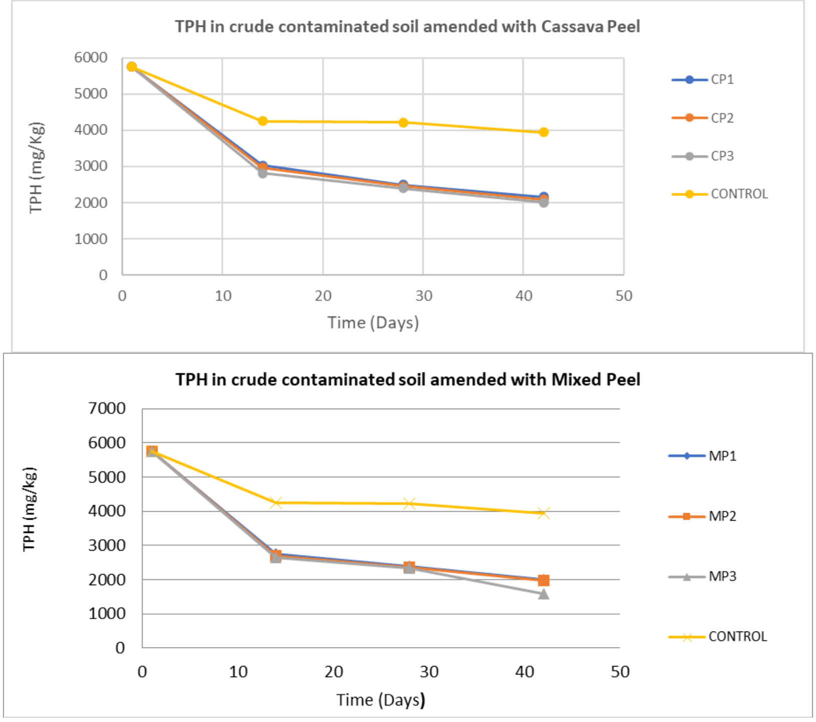
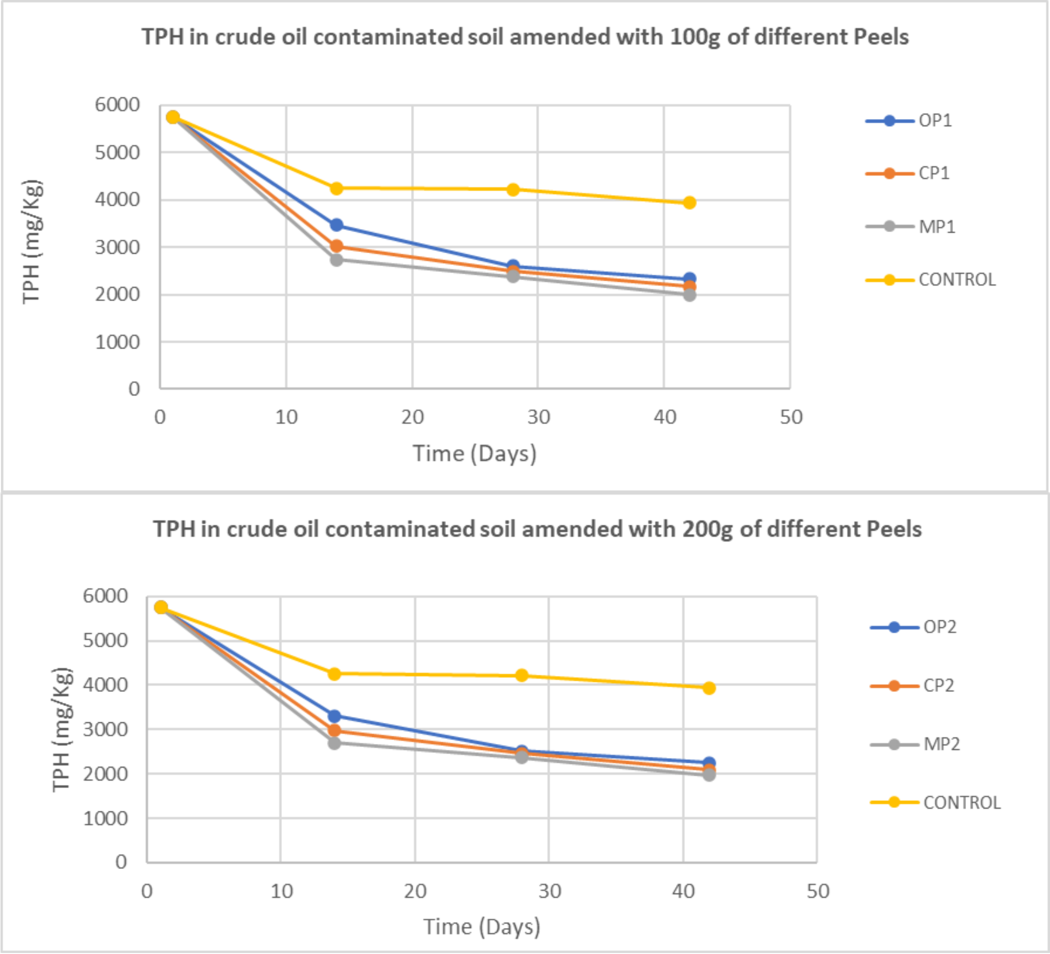


