Effect of Oxygen Diffusion on Physicochemical Properties of Petroleum Contaminated Sandy Soil

Umeda, U., Puyate Y. T., Dagde, K. K. & Ehirim, E.O.
Department of Chemical/ Petrochemical Engineering
Rivers State University, Port Harcourt,
Nigeria.
umexil@yahoo.com

Abstract

Crude oil pollution of the soils in Niger Delta region of Nigeria is common due to oil exploration, exploitation and transportation. Crude oil spillage on soils is an environmental problem which has to be prevented or controlled in order to achieve the basic need of soils for plants and animals usage and benefits. The objective of this study was to examine the effect of oxygen diffusion on the physicochemical properties of petroleum contaminated sandy soils at 100cm depth with the availability of indigenous microorganism in the impacted soils. The soil samples were subjected to soil analysis after pollution with Bonny light crude oil. The purpose of the pollution of the soil samples was to simulate conditions of major crude oil spill. Oxygen was diffused through the impacted soils in reactor C. Analysis of physicochemical properties of the sandy soils includes pH, Electrical conductivity, Total organic carbon, Total Nitrogen, Moisture content, Phosphorous and Total petroleum hydrocarbon at two weeks interval for six weeks using standard methods. The analysis indicated that bioremediation was faster in the soils at the depth of 100cm with oxygen diffusion. The study showed 71% reduction in TPH concentration, pH increase from 5.48 to 7.28, Electrical conductivity increased from 98.6 to182.0μş, Moisture content decreased from 12 to 10%, Total organic carbon reduced from 2.210 to 1.693%, Total Nitrogen decreased from 0.191 to 0.082% and Phosphorous reduced from 0.84 to 0.15mg/kg at the end of the study. Physicochemical properties of the treated Sandy soils showed similar soil characteristics as compared with the initial conditions of the soil before contamination with Bonny light crude oil, which indicated a positive results of the role of oxygen diffusion on bioremediation of petroleum contaminated Sandy soil at 100cm depth.

Keywords: Hydrocarbon; Oxygen diffusion; Pollution; Sandy soils.

Introduction

Bioremediation is a process that involves the use of microorganism to degrade harmful substances, and is one of the best technologies for the treatment of soil and groundwater contaminants (Jelena *et al.,* 2009). Bioremediation is a modern technology because natural potential of microorganisms is applied for reduction of concentration and toxicity of numerous chemical substances, such as petroleum derivatives, aliphatic and aromatic hydrocarbons, industrial solvents, pesticides and metals (Jelena *et al.,* 2009). Crude oil bioremediation in soil is enhanced by stimulation of indigenous microbial population, through introduction of nutrients and oxygen into the soil (Bento et al., 2005). Nutrients are easily assimilated by soil microorganisms in soil pollution with crude oil, thus reducing the nutrient reserves (Rahman *et al.,* 2002). The addition of inorganic or organic nitrogen-rich nutrients (bio-stimulation) is an effective approach to enhance bioremediation processes (Margesin *et al.,* 2001). The contamination of soils by crude oil and petroleum products have become a serious problem that represents global concern for the potential consequences on

ecosystem and human health (Onwurah *et al.,* 2007). The amount of hazards imposed on the natural environment depends on the surface of the area contaminated by the petroleum products, their chemical composition, and the depth at which pollutants occur (Wolicka *et al.,* 2009). Hydrocarbons from crude oil are substrates for microorganisms, hence, when an accidental oil spill occurs, the number of hydrocarbon degrading microorganisms in the ecosystem increases. The speed and efficiency of bioremediation of a soil contaminated with petroleum and petroleum products depend on the number of hydrocarbon-degrading microorganisms in the soil. The most important factors for population growth are temperature, oxygen, pH, content of nitrogen and phosphorus, hydrocarbon class and their effective concentration. Also, the degree and rate of biodegradation are influenced by the type of soil in which the process occurs (Van hmm *et al.,* 2003).

