Transactions on Engineering and Computing Sciences - Vol. 12, No. 3
Publication Date: June 25, 2024
DOI:10.14738/tecs.123.16957.
Douglas, R. K., Lawrence, C. A., & Ebiundu, K. (2024). Pristine Plantain Peels Biochar and Effect of Weathering on Polycyclic Aromatic Hydrocarbon Biodegradation in Crude Oil-Contaminated Soils. Transactions on Engineering and Computing Sciences, 12(3). 64-72.
SERVICES FOR SCIENCE AND EDUCATION

Pristine Plantain Peels Biochar and Effect of Weathering on Polycyclic Aromatic Hydrocarbon Biodegradation in Crude Oil-Contaminated Soils

Douglas, R. K.
Department of Chemical Engineering Niger Delta University,
Wilberforce Island, Nigeria

Lawrence, C. A.
Department of Chemical Engineering Niger Delta University,
Wilberforce Island, Nigeria

Ebiundu, K.
Department of Chemical Engineering Niger Delta University,
Wilberforce Island, Nigeria

ABSTRACT

The current research compared the potential of an agricultural waste-plantain peels derived biochar and weathering for the remediation of polycyclic aromatic hydrocarbons (PAHs) contaminated soil at laboratory scale. PAHs concentrations ranged from 0.245 to 348.04 mg/kg for the control sample (concentrations obtained without amendment after 4 day incubation period). Benzo(a)pyrene had the least concentration, while Chrysene has the highest concentration. Under weathering conditions, the sum concentration of PAHs was observed to be 694.213, 687.892, and 670.866 mg/kg after 30, 60, and 90 days experiment, respectively. More PAHs concentration degradation was observed with the PPB amendment option. That is, with PPB amendment option, the sum concentration of PAHs obtained were 649.743, 634.532, and 550.369 mg/kg after 30, 60, and 90 day experiment, respectively. Furthermore, first-order kinetics was used to determine the kinetics of PAHs degradation, which was applied on both the weathering and the PPB amendment options. With weathering, PAHs degradation rate constant (K) increased with decreasing PAHs concentrations; which shows that PAHs degradation in contaminated soil is slow under the influence of weathering. With PPB amendment option, the K value decreased between K_{30} and K_{60} with decreasing PAHs concentrations, which implies faster degradation of PAHs. However, reverse was the case between K_{60} and K_{90}. This shows slow degradation of PAHs. Results suggest that the PPB option is promising for the restoration and/or reclamation of soil polluted with PAHs.

Keywords: Soil, Hydrocarbons, Weathering, Biochar, Biodegradation, Kinetics

INTRODUCTION

Environmental contamination is currently a critical challenge globally, and a serious threat to human and environment health [1]. According to [2], crude oil exploration and exploitation