Figure 1: Total Petroleum Hydrocarbon Profiles for Crude Contaminated Soil Amended with the Organic Wastes (Cassava Peel, Orange Peel, Mixed Peel) and Control



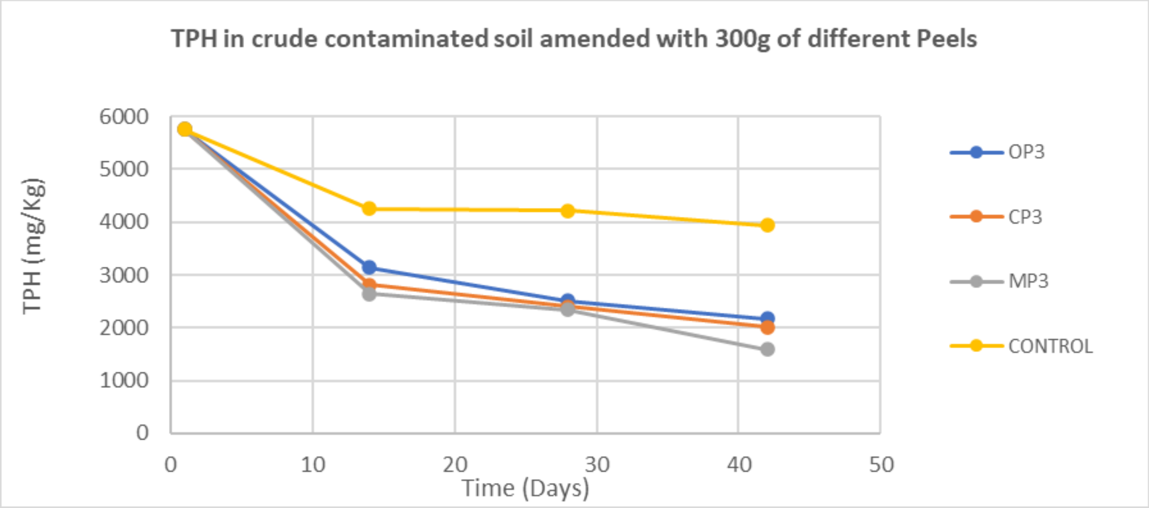


Figure 2: Total Petroleum Hydrocarbon Profiles for Crude Contaminated Soil Amended with the Different Weights of the Organic Wastes (100g, 200g, and 300g) and Control

As reported in Table 1, the PAH value of <0.01mg/kg was recorded for the uncontaminated soil and before the organic wastes treatment was applied to the contaminated soil, the PAH result was 2.77mg/kg. Tables 2 and 4 recorded the PAH concentrations for the crude contaminated organic wastes treated soil from day 14 to 42. The results shown in Table 2 recorded a decrease in concentration from 0.830 to 0.62mg/kg for soil amended with 100g of orange peel (OP1) to 300g of orange peel (OP3), 0.61 to 0.59mg/kg for soil treated with 100g of cassava peel (CP1) to 300g of cassava peel (CP3) and 0.57 to 0.51mg/kg for soil amended with 100g of mixed peel (MP1) to 300g of mixed peel (MP3). While the PAH result of the control for the day 14 treatment was 0.91mg/kg.

