

# Modeling the Effect of Biochar on Volatile Petroleum Hydrocarbon Biodegradation and Emanation from Soil

Arimieari, L.W.<sup>\*1</sup> and Ezeilo, F.E.<sup>2</sup>

<sup>1,2</sup>Department of Civil Engineering, Faculty of Engineering, Rivers State University, Port Harcourt, Nigeria.

## Abstract

The purpose of this study is to model the effect of biochar on soil polluted with petroleum using plantain peel to prepare the biochar by method of local pyrolysis. The soil was collected from an agricultural farm land; it was contaminated with petroleum product and mixed properly to achieve proper contamination. A microcosm system was constructed consisting of four plastic buckets containing 1 kg of soil, artificially contaminated with petroleum. Biodegradation was monitored over 42 days by determining the total petroleum hydrocarbon content of the soil. The results showed that plantain peel biochar amendment technique was the most effective, reaching up to 29.46% (14 days), 40.63% (28) and 54.86% (42 days) of petroleum percentage biodegradation from contaminated soil. A first-order

kinetic model was fitted to the biodegradation data to model the biodegradation rate and the corresponding half-life time was estimated. The model revealed that petroleum contaminated-soil microcosms under plantain peel amendment had higher biodegradation rate constants ( $k$ ) as well as lower half-life times ( $t_{1/2}$ ) than unamended soil remediation systems. ANOVA statistical analysis revealed that petroleum biodegradation in soil was significantly ( $p = 0.002$ ) influenced by the addition of plantain peel biochar amendment agents. The amendment of soils with biochar has the potential to be an effective, economical, environmentally friendly and relatively different approach to remediate organic compound contaminated soil.

**Keywords:** Biodegradation, Plantain Peel Biochar, Petroleum, First-order kinetics.

## I. INTRODUCTION

Petroleum is a very complex mixture of aliphatic and aromatic hydrocarbons, containing volatile constituents of gasoline, petrol, kerosene, lubricating oil and solid asphaltene residues. Petroleum when released into the environment causes a variety of risks. Biochar is the pyrolysis product of biomass. Reference [1] described pyrolysis as heating biomass in the absence of air, which drives off many constituent parts, such as oil tars, but leaving carbon behind in a solid form. The solid form of carbon left in the reactor is what is being referred to as bio-char. As a soil amendment, biochar can greatly influence various soil properties and processes [2]. With the addition of biochar, the increase of the availability of soil organic matter, the water holding capacity, and the bioavailable nutrition elements can significantly improve the microbial activities and thereby the soil aggregate formation and stability[3]. Reference [4] reported that the formation of complexes of biochar with minerals, as the result of interactions between oxidized carboxylic acid groups at the surface of biochar particles, should be responsible for the improved soil aggregate stability. The ability of biochar to serve as a shelter for microbes is also exhibited by the appearance of microbial attachment

to its surface [5], and therefore decreasing the rate of microbial leaching in soil [6].

Charred carbonaceous matter is more resistant to microbial degradation than other forms of organic matter, and adding biochars to soils may lastingly store CO<sub>2</sub> captured from the atmosphere in the terrestrial environment [7]. The use of biochar as an amendment for the remediation of contaminated soil [8] offers benefits in addition to those of storing CO<sub>2</sub> captured from the atmosphere. The application of biochars as sorbents for soil remediation is motivated by the successful use of coal-derived activated charcoals for the in-situ sequestration of hydrophobic organic compounds (HOCs) [9]. Activated or non-activated charcoals were shown to reduce hydrophobic organic pollutant leaching [10], pollutant loss to the atmosphere [11], and uptake from soil by plants [12], [13], [14], and earthworms [15], [13], [16]. Replacing coal-derived charcoal in soil remediation applications with biochar would improve the sustainability of remediation efforts by combining the benefits of HOC risk reduction and carbon capture and storage, and also by reducing economic costs [17].

