

Effect of Oxygen Diffusion on Physicochemical Parameters of Petroleum Contaminated Clay Soil

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ABSTRACT: This study is aimed at investigating the effect of oxygen diffusion on physicochemical parameters of petroleum contaminated clay soils at 100cm depth in the presence of indigenous microorganism. Soil analysis was carried out on the impacted clay soils after polluting the soils with crude oil. The purpose of pollution of the soil was to simulate condition of major crude oil spill. Oxygen was diffused through the soils. Analysis of physicochemical properties of the clay soils (pH, Electrical conductivity, Total organic content, Nitrogen, Moisture content, Phosphorous and Total petroleum hydrocarbon) at two weeks interval for six weeks using standard methods of laboratory analysis revealed that bioremediation occurred faster in the soils at the depth of 100cm with oxygen diffusion through the impacted soils. The study showed 85% reduction in TPH concentration, pH increase from 6.42 to 6.95, Electrical conductivity decreased from 146.3 to 113.8 μS , Moisture content decreased from 31 to 22%, Total organic content reduced from 2.730 to 1.213%, Nitrogen decreased from 0.236 to 0.006% and Phosphorous reduced from 1.41 to 0.85 mg/kg at the end of the study period. Final analysis demonstrated that, physicochemical properties of the treated clay soils have close soil characteristics compared with initial conditions of the soil before contamination with crude oil, which indicated that oxygen diffusion is an effective method for bioremediation of petroleum contaminated clay soil at 100cm depth.

KEYWORDS: Bioremediation, Oxygen diffusion, Petroleum contaminated soil and Pollution

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I. INTRODUCTION

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). The technologies used for soil remediation are mechanical, burying, evaporation, dispersion, and washing. These technologies are very expensive and can lead to incomplete decomposition of hydrocarbon contaminants (Das and Chandra, 2010). In oil pollution, nutrients are rapidly assimilated by soil microorganisms thus depleting 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). Bioremediation is a process that utilizes the ability of microorganism to degrade toxic waste, and is emerging as a promising technology for the treatment of soil and groundwater contamination. Bioremediation is considered a modern technology because natural ability of microorganisms is employed for the reduction of the concentration and toxicity of various chemical substances, such as petroleum derivatives, aliphatic and aromatic hydrocarbons, industrial solvents, pesticides and metals (Jelena et al., 2009). Crude oil bioremediation in soil can be promoted by stimulation of the indigenous microbial population, by introducing nutrients and oxygen into the soil through inoculation of an enriched microbial consortium into soil (Bento et al., 2005). 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 depends 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).

II. MATERIALS AND METHODS.

Soil Sampling.

The Soil samples for this study were collected from Kolo creek in Bayelsa State, Oshie oil field, Ahoada west and Abua odua in Rivers state. It was collected using hand soil auger. 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 Of Oxygen Diffusion Rate In Clay Soil.

Fifty kilogram(50kg) of soil samples were weighed into three bowl 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 physicochemical 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. Thereafter, the three soil sample were transferred into three separate batch reactors labelled A, B, and C, of 1 meter depth and $4 \times 10^{-2} \text{m}^3$ 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 0.42mm in diameter of four perforation 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. 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 determined before contamination of the soil with crude oil by hydrometer method using sodium hexametaphosphate as the dispersing agent (Ayotamuno et al.,2011). 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 Risdonet al.(2008). Total nitrogen was determined by using APHA (1998) method, 4500-NO₃ B. Phosphorous was analyzed by using APHA (1998) method, 4500-PO₄³⁻.