Table 4: Percentage Loss of PAH in Crude Oil Contaminated Soil Amended with Organic Wastes

Treatment	**Time (Days)**				**% loss after 42 days**
	1	**14**	**28**	**42**	
OP1	2.77	0.83	0.50	0.37	86.64
OP2	2.77	0.66	0.49	0.33	88.09
OP3	2.77	0.62	0.47	0.29	89.53
CP1	2.77	0.61	0.44	0.28	89.89
CP2	2.77	0.60	0.41	0.22	92.06
CP3	2.77	0.59	0.40	0.19	93.14
MP1	2.77	0.57	0.39	0.19	93.14
MP2	2.77	0.55	0.38	0.13	95.31
MP3	2.77	0.51	0.37	0.13	95.31
Control	2.77	0.91	0.89	0.77	72.20

As shown in Tables 2 and 4, for the day 28 treatment plan for the crude contaminated soil, the PAH values of soil treated with orange peel ranged from 0.50 to 0.470mg/kg for OP1 to OP3. The same trend was recorded for the CP1 to CP3 treated soil, where the PAH results ranged from 0.44 to 0.40mg/kg and PAH concentration for soil treated with MP1 to MP3 ranged from 0.39 to 0.37mg/kg and PAH concentration of the control soil for the 28th day treatment plan was 0.89mg/kg. Finally, as recorded in Table 2 for the day 42 treatment plan, the PAH values for the contaminated soils amended with orange peel wastes ranged from 0.37 to 0.29 mg/kg for OP1 to OP3 treated soils. Subsequently, for the cassava peel treated soil, the PAH values decreased from 0.28 to 0.19mg/kg for the soil treated with OP1 to OP3, while the soils amended with mixed peel organic wastes recorded PAH value ranging from 0.19 to 0.13 mg/kg for MP1 to MP3. The control, untreated soil recorded a PAH concentration of 0.77 mg/kg.

As reported by Malawska and Wilkomrski (2001), a soil is regarded as slightly polluted, polluted, heavily polluted and very highly polluted, when the total PAHs content ranges between 0.6 - 1, 1 – 5, 5 – 10 and > 10 mg/kg respectively. The results from the present study showed the crude contaminated soil is polluted. The results revealed that the rate of PAH degradation in soil amended with the natural organic wastes (MP, CP, OP) were more compared to the unamended control soil after 42 days of treatment. As shown in Tables 2 and 4, the crude contaminated soils treated with MP (mixed peel) showed higher degree of PAH degradation and followed by that treated with CP (cassava peel) and then the OP (orange peel). Hence the soil treated with MP3 showed the highest rate of PAH degradation, followed by that treated with CP3 and OP3 respectively.

As reported in Table 4, there was a significant difference on the 42nd day amendment between the percentage of PAH reduction in MP3 amended soil and OP3 amended soil. It is therefore evident that the crude oil contaminated soil amended with organic wastes has greater PAH biodegradability compared to the unamended control soil. Figures 3 and 4 showed that within 14 to 42 days treatment, the PAH degradation caused by biostimulation exhibited a significant difference between the crude contaminated soil treated with organic wastes and the unamended control soil.