Weathered Bonny light crude oil (WBLCO) contaminated-soil microcosms amended with commercial activated carbon (CAC) and plantain peel-derived biochar (PPBC) had higher



biodegradation rate constants ( $k$ ) as well as lower half-life times ( $t_{1/2}$ ) than unamended soil (natural attenuation) remediation system [18]. Pyrogenic or “black” carbon is a soil and sediment component that may control pollutant migration. Biochar, black carbon made intentionally by biomass pyrolysis, is increasingly discussed as a possible soil amendment to increase fertility and sequester carbon [7]. The use of biochar as an amendment for the remediation of contaminated soil [8] has been found to be effective for three basic reasons: (1) it adsorbs and holds metals and organic compounds thereby removing the material from contact with plants, animals and humans; (2) it fosters the introduction of beneficial microbes which also promote remediation; and (3) it improves the overall soil quality and fertility by acting as fertilizer [19], [20] as well as other ecosystem services and appropriate carbon (C) to mitigate climate change [21], [22], [23].

The crude oil samples spiked on the soil samples of sufficient clay and organic matter content vaporized within few days and the other way round used to investigate vaporization kinetics of various crude oil samples of Niger Delta from different soil samples of the same area [24]. Bacteria use the petroleum hydrocarbons as a source of carbon for assimilation and for energy production. To make degradation of hydrocarbons possible the presence of other compounds is sometimes necessary [25]. The results of the study indicate the dependence of the kinetic order model to the crude oil hydrocarbon concentration and the textural properties of the soil [26]. Reference [27] proposed that first order kinetic behaviour was equally observed in the photochemical degradation of crude oil in seawater carried. Cumene and all low-boiling aromatics got from south shore of Grand Bahama Island disappeared within 90 minutes of exposure to ambient temperature and the disappearance of these hydrocarbons is a good first order estimate of the vaporization [28]. Reference [29] observed that the photochemical degradation of light crude oil in seawater. Disappearance of light crude oil spiked in the soil amended with nutrients also obeyed the first order kinetic process [29].

## II. MATERIALS AND METHODS

### A. Experimental Design and Soil Treatment

Soil samples (1 kg) was put into four (4) different plastic bins with a volume of about 3 L and labeled A to D, respectively. The soil in each plastic bin was added with 10% (w/w) crude oil and thoroughly mixed together to achieve complete artificial contamination. 10% addition was adopted in order to achieve severe contamination because above 3% concentration, oil has been reported to be increasingly deleterious to soil biota and crop growth [30]. The soil in each plastic bins A, B, C, D was correspondingly adjusted by the addition of 60 g each of biochar having the same particle size (4.75 mm) It was assumed that the aforementioned quantity of

biochar applied to the relevant treatment plastic bin were well worked to at least 1.5 m depth in each plastic bin. The moisture content was adjusted to 50% water holding capacity by the addition of sterile distilled water and incubated at room temperature ( $28 \pm 2$  °C). Plastic bin D with soil and crude oil without biochar (amendment agents) served as control. Periodic sampling from each plastic bin was carried out at 14-day intervals for 42 days to determine the residual total petroleum hydrocarbon (TPH). The samples of dried plantain peel and plantain peel biochar are shown in Figures 1 and 2.



**Fig. 1: Sample of Dried Plantain Peel**



**Fig. 2: Sample of Dried Plantain Peel Biochar.**

### B. Total petroleum hydrocarbon determination

The total petroleum hydrocarbon (TPH) content of the soil samples was extracted using solvent extraction method of Reference [31]. Soil samples (approximately 10 g) was taken from each microcosm and put into a 50-ml flask and 20 ml of n-hexane was added. The mixture was shaken vigorously on a magnetic stirrer for 30 minutes to

allow the hexane extract the oil from the soil sample. The solution was then filtered using a Whatman filter paper and the liquid phase extract (filtrate) diluted by taking 1ml of the extract into 50 ml of hexane. The absorbance of this solution was measured spectrophotometrically at a wavelength of 400 nm HACH DR/2010 Spectrophotometer using n-hexane as blank. The total petroleum hydrocarbon in soil was estimated with reference to a standard curve derived from fresh crude oil of different concentration diluted with n-hexane. Percent degradation (D) was calculated using Eq. 1:

$$D = \frac{TPH_i - TPH_r}{TPH_i} \times 100 \quad (1)$$

Where  $TPH_i$  and  $TPH_r$  are the initial and residual TPH concentrations, respectively.