Materials and Methods
Soil Sampling
The Soil samples for this study were collected from Oshie Oil Field in Ahoada West Local Government Area of Rivers state. It was collected using hand soil auger. This location was considered because of frequent crude oil spill occurrence due to high rate of illegal refining activities. The soil samples collected were bulked together and put in a well labelled Polyethylene bags and glass bottles, sealed with aluminum foil, for Total Petroleum Hydrocarbon (TPH) analysis.

Experimental Design for Oxygen Diffusion through Petroleum Contaminated Sandy Soil.
Fifty kilogram(50kg) of soil samples were weighed into three bowel and contaminated with 5000mls (5litre) of Bonny light crude oil each , measured using 1000mls measuring cylinder five times by using standard pollution volume of 100mls of crude oil to 1kg of soil. This was done after collection of soil samples for determination of physiochemical properties. The objective was to simulate condition of major crude oil spill. Each of the mixture was properly mixed to ensure uniform concentration of the crude oil in the soil samples. It was left for three days to settle without any disturbance. The treatment of the soil commenced after three days by application and mixing of 340g of 27:13:13 NPK fertilizer with the soil samples B and C, while sample A had no Fertilizer application because it served as control unit or sample for the process. The three treated sandy soil samples were transferred into three separate batch reactors labelled A, B, and C, of 1 meter depth and $4 \times 10^{-2} m^3$ volume, with application of 200mls of water every two days for 6 weeks to effect quick compartment and settlement of the soil samples. Soils in reactor C had a PVC pipe which transferred oxygen gas from the gas cylinder into soils in reactor C. The PVC pipe had perforation of 4.2mm in diameter of four perforations per 10 cm intervals along the length of the Pipe. The purpose of the perforation was to allow the transfer of oxygen gas from the PVC pipe into the soil samples. A gas flow meter was fixed on the flow line into the reactors to measure the volume of oxygen transferred into the system. $14m^3$ of oxygen was delivered into soils in reactor C at an interval of 10minutes for 48hours and left to diffuse into the soil for a period of 42 days. (Umeda *et al.,* 2017). Soil samples were collected from the reactors at intervals of 2, 4 and 6 weeks for physicochemical properties and hydrocarbon utilizing bacteria analysis. Standard deviation (SD), using the STDEV function in Microsoft® Excel 2013, simple percentages and ANOVA were used to analyze the data.

Determination of Physicochemical Properties
The soil samples were characterized for particle size and classification, pH, electrical conductivity, total petroleum hydrocarbon, moisture content, total organic content, total

nitrogen, and phosphorous Physicochemical properties were determined before and after contamination with crude oil using standard methods adopted from relevant literatures. Particle size analysis was carried out before contamination of the soil with crude oil by hydrometer method using sodium hexametaphosphate as the dispersing agent (Bouyoucos, 1962). Soil type classification was obtained, using the United State Department of Agriculture (USDA, 1987) soil textural classification scheme using TAL$^®$ for Windows software., The pH level of the soil samples were determined in the laboratory using Hanna HI 2211 pH/ORP meter according to ASTM (1999) method D4972. The pH was determined by dipping the electrode into a 1:25 soil: water suspension that was stirred and allowed to equilibrate for one hour. Electrical conductivity of the soil samples were measured using, Hanna EC 214 conductivity meter. Total organic carbon was determined using wet combustion method as reported by Ayotamuno *et al.* (2006). Soil Moisture Content was obtained by application of APHA (1998) standard as described in Ayotamuno *et al.* (2011). Total petroleum hydrocarbon was analyzed by using Gas Chromatograph-Flame Ionization Detector (GC-FID) Model, HP 5890 Series II, U.S.A., after extraction of hydrocarbon content by applying ASTM (1999) method D3921 as reported by Umeda *et al*. (2017). Total nitrogen was determined by using APHA (1998) method, 4500-NO$_3$ B. Phosphorous was analyzed by using APHA (1998) method, 4500-PO$_4$$^{3-}$

Results and Discussion

Table1 shows the initial conditions of the soil before pollution with crude oil. The results of particle size distribution and soil classification showed that the soil was sandy soil with 88.4% of sand, 2.94% silt and 8.68% clay. The sandy soil has bulk density of 1.269g/cm^3 and porosity of 0.521.