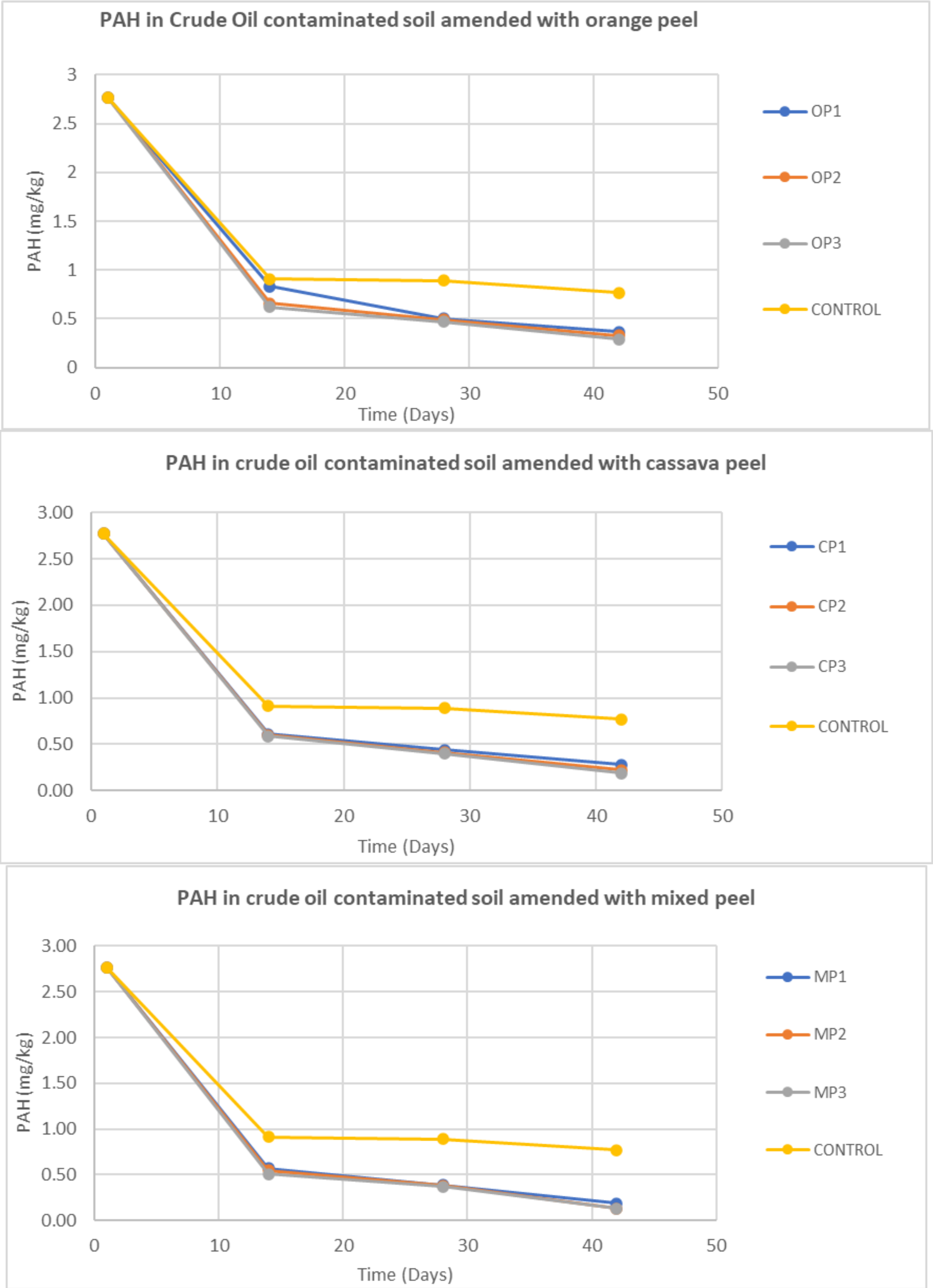


Figure 3: Polycyclic Aromatic Hydrocarbon (PAH) Profiles for Crude Contaminated Soil Amended with the Organic Wastes and Control