III. RESULTS AND DISCUSSION

The results in Table 1 shows the initial conditions of the soil before contamination with crude oil. The soil has bulk density, 1.424g/cm^3 and porosity, 0.463

Table 1. Physicochemical characteristics of Clay soil before contamination (Result represent mean \pm standard deviation of three replicates)

Sand (%)	Silt (%)	Clay (%)	MC (% by mass)	pH	EC (μs)	TPH (PPM)	TOC (%)	TN (%)	P (mg/kg)
30	10	60	42 ± 2	6.25 ± 1	112.0 ± 2	3.70 ± 0.02	1.314 ± 0.097	0.142 ± 0.001	0.58 ± 0.02

Bulk density = 1.424g/cm³, Porosity = 0.463

The results of particle size distribution and soil classification showed that the soil was clay soil with sand 30%, silt 10% and clay 60%. Results of initial conditions of the soil showed Moisture Content (MC) 42%, Soil acidity (pH) 6.25, Electrical Conductivity (EC) 112.0 μs , Total Petroleum Hydrocarbon(TPH) 3.70(ppm), Total Organic Carbon(TOC) 1.314(%), Total Nitrogen (TN) 0.142(%) and Phosphorous (P) 0.58 (mg/kg).

Table 2 shows the conditions of the clay soil after three days of contamination with crude oil.

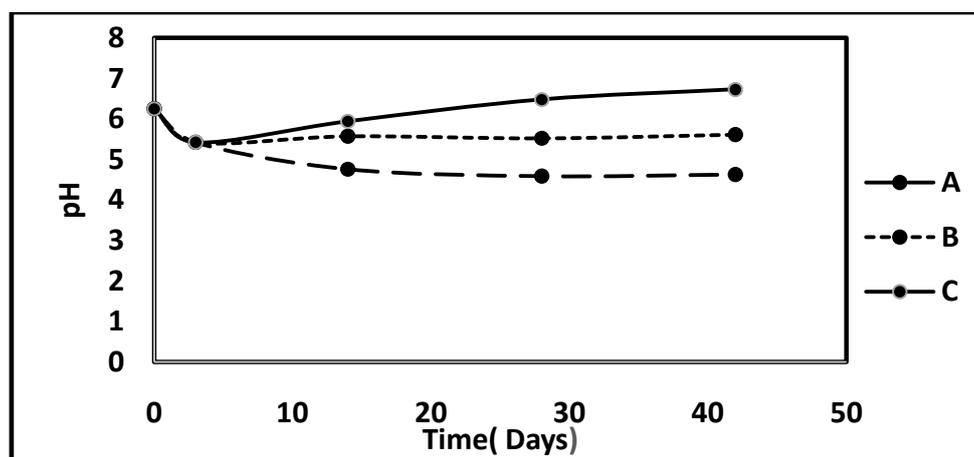
Table 2. Physicochemical characteristics of Clay soil, 3days after contamination, prior to remediation (Result represent mean \pm standard deviation of three replicates)

MC(% by mass)	pH	EC (μs)	TPH (PPM)	TOC (%)	TN (%)	P (mg/kg)	Oxygen Conc.(mg/l)
31 ± 1	6.42 ± 0.14	146.3 ± 2	1446.75 ± 0.88	2.730 ± 0.003	0.236 ± 0.002	1.41 ± 0.73	
A							1.45 ± 2
B							1.62 ± 0.02
C							2.50 ± 4

It was observed that the physicochemical properties of the soil increased in concentration with time, except moisture content that decreased. The pollution of the soils with crude oil caused the changes in the physicochemical properties

Variation Of Ph With Time

Figure 1, showed the variation of pH with time. The pH values in the soils in reactor A, B and C decreased after contamination with crude oil. These were as a result of introduction of contaminants into the soils by the crude oil pollution. Also, the Figure showed a continuous decrease in pH value in soils in reactor A and B with Time while soils in reactor C showed an increase in pH value with time for the entire period of bioremediation.

**Figure 1: Variation Of Ph With Time.**

The increase in acidity level in soils in reactor A and B were due to introduction of metabolites by microorganism as a result of limited oxygen which promoted bioremediation of petroleum contaminated soils by anaerobic conditions. The decrease in acidity level in reactor C were due to the process of complete aerobic conditions experienced by the microorganism as explained by Ekperusi & Aigbdion (2015). This arose as a result of availability of sufficient oxygen due to oxygen diffusion which enhanced effective bioremediation of petroleum contaminated soils by aerobic conditions.