Table 1: Physicochemical characteristics of Sandy soil before pollution. (Results represent mean ± standard deviation of three replicates)

Sand (%)	Silt (%)	Clay (%)	pH	EC (µş)	TPH (PPM)	TOC (%)	N (%)	P (%)	MC (%)
88.4	2.94	8.66	6.25 ±0.18	133 ±2	5.95 ±0.22	1.599 ±0.13	0.138 ±0.002	0.40 ±0.06	30 ±2

Bulk density =1.269g/cm^3, Porosity = 0.521

Table 2: Physicochemical characteristics of Sandy soil 3days after pollution, prior to remediation. (Results represent mean ± standard deviation of three replicates)

pH	EC (µş)	TPH (PPM)	Moisture content (%)	TOC (%)	Nitrogen (%)	Phosphorus (%)	Oxygen Conc. (mg/l)
5.48 ±0.19	98.6 ±1	1136.79 ±0.23	12 ±2	2.210 ± 0.002	0.191 ±0.002	0.84 ± 0.05	
A							1.15 ± 1
B							1.22 ± 3
C							2.5 ± 3

Table 2, shows the conditions of the sandy soil, three day after contamination with crude oil prior to remediation. Comparison of Table 1 and 2, indicated that, the TPH value increased from 5 .95ppm – 1136.79ppm. The   pH value decreased from 6.25 – 5.48, Total organic carbon (TOC) increased from 1.599% to 2.210%. Total nitrogen increased from 0.138% - 0.191%. Phosphorus increased from 0.40% -0.84% and the Electrical Conductivity (EC) decreased from 133-98.6µş. The change in the initial conditions of the soil properties were

due to Pollutants injected into the soils from the Crude oil pollution (Umeda et al., 2017)

Variation of pH With Time

Figure 1 shows the variation of pH with time. The pH values for sandy soil within the period of remediation increased from 5.05 -5.12 within second and fourth weeks, but decreased to 5.08 at the end of sixth week of remediation for soils in reactor A.
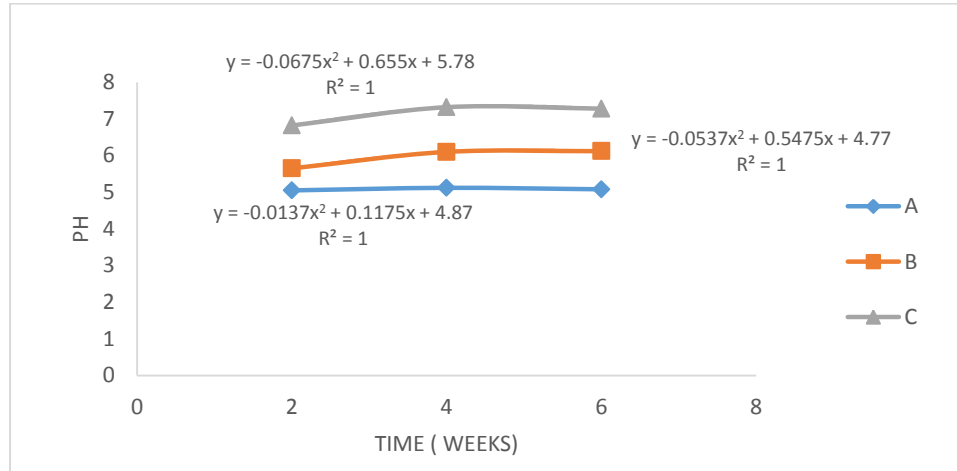

Figure 1 pH chart with equations:
$y = -0.0675x^2 + 0.655x + 5.78$, $R^2 = 1$
$y = -0.0537x^2 + 0.5475x + 4.77$, $R^2 = 1$
$y = -0.0137x^2 + 0.1175x + 4.87$, $R^2 = 1$