activities, accidental spills, sabotage etc, are critical issues accountable for environmental pollution and degradation from petroleum hydrocarbons (PHCs) and its derivatives. Crude oil is a complex mixture-comprising aliphatic and aromatic hydrocarbon compounds, and traces of heterocyclic compounds-comprising sulphur, nitrogen, oxygen; which are acknowledged environmental contaminants [3; 4]. PHC compounds are generally toxic, and impacts negatively on soil's physicochemical properties [5]. PHC induced pollution is a grave environmental problem due its immobilization and consequent buildup nature in the environment [6]; and is severely impacting the ecosystems wellbeing and humans [5; 7]. It was reported that the micro-organisms population in the soil was greatly depends on the level of PHC concentration [8]. Crude oil also contains potentially toxic elements (PTEs) including silver, Ag; titanium, Ti; arsenic, As; nickel, Ni; cobalt, Co; lead, Pb; manganese, Mn; copper, Cu; iron, Fe; zinc, Zn; cadmium, Cd; magnesium, Mg; chromium, Cr; amongst others [9]. Soil contamination by PTEs has attracted substantial ecological concern due to their toxicity and bioaccumulation. Nigeria has been ranked largest natural gas reserve and the second largest oil reserve in Africa. In the Niger Delta region of Nigeria (Ogoni land in Rivers State), [10] reported that crude oil pollution has deeply affected soil, air, and water quality criteria and thus posing a serious threat to both human health and the environment. This is same in the other crude oil producing states, especially, Bayelsa, Delta, Akwa Ibom, and Ondo states in the region. The devastating environmental pollution and degradation and associated impacts in the Niger Delta, Nigeria are primarily due oil theft; oil bunkering; artisanal (illegal) refining of crude oil in Nigeria; technical or operational error; un-serviced oil infrastructure; and hazardous waste management. Thus, there is need for contaminated land management in the region; which is the responsibility of the Environment Unit at the Department of Petroleum Resources (DPR), and the National Oil Spill Detection and Response Agency (NOSDRA). DPR is responsible for managing legacy sites and NOSDRA is responsible for the detection and management of emerging oil spills [11; 12; 13]. However, Nigeria lacks the necessary funds and the expertise to handle these critical issues of environmental pollution and degradation caused by the activities of the oil and gas industries in the Niger Delta region. Therefore, there is need to develop simple, cost-effective, low-carbon, and sustainable means and/ or methods (e.g., bioremediation by agricultural waste) to address the issues of PHCs-contaminated soils and/or land sites in the laboratory first, and later take the laboratory to the field to address this alarming and devastating problem of land pollution and degradation in the region.

Remediation of PHCs-contaminated land sites has become a global concern due to the negative effects of PHCs on the environment (soil, water, and air) and human health. Considerable efforts have been dedicated to developing simple adoptable methods for the remediation of PHCs-contaminated soils and/or land sites. Currently used PHCs-contaminated soil remediation methods include excavation, burning (i.e., physical, chemical approaches); chemical (detergent, surfactant, degreaser), phytoremediation (the use of plants), and biological (bioremediation) [5; 14]. However, there are shortcomings associated with existing remediation techniques. For instance, thermal desorption is costly and prone to secondary pollution [15].

Contaminated soil remediation by phytoremediation is the application of plants to remove and/or mitigate contaminants in the environment [16]. This technique has been proven effective for the remediation of environmental contaminants including petroleum products,

and heavy metals. However, plant for phytoremediation should tolerate both the climatic and soil conditions of the prevailing polluted environment [5]. According to [17], for a plant to be fit for the phytoremediation of contaminated soils, such plant should have the potential to accumulate the extracted contaminant; should be tolerant enough not only to survive in the contaminated environment, but also adsorb contaminants into their shoots; be able to grow rapidly with the capacity to accumulate possible toxins; and be easily harvested and simply disposed.

Bioremediation by the use of agricultural wastes have been reported cost-effective and a simple approach for contaminated soil remediation [18; 19]. Consequently, the current research aims to assess the potential of pristine plantain peels-based biochar (PPB); which might constitutes environment pollution if not properly dispose of for PAHs biodegradation in crude oil-contaminated soil. Furthermore, the specific objective was to compare the biochar induced degradation with the effect of weathering.

MATERIALS AND METHODS

Soil Sample Collection

1kg pristine soil sample was collected from the Niger Delta University, Department of Agricultural and Environmental Engineering Research Farm, Amassoma, Bayelsa State, Nigeria. The sampling site has no history of hydrocarbon pollution. A subsurface soil sample was collected from top 0-20cm layer using a hand trowel and taken with polythene bags to the laboratory. Pristine soil was sieved using 4 mm sieve, and analyzed for hydrocarbon contamination.