Variation Of Electrical Conductivity With Time

The initial concentration of Electrical Conductivity (EC) in the soil increased after contamination with Crude oil. This is due to introduction of trace ionic elements or metals into the soils from the crude oil thereby changed the initial conditions of the Electrical Conductivity of the soil (Obiri &Nwanbete, 2001). Electrical Conductivity (EC) is a measure of the salinity of the soil.The applied Fertilizer (NPK 27:13:13) is a salt, so the treated options (soils in reactors B and C) are expected to have higher level of Electrical Conductivity due to the application of NPK 27:13:13 as nutrients. (Ayotamuno et al., 2009).

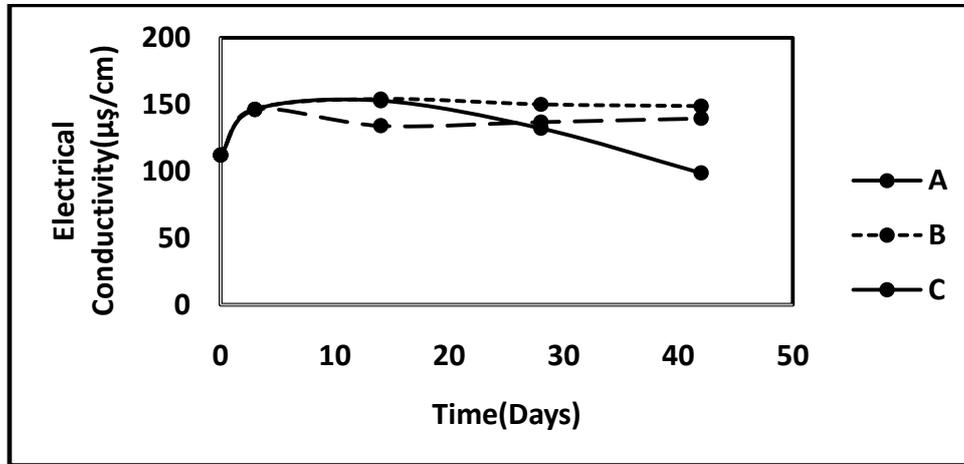


Figure 2: Variation Of Electrical Conductivity With Time.

Figure 2, shows an increase in the level of electrical conductivity of the clay soils in reactor A, B but with a decrease in soils in reactor C. This may be as a result of reduction in the salinity of the soils due to insufficient nutrient in soils in reactor A since it did not receive NPK as nutrient to the soils while the increase in soils in reactor B where as a result of limited microorganism to utilize the nutrients due to insufficient oxygen to promote microbial growth.The decrease in concentration of Electrical Conductivity in soils in reactor C may be as a result of the utilization of NPK as nutrient by the microorganisms in the soils due to sufficient oxygen concentration as a result of oxygen diffusion thereby increasing microbial population in the soil which provided fast usage of the nutrients which led to a depletion in the level of electrical conductivity in the soils.

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. The graphs below indicated that the initial concentration of Total Petroleum Hydrocarbon (TPH) in the soil increased after pollution with Crude oil. This is because of the introduction of carbon compounds into the soils by pollution with crude oil (Obiakalaje et al., 2015). Also, the graphs revealed that, there were decrease in concentration of hydrocarbons in the soil samples with Time after three days of contamination of the soil with crude oil for the entire period of bioremediation.Total Petroleum Hydrocarbon in soils in reactor A reduced from 1446.75 to 1415.96 ppm, while TPH in soil in reactor B reduced from 1446.75 to 488.20ppm. Soil in reactor C reduced from 1446.75 to 219.20ppm at the end of the six weeks of remediation.