Figure 1: Variation of pH With Time, Sandy soil

Soil in reactor B showed an increase from 5.65-6.12 for the six week period of remediation and Soil in reactor C indicated an increase from 6.82 – 7.32 in the second and fourth week, but reduced to 7.28 at the end of the sixth week. This showed that, there was fluctuation in the values of pH with time for soils in reactor A, and C but soils in reactor B noticed an increase in pH with time. The fluctuation in pH values of soil in reactor A and C are because of the release of Metabolites by microorganisms during the bioremediation process (Obiakalaije et al., *2015*). The pH values for soils in reactor C, falls within the range for a better bioremediation exercise than soils in reactor A and B (Ayotamuno et al., *2006*). Statistical evaluation showed that, soils in reactor C has significant difference at $P<0.05$, which was greater than soils in reactor B. This may be attributed to sufficient Oxygen availability in the soils in reactor C.

Variation of Electrical conductivity with time

Figure 2, shows the variation of Electrical conductivity in soil A, B and C with Time. The Electrical Conductivity (EC) was between the ranges of 125.0 – 128.9μş for soils in reactor A.
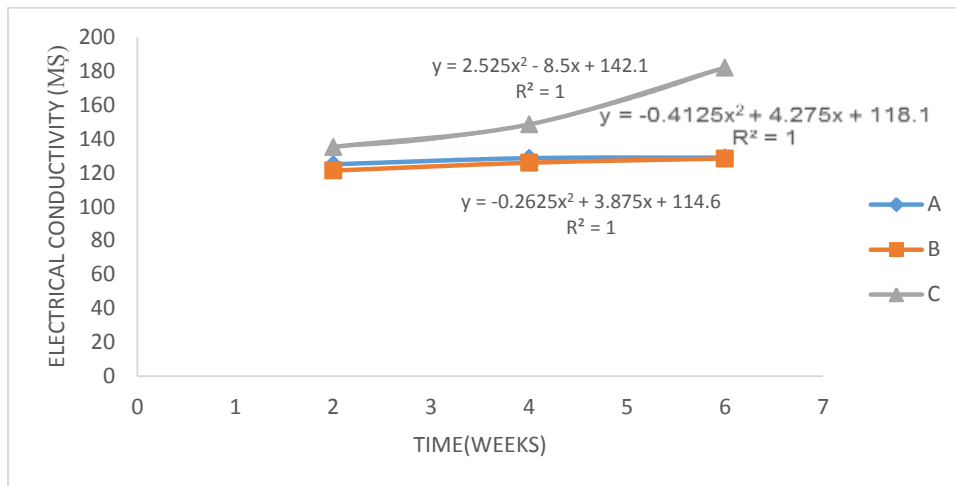
Figure 2: Variation of Electrical conductivity with time, Sandy soil

The soils in reactor B had 121.3-128.4µş while the soil in reactor C had 135.2-182.0µş.The Electrical conductivity increases with time for soils in the three reactors but the soil in reactor C recorded the highest value of electrical conductivity. This is expected because Electrical conductivity is used to measure the salinity of the soil. The applied fertilizer is a salt, so the treated options are expected to have higher level of electrical conductivity (Ayotamino *et al.,* 2009). There was no significant difference with time at $P<0.05$ for soil in reactor B and C respectively.