### C. Bioremediation kinetics

Kinetic analysis is a significant factor for understanding biodegradation process, bioremediation speed measurement and development of efficient clean up for a petroleum contaminated soil. The information on the kinetics of soil bioremediation is of great significance because it characterizes the concentration of the contaminant remaining at any time and permit estimate of the level likely to be present at some future time. Biodegradability of petroleum is usually explained by first order kinetics [32], [33] as cited in [18] and this is given as in Eq. 2.

$$C_t = C_o e^{-kt} \quad (2)$$

Where

$C_o$  - is the initial TPH content in soil (mg/kg),

$C_t$  - is the residual TPH content in soil at time t, (mg/kg),

k - is the biodegradation rate constant ( $day^{-1}$ )

t - is time (day).

Plotting the logarithm of TPH concentration versus time represents appropriate information about biodegradation rate.

## III. RESULTS AND DISCUSSION

### A. Total hydrocarbon content evaluation

The rate of biodegradation of petroleum contamination at 29.46% (14 days), 40.63% (28 days) and 54.86% (42 days) concentrations were analysed for the plantain peel from the data gathered. The abstraction result of total hydrocarbon content which was used as a pointer parameter for remediation at several levels of petroleum contamination, ranging from 29.46, 40.63 and 54.86% and these were detected to reduce with time

for the plantain peel biochar applied. This indicates that there was a progress in the effectiveness or rate of remediation offered by the plantain peel biochar.

### B. Application of first order reaction for bioremediation kinetics

The rates of biodegradation were compared using biodegradation rate constants, from the First Order Kinetics Model, which was achieved using the linear function of Microsoft Excel Statistical tool pack. The graphs of the kinetic form for total hydrocarbon content decrease at 29.46, 40.63 and 54.86% contamination levels for plantain peel biochar when refined for a remediation period of 42days, are shown in Figure 3. It was observed that the first order kinetic model (Eq. 2) fitted well to the biodegradation offered by the plantain peel biochar. The degree of biodegradation shows a positive correlation coefficient  $R^2$  for the reduction in total hydrocarbon content, with a higher biodegradation rate at a reduced time. From the result, the biodegradation rate constant (k) was high for plantain peel biochar, k (2.90) with the lowest half-life, i.e.,  $t_{1/2}$  (0.24).

It is realized from Figure 3 that the soil amendment with plantain peel biochar generally improved the TPH biodegradation in comparison with the unamended contaminated soil. This observation could be due to the fact that plantain peel biochar acted as an adsorbent in the soil by allowing the contaminant to be strongly bound to it, thus producing favourable conditions for degrading organisms' growth. The data were subjected to one – way analysis of variance (ANOVA) at level of significant difference of P- value 0.002.

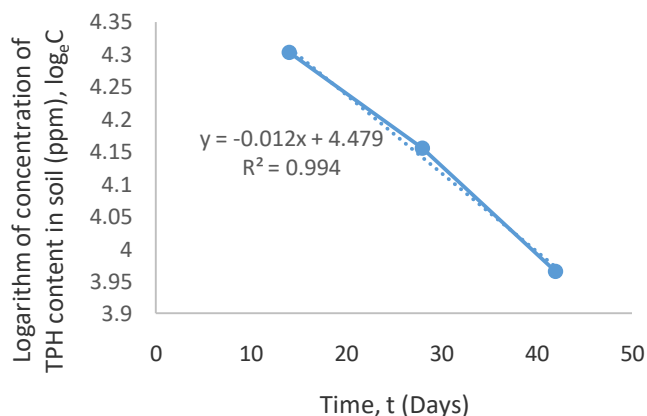


Fig. 3: A plot of log of TPH concentration versus time

## IV. CONCLUSION

The results from the study confirm that the use of plantain peel biochar enhanced the degree of biodegradation in microcosms simulating soil polluted with petroleum. At the end of 42 days remediation period, the maximum total petroleum



hydrocarbon (TPH) removal that ranged from 29.46, 40.63 and 54.86% was obtained for petroleum contaminated with soil amended with plantain peel biochar. The rate of biodegradation constant achieved from the application of first order kinetics described the rate of petroleum biodegradation in soil with and without amendment. The rate constant  $k$  (2.90) for plantain peel biochar amended soil microcosm with the lowest half-life, i.e.,  $t_{1/2}$  (0.24).