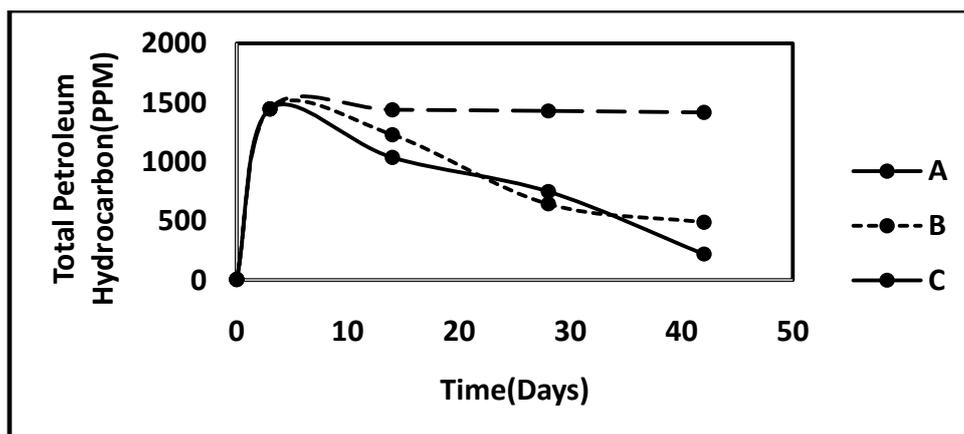


Figure 3. Variation Of Total Petroleum Hydrocarbon With Time

Results showed that at the end of the remediation exercise, the soils in reactor A, had 2.1% reduction in TPH concentration, those in reactor B recorded 66% reduction and the soils in reactor C reduced by 85%. The decrease in Total Petroleum Hydrocarbon concentration in the soils showed that, the indigenous bacterial in the impacted soils have the ability to degrade petroleum hydrocarbon (Obiakalaje et al., 2015). The highest percentage degradation of Total Petroleum Hydrocarbon noticed in soils in reactor C in the soil samples may be attributed to an increase in population of microorganism because of availability of sufficient oxygen concentration in the soils at 100cm depth as a result of oxygen diffusion, thereby using the carbon for energy.

Variation Of Moisture Content With Time

Figures 4, show the variation of Moisture Content with Time in soils in reactor A, B and C for Clay soils. Figures 4 revealed that the Moisture Content reduced in the soils after contamination with crude oil. This was because, the contaminated soil water droplet adhered to the hydrophobic layers formed and this prevented the wetting of the inner part of the soil aggregates (Ayotamuno et al., 2006).

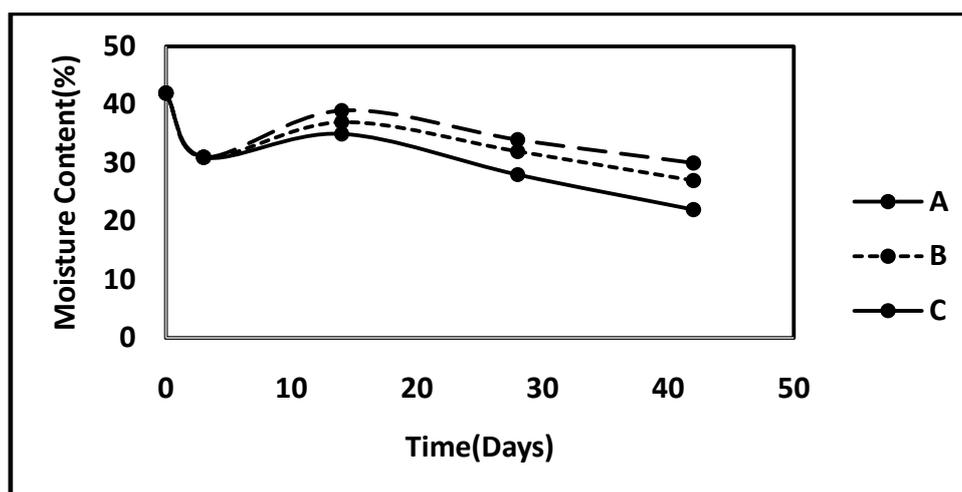


Figure 4: Variation Of Moisture Content With Time.

The soil moisture content increased within the second week of bioremediation process but later decreased as bioremediation process progressed to the sixth week. These were as a result of evaporation and continuous drying of the soils which maintained an optimum moisture level for biodegradation process (Ayotamuno et al., 2006). However, clay soils in reactor C experienced more appreciable reduction in moisture content. This may be as a result of biochemical reactions which arose from fast bioremediation of petroleum contaminated soils at 100cm depth due to availability of oxygen for the microorganisms through oxygen diffusion in the impacted soils.