Plantain Peel Collection and Biochar Preparation

A bounce of plantain (fresh) was bought from Swali Ultra-Modern Market (SAM), Bayelsa State, Nigeria. The plantains were peeled to obtain the peels. The peels were sliced to smaller pieces and sun dried at ambient condition for 2-3 days. The dried plantain peels were packaged and taken to the Reaction Kinetics laboratory, Department of Chemical Engineering, Niger Delta University, Wilberforce Island, Amassoma, Bayelsa State, Nigeria for the production of plantain peel derived biochar (PPB). The PPB was produced at low-temperature (T = 300^{o}C) at the Niger Delta University Chemical Engineering Laboratory using a furnace.

Experimental Design

Two (n = 2) soil microcosms (labelled A and C) were set up using 2k soil, and spiked with 250ml crude oil. The two soil samples were allowed to equilibrate at laboratory conditions for 4 days. Sample A was amended with 500g PPB, while Sample C was kept as a control (i.e., no amendment was added to it). All the microcosms were mixed manually to obtain homogenous samples and kept in the laboratory at laboratory conditions. The soil moisture was adjusted twice a week by adding deionized water to mimic ambient conditions. Sample B (i.e., the control sample) was taken for petroleum hydrocarbon analysis by gas chromatography coupled with mass spectrometry (GC-MS) after the 4 day incubation period. Samples A and B were further subjected to hydrocarbon analysis by GC-MS at thirty day time intervals (i.e., 30 days, 60 days and for 90 days) to determine the effect of the amendment option (PPB) on the concentration of polycyclic aromatic hydrocarbons (PAHs). Furthermore, the influence of weathering and /or

aging on the concentration of PAHs in crude oil contaminated soil was investigate at each of the hydrocarbon concentration measurement time.

PAHs Analysis by GC-MS

A Buchi Speed Extractor E-916 (BUCHI Labortechnik AG, Flawil, Switzerland) was applied to carry out the hydrocarbon extraction process. It functions by 20 mL steel cells; with each cell filled with a bed of diatomaceous earth and 10g of sample diluted with quartz. The extraction solvent was hexane/dichloromethane 9:1 v/v mixture. To carry out the hydrocarbon extraction, each cell was held at 50^{o}C and 50 bar for 5 min, washed with fresh solvent for 3 min and washed again with nitrogen for 3 additional minutes. The process was repeated for 10 times for each cell. The extract obtained was concentrated to below 10 mL by a 40^{o}C bath under nitrogen flow. Pure hexane was used to wash the vials and raise the volume to 10 mL. An Agilent 7820A GC using an MSD5977E mass selection detector (MSD) operating in split mode was used for analysis of the extracts. The column was an Agilent HP5 MS30 m, 0.25 mm, 0.25 mm column; using thermal gradient of 40^{o}C (isothermal for 2 min) with a ramp of 7^{o}C/min up to 270^{o}C; Tamp of 15^{o}C/min up to 320^{o}C; 320^{o}C isotherm for 10 min; and "SCAN" mode (mass from 50 to 600).

RESULTS AND DISCUSSION

Effect of Weathering and Biochar Enhanced Hydrocarbon Degradation

The current study evaluated the effects of weathering and/or aging; and amendment on PAHs concentrations in crude oil contaminated soils at laboratory scale. Three separate scenarios for PAHs were considered in the current study-remediation by weathering and /or aging; PPB enhanced degradation. The amendment option performed better than degradation due weathering. This was considered in 13 PAHs present in the contaminated soil analyzed. The PAHs concentrations ranged from 0.245 to 348.04 mg/kg for the control sample (that is, the concentrations obtained without amendment for 4 day). The Benzo(a)pyrene had the least concentration (that is 0.245 mg/kg), while Chrysene has the highest concentration value (348.04 mg/kg). These concentrations were reduced to 347.469 mg/kg, 346.892 mg/kg, and 339.689 mg/kg after 30 day, 60 day, and 90 day, respectively. Expectedly, more hydrocarbons (PAHs) concentration degradation and /or reduction was observed in the amendment option. That is, for PPB, the control concentration reduced to 340.473 mg/kg after 30 day, 336.897 mg/kg after 60 day, and 334.278 mg/kg after 90 day. The results are presented in Table 4.1 below. From the results obtained, PPB amendment option performed better than the weathering and /or aging option.