Statistical analysis using ANOVA to determine significance effect of the amendment agents on petroleum biodegradation revealed that petroleum biodegradation in soil was highly influenced by the addition of plantain peel biochar as amendment agents. Amendment of soils with biochar has the potential to be an economical, relatively different approach to remediate the risk of organic compound contamination and contact in soils. The bioremediation method recommended here for soils contaminated with petroleum could be apt in field, for its inexpensive and low environmental risk related with volatile hydrocarbon damages. However, these results do not represent an overall rule and site detailed studies are required, the method adopted here can be a significant maintenance device when planning bioremediation approaches on site.

#### ACKNOWLEDGMENTS

This research work was sponsored by TETFund Institution Based Research (IBR) through Rivers State University, Port Harcourt, Nigeria.

#### REFERENCES

- [1] M. Fowles., Black carbon sequestration as an alternative to bioenergy, Biomass and Bioenergy, doi: 10.1016/j.biombioe.2207.01.012, (2007).
- [2] J. Lehmann and S. Joseph, In Biochar for environmental management: Science, Technology and Implementation, ed Earthscan from Routledge, London and New York, (2009), 89-109.
- [3] A. Downie, A. Crosky, and P. Munroe, Physical properties of biochar, In: Lehmann, J., Joseph, S. (eds), Biochar for Environmental Management: Science and Technology, Earthscan, London., (2009), 13-29.
- [4] B. Glaser, J., Lehmann, W. Zech, Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review, Biol. Fert. Soils. 35, (2002), 219-230.
- [5] J.E. Thies, and M.C Rillig, Characteristics of biochar—biological properties. In: Lehmann JSJ (ed) Biochar for environmental management: science and technology, Earthscan, London, (2009).
- [6] J. Pietikäinen, O. Kiikkilä, and H. Fritze, Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus., Oikos 89(2), (2000), 231–242. doi:10.1034/j.1600-0706.2000. 890203 x.
- [7] A.R. Zimmerman, Abiotic and microbial oxidation of laboratory-produced black carbon (biochar), Environ. Sci. Technol. 44, (2010), 1295-1301.
- [8] L. Beesley, E. Moreno-Jiménez, and J. L. Gomez-Eyles, Effects of biochar and green waste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil., Environ. Pollut. 158, (2010), 2282-2287.
- [9] U. Ghosh, R.G. Luthy, G. Cornelissen, D. Werner, and C. A. Menzie, In-situ sorbent amendments: a new direction in contaminated sediment management., Environ. Sci. Technol. 45, (2011), 1163 - 1168.
- [10] S.E. Hale, M. Elmquist, R. Brändli, T. Hartnik, L. Jakob, T. Henriksen, D. Werner, and G. Cornelissen, Activated carbon amendment to sequester PAHs in contaminated soil: a lysimeter field trial., Chemosphere 87, (2012), 177-184.
- [11] K. M. Bushnaf, S. Puricelli, S. Saponaro, and D. Werner, Effect of biochar on the fate of volatile petroleum hydrocarbons in an aerobic sandy soil., J. Contam. Hydrol. 126, (2011), 208-215.
- [12] I. Hilber, G.S. Wyss, P. Mäder, T.D. Bucheli, I. Meier, L. Vogt, and R. Schulin, Influence of activated charcoal amendment to contaminated soil on dielrin and nutrient uptake by cucumbers. Environ. Pollut. 157, (2009), 2224 – 2230.
- [13] L. Jakob, T. Hartnik, T. Henriksen, M. Elmquist, R.C. Brändli, S.E. Hale, G. Cornelissen, G., PAH-sequestration capacity of granular and powder activated carbon amendments in soil, and their effects on earthworms and plants., Chemosphere 88, (2012), 699-705.
- [14] W. Verstraete, and W. Devliegher, Formation of non-bioavailable organic residues in soil: Perspectives for site remediation., Biodegradation 7(6), (1996), 471-485.
- [15] S.K. Fagervold, Y.Z. Chai, J.W. Davis, M. Wilken, G. Cornelissen, and U. Ghosh, Bioaccumulation of polychlorinated dibenzo-p-dioxins/dibenzofurans in *E. fetida* from floodplain soils and the effect of activated carbon amendment.” Environ. Sci. Technol. 44, (2010), 5546-5552.
- [16] V. Langlois, A. Rutter, and B. Zeeb, Activated carbon immobilizes residual polychlorinated biphenyls in weathered contaminated soil., J. Environ. Qual. 40, (2011), 1130 - 1134.
- [17] M. Sparrevik, T. Saloranta, G. Cornelissen, E. Eek, A.M. Fet, G.D. Breedveld, and I. Linkov, Use of life cycle assessments to evaluate the environmental footprint of contaminated sediment remediation., Environ. Sci. Technol. 45, (2011), 4235-4241.
- [18] S.E. Agarry, K.M. Oghenejoboh, and B.O. Solomon, Kinetic Modelling and Half Life Study of Adsorptive Bioremediation of Soil Artificially Contaminated with Bonny Light Crude Oil. Journal of Ecological Engineering, 16(3), (2015), 1-13.
- [19] B. Glaser, L. Haumaier, G. Guggenberger, and W. Zech, The ‘Terra Preta’ phenomenon: a model for sustainable agriculture in the humid tropics., Naturwissenschaften 88, (2001), 37–41.
- [20] E. Marris, Putting the carbon back: black is the new green. Nature 442, (2006), 624–626.
- [21] J. Lehmann, Bio-energy in the black. Front Ecol. Environ. 5(7), (2007), 381–387.
- [22] D.A. Laird, The charcoal vision: a win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality., Agronomy J., 100, (2008), 178–181.
- [23] S. Sohi, E. Krull, E. Lopez-Capel, and R. Bol., A review of biochar and its use and function in soil., Adv. Agronomy 105, (2010), 47–82.
- [24] A.P. Uzoije, Vaporization kinetics of Nigerian crude oil from different soil samples of Niger delta. Agric. J., 3, (2008), 278-282.
- [25] Z. Wang, M. Fingas, S. Blenkinsopp, G. Sergy, M. Landriault, L. Sigouin, J. Foght, K. Semple, and D.W. Westlake, Comparison of oil composition changes due to biodegradation and physical weathering in different oils., Journal of Chromatography A (1998), 809(1-2), 89-107.
- [26] A.P. Uzoije, F.N. Uzundu, and P.C. Agu, Vaporization Models of Varying Crude Oil Characteristics. Journal of Environmental Science and Technology, 4, (2011), 150-157.
- [27] Z. Wang, M. Fingas, and K. Li, Fractionation of a light crude oil and identification and quantitation of aliphatic, aromatic, and biomarker compounds by GC-FID and GC-MS.I., J. Chromatogr. Sci., 32, (1994), 361-366.