Variation Of Total Organic Carbon With Time

Figures 5 shows the variation of Total Organic Carbon with time in soils in reactor A, B and C for Clay soils. Also, it shows an increase in concentration of Total Organic Carbon after pollution with crude oil. This implied that, the Crude oil contamination increased the organic contents of the soils (Ayotamuno et al., 2006).

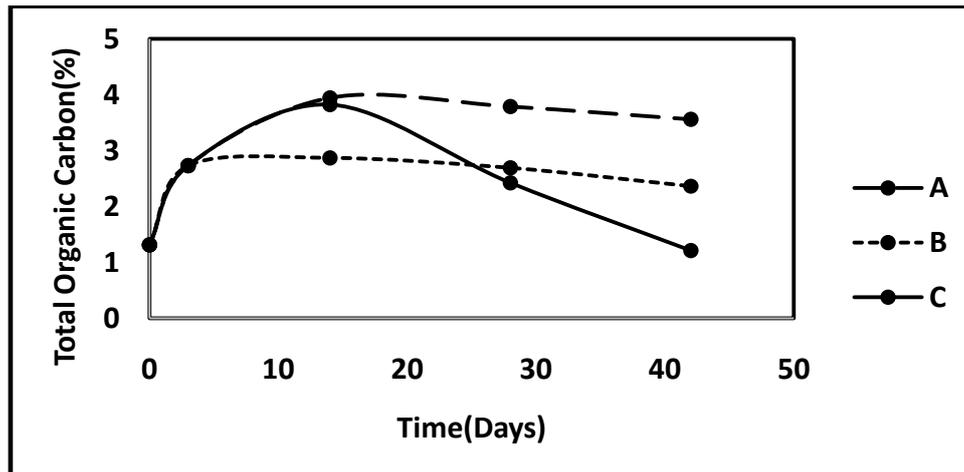


Figure 5: Variation Of Total Organic Carbon With Time.

Furthermore, it indicated that the soils in reactor A and B showed a slight decrease in concentration of Total Organic Carbon, but the soils in reactor C showed rapid decrease in concentration of Total Organic Carbon compared to soils in reactor A and B. The rapid and appreciable decrease in Total Organic Carbon in reactor C unlike A and B may be attributed to availability of sufficient oxygen at 100cm depth in the soil due to oxygen diffusion which enhanced the increase in population of microorganism which utilized more organic carbon for energy during biodegradation of hydrocarbons.

Variation Of Total Nitrogen With Time

Figures 6, shows the variation of Total Nitrogen with time in soils in reactors A, B and C for Clay soils. The graph indicated that soils in reactor A had aslight decrease in concentration of Total Nitrogen after three days before it increased further. This is as a result of depletion in concentration of nitrate in the soil due to crude oil pollution after a certain period of time without any replacement (Ayotamuno et al., 2006). Also, the soils in reactor B showed a constant increase in the concentration of nitrogen in the entire period of bioremediation. This may be attributed to low population of microorganism at 100cm depth to utilize the nitrate added to the soil through the application of NPK as nutrient, due to insufficient oxygen to enhanced microbial growth in the soil at 100cm depth.

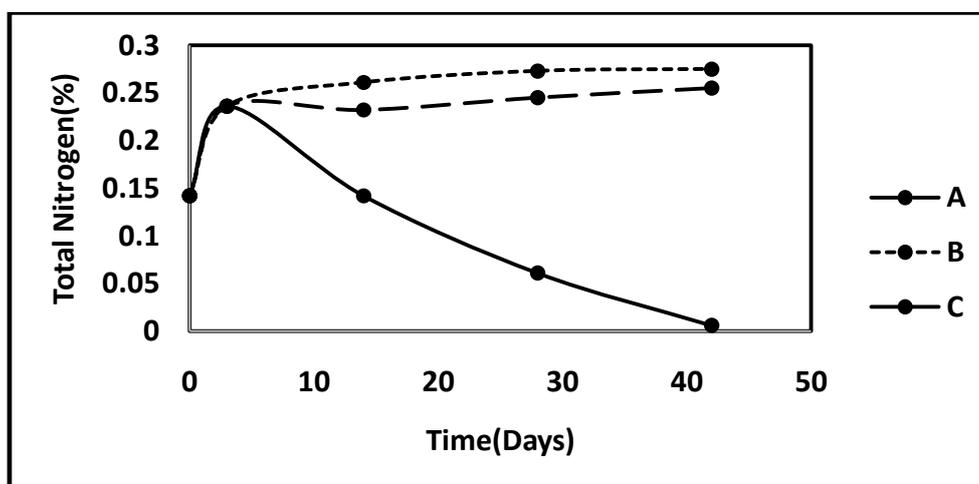


Figure 6: Variation Of Total Nitrogen With Time.