Variation of Total Petroleum Hydrocarbon with time
Figure 3, shows the variation of Total Petroleum Hydrocarbon (TPH) in soils in reactor A, B and C with time. Total Petroleum Hydrocarbon (TPH) level decreased from 1136.79 - 1056.74ppm for soil in reactor A, while soils in reactor B recorded 1136.79 – 536.3ppm, and 1136.79 – 325.00ppm was recorded for soils in reactor C within the study period of six weeks.
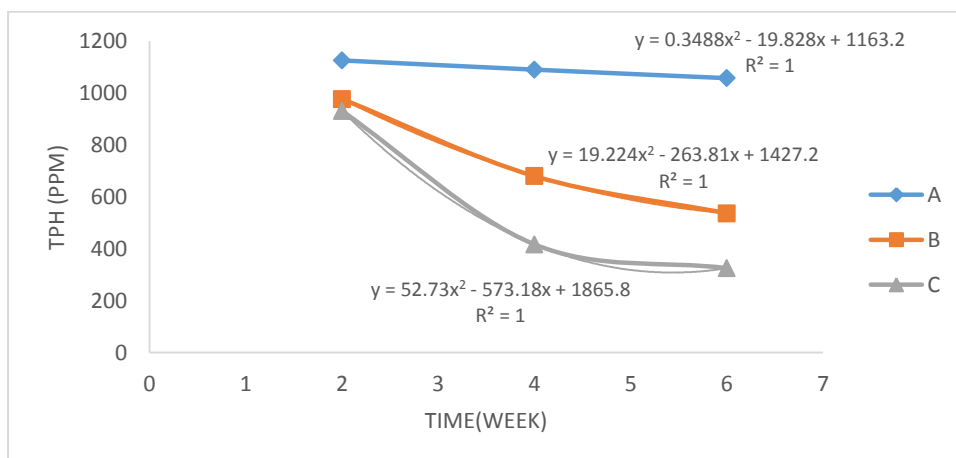

Figure 3: Variation of Total Petroleum Hydrocarbon with time, Sandy soil

The reduction of hydrocarbon level in the soils indicates that, the indigenous bacterial communities in the hydrocarbon impacted soil have the ability to degrade petroleum hydrocarbon since they could use it as source of carbon and energy (Obiakalaije *et al,* 2015). Soils in reactor A recorded TPH reduction of 7%, soils in reactor B, had 53% and soils in reactor C registered 71% at the end of six week. The higher rate of percentage degradation in

reactor C, may be attributed to higher growth in population of micro -organism because of the presence of sufficient Oxygen concentration in the system. The effect of time was highly significant at $P<0.05$ in reactor C.

Variation of Moisture Content with time

The moisture content reduced in sandy soil after contamination with crude oil. This was because, the contaminated soil water droplet adhered to the hydrophobic layers formed and these prevented wetting of the inner part of the soil aggregates (Ayotamuno *et al.,* 2006).
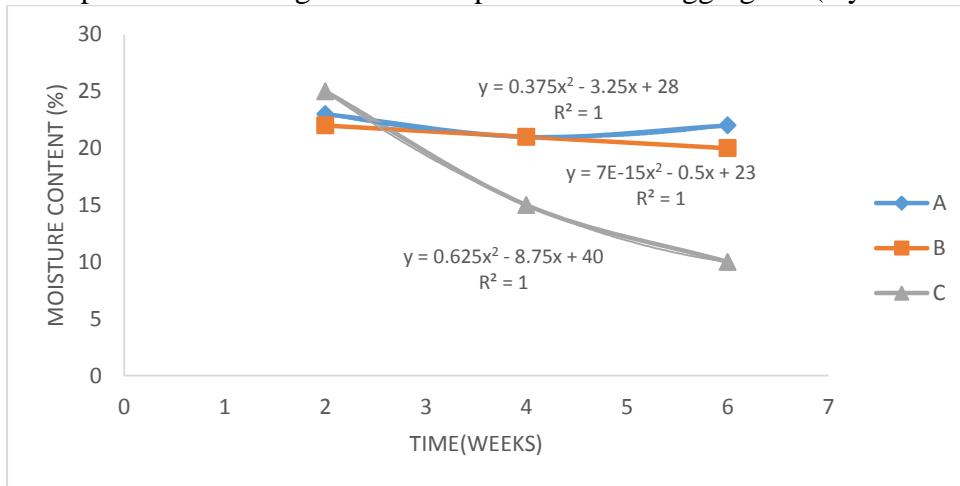
Figure with y-axis "MOISTURE CONTENT (%)" from 0 to 30, x-axis "TIME(WEEKS)" from 0 to 7. Equations shown: $y = 0.375x^2 - 3.25x + 28$, $R^2 = 1$; $y = 7E\text{-}15x^2 - 0.5x + 23$, $R^2 = 1$; $y = 0.625x^2 - 8.75x + 40$, $R^2 = 1$. Legend: A, B, C.