Table 4.1: Results for weathering and biochar-enhanced biodegradation of PAHs in crude oil contaminated soils at laboratory scale.

Hydrocarbon	Weathering of PAHs at Different Time Intervals (in days)				Amendment: PPB		
PAHs (mg/kg)	T, 4d	T, 30d	T, 60d	T, 90d	T, 30d	T, 60d	T, 90d
Acenaphthylene	35.089	34.149	32.792	30. 875	29.56	27.859	26.415
Acenaphthene	6.987	6.406	6.024	5.786	4.954	4.274	4.022
Fluorene	0.735	0.701	0.668	0.579	0.516	0.468	0.397
Phenanthrene	77.018	76.615	74.872	72.286	69.135	67.451	65.941

Fluoranthene	70.021	69.871	68.924	67.051	63.142	61.587	59.082
Pyrene	82.978	82.396	82.020	80.486	75.421	73.847	71.206
Benz(a)anthracene	69.987	69.562	69.187	68.012	60.659	57.451	56.012
Chrysene	348.04	347.469	346.892	339.689	340.473	336.897	334.278
Benzo(k)fluoranthene	5.861	5.443	5.117	4.877	4.976	4.107	3.814
Benzo(a)pyrene	0.245	0.218	0.194	0.172	0.104	0.097	0.054
Indeno (1, 2, 3-c, d) pyrene	0.578	0.536	0.497	0.387	0.309	0.196	0.105
Dibenz (a, h) anthracene	0.296	0.260	0.203	0.198	0.107	0.089	0.062
Benzo (g, h, i) pyrylene	0.624	0.587	0.502	0.468	0.387	0.209	0.187
Summation (Σ) of PAHs	**698.459**	**694.213**	**687.892**	**670.866**	**649.743**	**634.532**	**550.369**

PPB = Plantain peel derived biochar.

PAHs concentrations decrease was experienced in the two options evaluated. Faster degradation of PAHs was achieved with PPB, while least PAHs concentrations decrease was achieved via the effect of weathering and/or aging. This of course was expected as it is a natural condition which is solely depended on soil microorganisms and environmental conditions.

Removal efficiency (%) of the two options were investigated for PAHs in contaminated soils. Results show that PPB option outperformed that of weathering and/or aging. While the removal efficiency of PPB was 6.97, 9.15, and 21.2 % after 30, 60, and 90-day laboratory experiment, respectively; that of weathering (W) was 0.61, 1.51, and 3.95% after 30, 60, and 90-day laboratory experiment, respectively. From the literature review investigated for contaminated soil bioremediation, no study yet on the application of PPB for the bioremediation and weathering and/or aging of PAHs in contaminated soils.

Furthermore, first-order kinetics was used to determine the kinetics of PAHs bioremediation in this study. The equation of the first-order kinetics is as follows:

$$C_t = C_0 . \exp(-kt) \quad (1)$$

where C_t represents the contaminant's concentration at time t (mg/kg), k is the first-order kinetic constant (day^{-1}), C_0 represents the initial concentration (mg/kg) of the contaminant, and t is the time (day). The degradation constant (K) for the three (2) different hydrocarbon degradation options were calculated for the different time intervals (that is, t = 30, 60, and 90 days) considered in the study.

Table 4.2: Kinetics results for petroleum hydrocarbon degradation by weathering (W); and by plantain peel based (PPB) biochar.

Degradation time	Means of degradation	Kinetics results
K_{30}	W	0.00020
K_{60}	W	0.00025
K_{90}	W	0.00045
K_{30}	PPB	0.00241

K_{60}	PPB	0.00159
K_{90}	PPB	0.00265

W = weathering; PPB = as defined at the foot of Table 4.1.