The soils in reactor C experienced a rapid decrease in concentration of Total Nitrogen for the entire bioremediation period. The decrease in concentration of Total Nitrogen in soils in reactor C indicated that the diffusion of oxygen at 100cm depth enhanced the increase in population of indigenous microorganism, hence, the higher demand for nitrate as nutrients by the microbes for biodegradation of hydrocarbons, thereby depleting the concentration of Total Nitrogen in the soils despite the addition of NPK to improve the soil nutrients.

Variation Of Phosphorous With Time

Figure 7 shows the Variation of Phosphorous with time in soils in reactor A, B and C for Clay soils. The soils in reactor A showed a constant increase in concentration of Phosphorous. The soils in reactor B indicated a constant increase in concentration of Phosphorous for the entire bioremediation period but with a rapid decrease in concentration of Phosphorous in soils in reactor C.

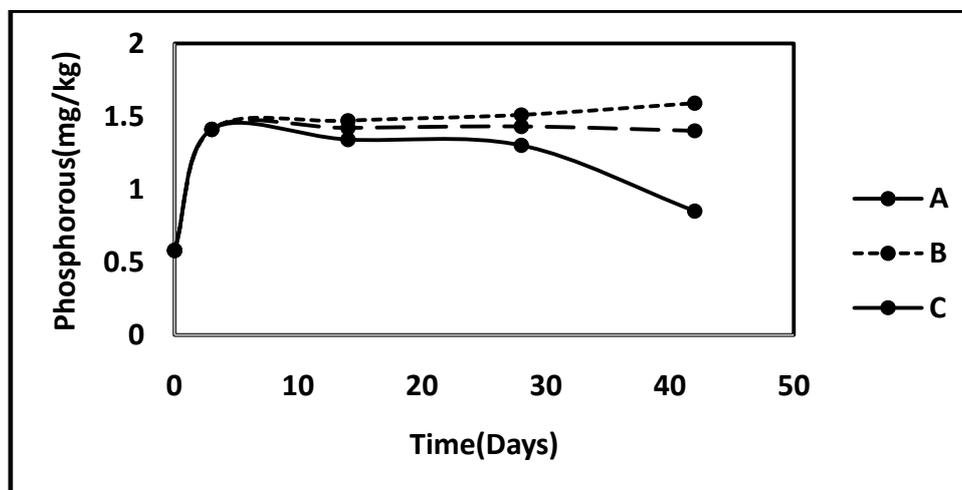


Figure 7: Variation Of Phosphorous With Time.

The increase in concentration of Phosphorous in soils in reactor A and B indicated low population of microorganism to utilize the phosphate at 100cm depth due to insufficient oxygen to enhanced their survival and growth in population, hence there was less demand for Phosphate as nutrient, unlike the soils in reactor C, where rapid decrease in concentrations of phosphate were experienced, because of high demand for phosphate by microorganism as nutrient during biodegradation of hydrocarbon. The high population of microorganism at 100cm depth were facilitated by oxygen diffusion which provided sufficient oxygen to enhanced increase in microbial population to degrade hydrocarbon content.

IV. CONCLUSION.

In line with the results obtained from this study, Oxygen diffusion through petroleum contaminated clay soils enhanced bioremediation of petroleum contaminated soils at 100cm depth. It is an effective method for bioremediation of petroleum contaminated clay soils in the Niger Delta region of Nigeria.