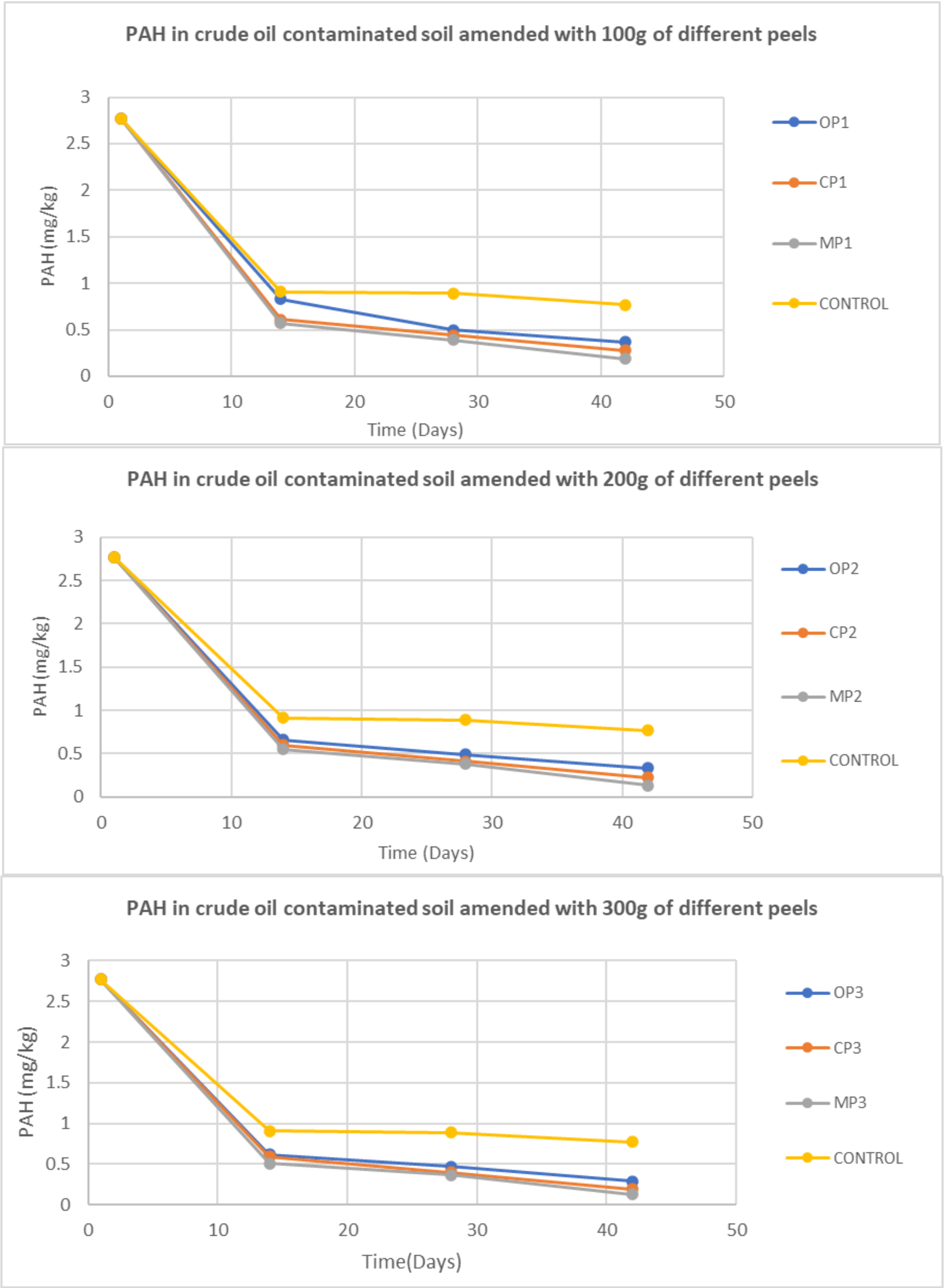


Figure 4: Polycyclic Aromatic hydrocarbon (PAH) Profiles for Crude Contaminated Soil Amended with the Different Weights of the Organic Wastesand Control

The reason for this could be as a result of bacteria activities which are greatly supported by the addition of the peels from the organic wastes. This is in support of the report by Juhasz and Naidu (2000); Stroud *et al.* (2007); Okere and Sample (2012); Cebron *et al*. (2013), who reported that the loss of PAH from contaminated soils are mostly achieved through degradation that are carried out by bacteria, fungi and algae.

Also, Mohan *et al* (2006) and Kuppusamy *et al* (2016d), have all demonstrated the use of biostimulation as the most suitable option to increase the treatment process. The increase in the population of the hydrocarbon utilizing bacteria after the addition of the peels from the organic wastes could be another factor that could lead to the biodegradation of the PAH following biostimulation as supported by the following authors (Safdari *et al.*, 2018; Wu *et al*., 2017). As reported by Mathieu *et al* (2013), PAH degradation are linked to the growth of microorganisms which are stimulated by the use of agricultural wastes.

In addition, Barathi and Vasudevan (2003) reported that the soil microorganisms could be given shelter by these organic substrates and this could improve the soil nutrients and aeration and hence, increase microbial activities and degradation of the organic pollutants like PAH.

These present results showed that CP and OP could enhance the biodegradation of PAH in the crude contaminated soils but the combined application of these organic wastes in form of mixed peel (MP) exhibited more effective removal of the PAH.

As reported in Figure 4, 300g of the mixed peel (MP) amendment proved to enhance its biodegradability strength more than the other organic wastes amendments. This could be as a result of the increase in the concentration of Nitrogen and Phosphorus in the 300g of the mixed peel which enhances the stimulation of the indigenous microorganisms.

IV. Conclusion

The potentials of organic wastes in the enhancement of bioremediation of crude oil contaminated soil were carried out and the results showed that these organic wastes in single (OP and CP) and their combined forms (MP) showed significant reduction in TPH and PAH levels and the mixture of these organic wastes (MP) showed a more significant reduction in TPH and PAH concentrations.

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