Option 1: this approach assessed the impact of weathering on PAHs degradation in crude oil contaminated soils. In this case, the K values (that is K_{30} after thirty days, K_{60} after sixty days, and K_{90} after ninety days) does not decrease; rather an increase was observed (Table 4.2). The results indicate that PAHs degradation in contaminated soil cannot be fast under the influence of weathering and/or aging. Results support the findings of [20].

Option 2: this remediation option evaluated the impact of PPB on PAHs degradation in crude oil contaminated soils. In this bioremediation option, a decrease in K value was observed from K_{30} to K_{60} only. This shows that with PPB biochar, PAHs degradation in contaminated soil is faster. This also support the results of [20]. In contrast, the K value increased between K_{60} and K_{90}. This means that with PPB amendment, the reduction of PAHs in polluted soil was slow between this period. The break in PAHs concentration reduction observed at 60 day of bioremediation needs further investigation in the course of time.

Furthermore, the study carried out regression analysis to evaluate the relationships that existed between the various approaches considered for the level PAHs degradation in contaminated soils. The results for the respective plots are presented in figures 4.1 and 4.2 below. A good relationship existed between the two remediation options. This is shown by the R-square values of 0.999 and 0.996 for PAHs concentration after 30-day PPB enhanced degradation versus weathering enhanced degradation of PAHs after day 30-day experiment; and 0.996 for PAHs concentration after 60-day PPB enhanced degradation versus weathering enhanced degradation of PAHs after day 60-day experiment;

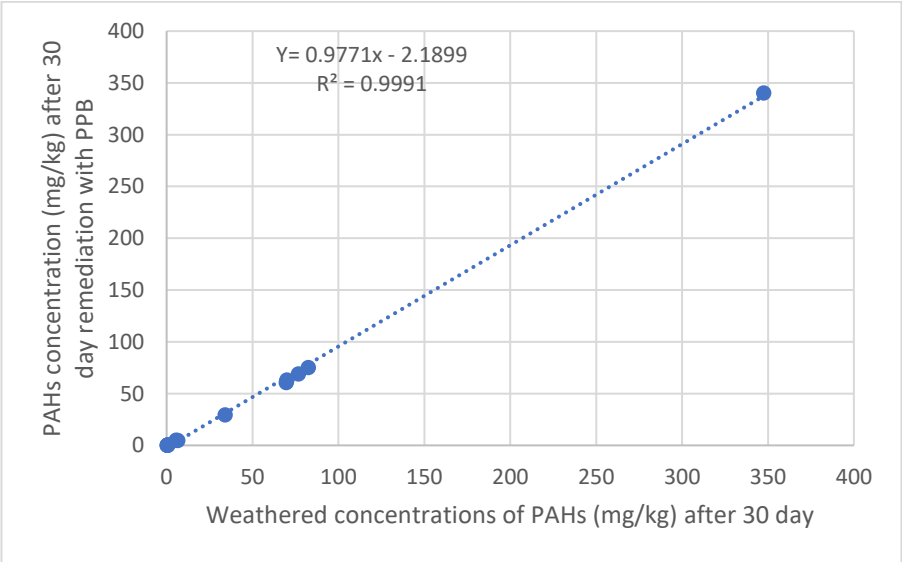


Figure 4.1: A plot of regression analysis showing the relationship that existed between PPB amendments and weathering for PAHs in crude oil contaminated soil after 30 day.