REFERENCES

- [1]. American Society for Testing and Materials (ASTM) (1999). Water (II). Volume 11.02. 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, 19428 – 2959.
- [2]. American Public-Health Association (APHA) (1998). Standard Methods for the Examination of Water and Wastewater (20th ed). Washington DC.
- [3]. Ayotamuno, M.J., Kogbara, R.B. and Agunwamba, J.C. (2006). Bioremediation of a petroleum hydrocarbon polluted agricultural soil at various level of soil tillage in Portharcourt. Nigeria Journal of Technology, 25, 44-51
- [4]. Ayotamuno, M.J., Kogbara, R.B. & Agoro, O.S. (2009). Biostimulation supplemented with phytoremediation in the reclamation of a petroleum contaminated soil. World Journal of Microbial Biotechnology, 25, 1567-1572
- [5]. Ayotamuno, J.M., Okparanma, R.N., and Amadi, F. (2011). Enhanced remediation of oil sludge with saline water. African Journal of Environmental Science and Technology, 5(4). 262-267
- [6]. Bentos, F.M., Carmago, F. A. O., Okeke, B.C. and Frankenberger, W.T. (2005). Comparative bioremediation of soil contaminated with diesel oil by natural attenuation, bio-stimulation and bio-augmentation. Bio-resources Technology, 96, 1049-1055
- [7]. Das, N. and Chandran, P. (2010). Microbial Degradation of Petroleum Hydrocarbon Contaminants: An overview. Biotechnology Research International, 1-3
- [8]. Ekperusi, O.A & Aigbodion, F.I. (2015). Bioremediation of Petroleum hydrocarbon from crude oil contaminated soil with earthworm. *Hyperiodrus africanus*. <http://www.nlm.nih.gov/pmc/article/PMC4624143>. Accessed on 20/05/2017
- [9]. Jelena, M.S., Beskoski, V.P. Ilic, M.V., Ali, S.A.M. (2009). Bioremediation of soil heavy contaminated with crude oil and its products. Composition of the microbial consortium. Journal of the Serbian Chemical Society, 74, 455-460
- [10]. Margesin, R. & Schinner, F. (2001). Biodegradation and bioremediation of hydrocarbons, in extreme environments, Applied Microbial Biotechnology, 56, 650 – 663
- [11]. Obire, O. & Nwanbete, O. (2001). Bioremediation of Refined Petroleum Hydrocarbon in soil. Journal of Applied Science and Environmental Management, 1, 43 – 46
- [12]. Obiakalaje U.M., Makinde O.A. & Amakoroma E.R. (2015). Bioremediation of crude oil polluted soil using Animal waste. International Journal of Environmental Bioremediation and Biodegradation, 3, 79-85
- [13]. Onwurah, I.N.E., Ogugua, V.N., Onyike, N.B., Ochongor, A.E. and Otitoju, O.F. (2007). Crude oil spills in the environment, effects, and some innovative clean up biotechnologies. International Journals of Environmental Research, 1, 307 – 320.

- [14]. Rahman, K.S.M., Thahira-Rahman, J., Lakshamapermamsamy, P., Banat, I. M. (2002). Towards efficient crude oil degradation by a mixed bacterial consortium. *Bio-resources Technology*, 85, 257 – 261.
- [15]. Risdon, G. C., Pollard, S. J. T., Brassington, K. J., McEwan, J. N., Paton, G. I., Sample, K. T., and Coulon, F. (2008). Development of an analytical procedure for weathered hydrocarbon contaminated soil within a UK risk-based framework. *Analytical Chemistry*, 80, 7090-7096.
- [16]. United State Department of Agriculture(USDA)(1987). Soil mechanics level 1, module3. Textural classification study guide
- [17]. Van Hamme, J.D., Singh, A. and Ward, O.P. (2003). Recent advances in petroleum microbiology. *Microbial Molecular Biology Review*, 67, 503-549.
- [18]. Wolicka, D., Suszek, A., Borkowski, A. and Bieleaka, A. (2009). Application of aerobic microorganism in bioremediation in-situ of soil contaminated by petroleum product. *Bio-resources Technology*, 100, 3221-3227.
- [19]. Prakash, M. & Karmegam, N. (2010). Vermistabilization of pressmud using *Perionyx ceylanensis* mich. *Journal of Bioresources Technology*, 10, 8464-8468

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