- [28] Duddy, J.E., L.I. Wisdom, S. Kressmann and T. Gauthier, Understanding and optimization of residue conversion in H Oil. Proceedings of the Third Bottom of the Barrel Technology Conference (BBTC), Oct. 20-21, Antwerp, Belgium,1003-1022, 2004.
- [29] W. Henry, and M.S. Kenneth, Potocatalytic oxidation of crude oil residues by mercury vapor lamp., *Chem. Eng. Sci.*, 62, (1991),5409-5417.
- [30] L.C. Osuji, E.J.G. Egbuson, and C.M. Ojinnaka, Chemical reclamation of crude-oil-inundated soils from Niger Delta, Nigeria., *Chem. Ecol.*, 21(1), (2005), 1–10.
- [31] J.K. Adesodun, and J.S.C Mbagwu, Biodegradation of waste-lubricating petroleum oil in a tropical alfisol as mediated by animal droppings., *Bioresource Technol.*, 99(13), (2008),5659–5665.
- [32] M.A. Zahed, H. Abdul Aziz H., M.H. Isa, L. Mohajeri, S. Mohajeri, and S.R.M. Kutty, Kinetic modeling and half - life study on bioremediation of crude oil dispersed by Corexit 9500, *J. Hazard Mater.* 185, (2011),1027–1031.
- [33] S.E. Agarry, M.O. Aremu, and O.A Aworanti, Kinetic modelling and half-life study on bioremediation of soil co-contaminated with lubricating motor oil and lead using different bioremediation strategies., *Soil and Sediment Contam. An Int. J.* 22 (7), (2013),800–816.
- [34] Ihab Hassan, Mustafa Abbas Mustafa and Basheer Elhassan, Use of Zinc Oxide Nanoparticle for the Removal of Phenol Contaminated Water, *SSRG International Journal of of Material Science and Engineering* 3(2) (2017) 1-5.