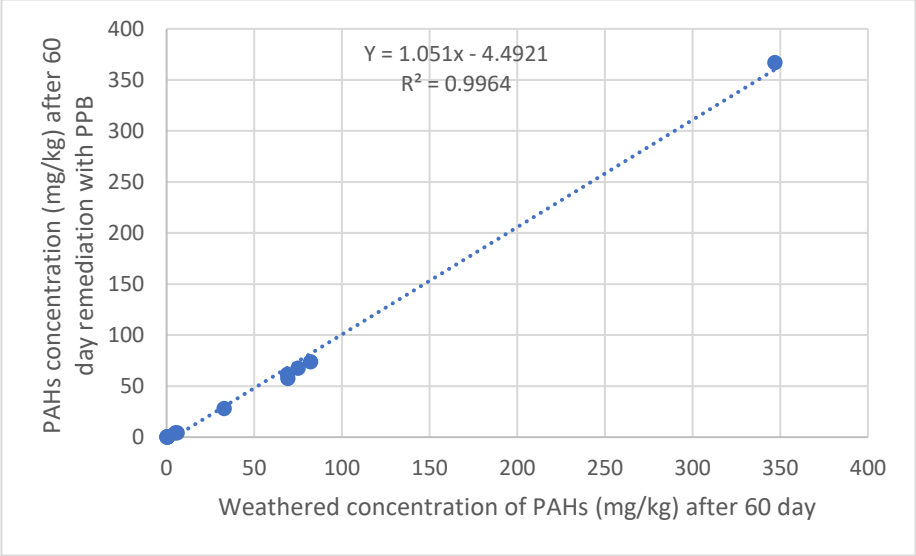


Figure 4.2: A plot of regression analysis showing the relationship that existed between PPB amendments and weathering for PAHs in crude oil contaminated soil after 60 day.

CONCLUSION

Industrial and technological advancements have impacted positively on human well-beings globally. However, their operational activities have impacted negatively on the environment (soil, water, and air) causing environmental pollution and degradation. Thus, there is need for appropriate redial actions. Consequently, the current research compared the efficacy of an agricultural waste-plantain peels derived biochar and weathering (a natural process) for the remediation of organic pollutant-polycyclic aromatic hydrocarbons (PAHs) contaminated soil at laboratory scale.

The PAHs concentrations ranged from 0.245 to 348.04 mg/kg for the control sample (that is, the concentrations obtained without amendment after 4-day incubation period). Benzo(a)pyrene had the least concentration, while Chrysene has the highest concentration. Under weathering conditions, the sum concentration of PAHs was observed to be 694.213, 687.892, and 670.866 mg/kg after 30, 60, and 90 days experiment, respectively. Expectedly, more hydrocarbons (PAHs) concentration degradation and /or reduction was observed in the amendment option. That is, with PPB amendment option, the sum concentration of PAHs obtained were 649.743, 634.532, and 550.369 mg/kg after 30, 60, and 90-day experiment, respectively.

Furthermore, first-order kinetics was used to determine the kinetics of PAHs bioremediation in this study. This was applied on both the weathering and the PPB amendment options. During weathering of PAHs, the degradation rate constant (K) increased with decreasing PAHs concentrations. This shows that PAHs degradation in contaminated soil is slow under the influence of weathering. In the case of the PPB amendment option, the K value decreased between K_{30} and K_{60} with decreasing PAHs concentrations, which implies faster degradation of PAHs. However, reverse was the case between K_{60} and K_{90}. This shows slow degradation of

PAHs. Consequently, this is the best option for the restoration and/or reclamation of soil polluted with PAHs. However, further research is needed to cover more time intervals.

References

[1] Suresh, B. and G. A. Ravishankar, Phytoremediation–A novel and promising approach for environmental cleanup. Critical Reviews in Biotechnology, 2004. 24, (2-3): 97-124.

[2] Ghosh, M. and S.P. Singh, A review on phytoremediation of heavy metals and utilization of its by-products. Applied Ecology and Environmental Research, 2005. 3: 1-18

[3] Wartini, Ng., P.M. Brendan., and M. Budiman, Rapid assessment of petroleum contaminated soils with infrared spectroscopy. Geoderma, 2017. 289, 150–160.

[4] Cozzolino, D, Near infrared spectroscopy as a tool to monitor contaminants in soil, sediments and water – state of the art, advantages and pitfalls. Trends Environ. Anal. Chem., 2015. 9, 1-7.