Figure 4: Variation of Moisture Content with time, Sandy soil

In Figure.4, the moisture content in soils in reactor A, decreased within the second and fourth week of remediation, but later increased as the process progressed to the sixth week. Soils in reactor B and C decreased with time for the entire remediation period. These were as a result of evaporation and continuous drying of soils in reactor B and C which maintained an optimum moisture level for biodegradation process (Ayotamuno *et al.,* 2006). However, soils in reactor C experienced more appreciable reduction in moisture content. This may be as a result of biochemical reactions aroused from faster bioremediation of the petroleum contaminated soils due to diffusion of oxygen through the impacted Soils. Statistical evaluation showed that there was no significant different in soils in reactor B and C.

Variation of Total Organic Carbon with time

Figure 5 shows the variation of Total Organic Carbon (TOC) for soils in reactor A.B and C with time. Total Organic Carbon (TOC) decreased with time in soils in the three reactors, but soils in reactor C showed more appreciable decrease.
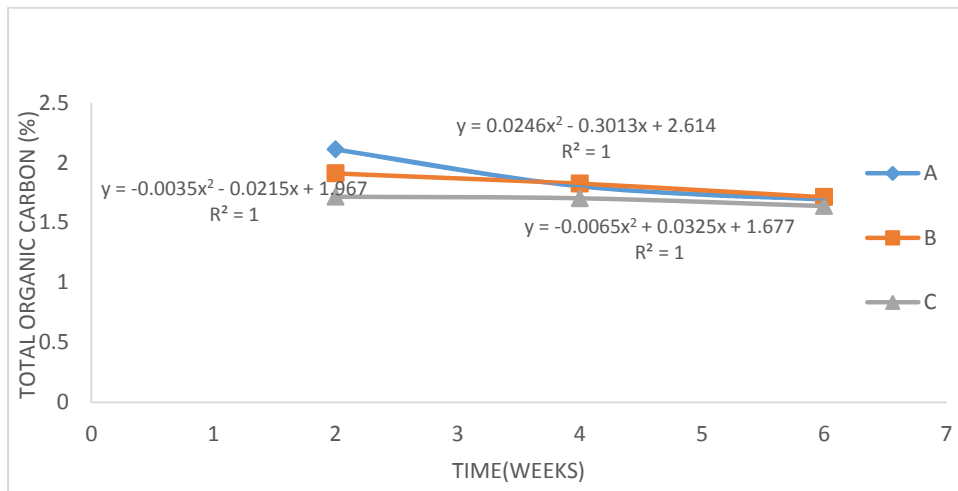
Figure 5: Variation of Total Organic Carbon with time, Sandy soils.

This may be as a result of the effect of oxygen on the micro-organism by increasing its population which resulted in the use of the total organic carbon for energy. The statistical evaluation showed that, there was no significant difference in the three samples in the reactors.

Variation of Total Nitrogen with time

Figure 6 shows the variation of Total Nitrogen for soils in reactor A, B and C with Time. Total Nitrogen increased with time in soils in reactor A and B but decreased with time in soils in reactor C. This implied that, there may be an increase in microbial population because of the presence of oxygen in reactor C which provided increase in population of micro-organism to utilize the nitrate during the bioremediation process.
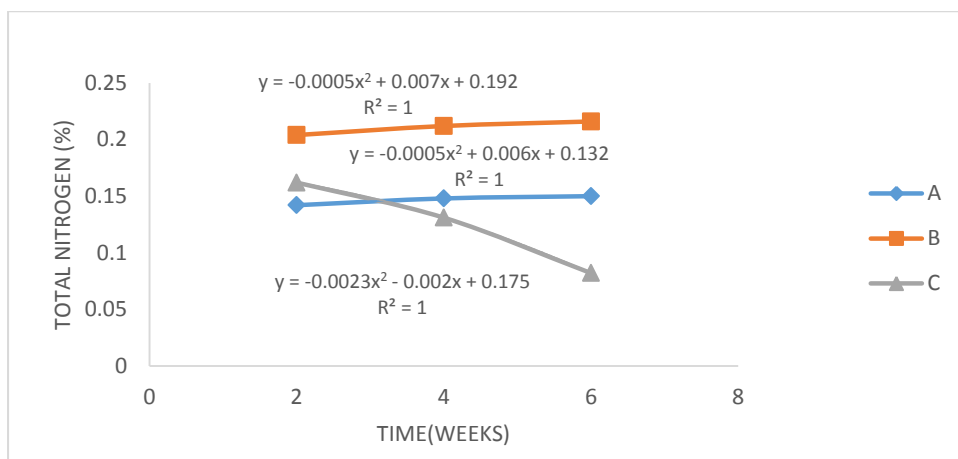

Figure 6: Variation of Total Nitrogen with time, Sandy soil

There was significant different in soils in reactor B as $P<0.05$, but no significant different in soils in reactor C as $P>0.05$. This may confirm the fact that, nitrate was used by the micro-organism in soils in reactor C, which reduced its concentration and made it to have no significant different when compared with reactor A.

Variation of Phosphorous with time

Figure 4.7 shows the variation of Phosphorous for soils in reactor A, B and C with Time. Phosphate increased with time in soils in reactor A and B, but decreased with time in soils in
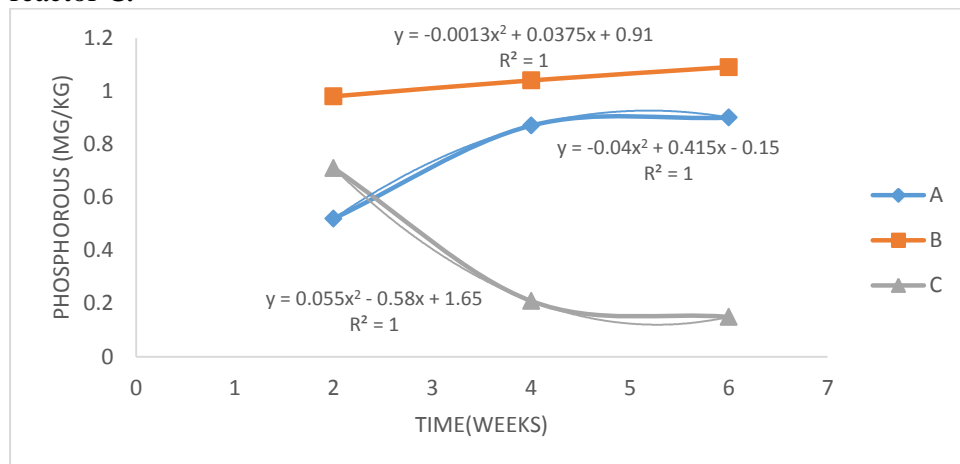
reactor C.

Figure 7: Variation of Phosphorous with time, Sandy soil

This showed that the phosphate was used in soils in reactor C by the microorganism as nutrient during bio degradation of hydrocarbon (Ayotamuno et al., 2006). Statistical evaluation showed that both soils in reactor B and C had significant difference of $P<0.05$, but the soil in reactor C had greater significant difference of $P\leq0.05$ as compared to soils in reactor B.

Conclusion
Diffusion of oxygen through petroleum contaminated Sandy soils enhanced the physicochemical properties of Sandy soil at 100cm depth. The results revealed that, the physicochemical properties of the treated Sandy soils have similar soil characteristics compared with initial or natural properties of the soils before contamination, which indicated that diffusion of oxygen through the impacted Sandy soil was effective and a good approach for bioremediation of petroleum contaminated Sandy soil at 100cm depth in Niger Delta region of Nigeria.

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