[5] Akpokodje O. I., and H. Uguru, Phytoremediation of petroleum products contaminated soil. Archives of Current Research International, 2019. 18 (1): 1-8

[6] Wang, X. Y., J. Feng, and J.M. Zhao, Effects of crude oil residuals on soil chemical properties in oil sites, Momoge Wetland, China. Environ. Monit. Assess., 2010. 161: 271–280.

[7] Liste, H.H., and D. Felgentreu, Crop growth, culturable bacteria, and degradation of petroleum hydrocarbons (PHCs) in a long-term contaminated field soil. Appl. Soil Ecol., 2006. 31: 43– 52

[8] Peng, S., Q. Zhou., Z. Cai, and Z. Zhang, Phytoremediation of petroleum contaminated soils by Mirabilis jalapa L. in a greenhouse plot experiment. J. Hazard. Mater, 2009. 168:1490–1496.

[9] R. K. Douglas; M. Obhuo and A. W. Opukumo Rapid estimation of heavy metals in crude oil contaminated soils by X-ray fluorescence (XRF) spectroscopy. Global Journal of Earth and Environmental Science, 2020, 5(2), pages 51-57.

[10] UNEP, Environmental Assessment of Ogoniland. UNEP, Switzerland, 2011.

[11] Oyefusi, A, Oil-dependence and Civil conflict in Nigeria. CSAE (University of Oxford), Oxford, UK, 2007.

[12] Ambituuni, A., J. Amezaga, and E. Emeseh, Analysis of safety and environmental regulations for downstream petroleum industry operations in Nigeria: problems and prospects. Environ, 2014. Dev. 9, 43–60. https://doi.org/10.1016/j.envdev.2013.12.002.

[13] Rim-rukeh, A, Oil spill management in nigeria: swot analysis of the joint investigation visit (JIV) process. J. Environ, 2015. Prot. 6, 259–271.

[14] Okoh, A. I, Biodegradation alternative in the cleanup of petroleum hydrocarbon pollutants. A review. Biotechnology and Molecular Biology, 2006. 1 (2): 38–50.

[15] Koshlaf, E., Ball, A.S, Soil bioremediation approaches for petroleum hydrocarbon polluted environments. AIMS Microbiol, 2017. 3(1), 25–49. https://doi.org/10.3934/ microbiol.2017.1.25

[16] Merkl, N., R. Schutze-Kraft., and M. Arias, Influence of fertilizer level on phytoremediation of crude oil contaminated soils with the tropical grass Brachiariabrizantha (Hochst. ex A. Rich.) Stapf. In: Merkl N (Eds). Phytoremediation of Petroleum-contaminated Soil. Margraf Publisher, 2005. Weikershim; 71–83

[17] Karenlampi, S., Schat, H., Vangronsveld, J., Verkleij, J.A.C., van der Lelie, D., Mergeay, M. and Tervahauta. A. I, Genetic engineering in the improvement of plants for phytoremediation of metal polluted soils. Environmental Pollution, 2000. 107: 225-231.

[18] Douglas, R.K., P. A. Peremelade., Fou, A., and H. Abarasi, Evaluation of the potential of agricultural wastes-cattle manure and poultry manure for bioremediation of crude oil-contaminated soil, Bioremediation Journal, 2024. DOI: 10.1080/10889868.2024.2322471.

[19] Douglas, R.K., Fou, A., and P.A. Peremelade, Use of Rice Husk Ash for Copper, Chromium, Zinc, and Lead Bioremediation in Crude Oil-Contaminated Soil. European Journal of Applied Sciences, 2022. 10(5), 27-33.

[20] Samuel, E. A., O. A. Mujidat., and A. A. Oluwafunmilayo, Kinetic Modelling and Half-Life Study on Enhanced Soil Bioremediation of Bonny Light Crude Oil Amended with Crop and Animal-Derived Organic Wastes. J Pet Environ Biotechnol, 2013. 4:2.