Effect of Maize Husk Biochar on Physicochemical Properties of Petroleum Polluted Soil

Arimieari, L.W.[1*] and Woyo, W. N.[2]

[1, 2]*Department of Civil Engineering, Faculty of Engineering, Rivers State University, Port Harcourt, Nigeria.*
**Correspondence author*

Abstract:-**This study considered the effect of biochar on soil polluted with petroleum using maize husk to prepare the biochar by method of local pyrolysis. The soil was collected from an agricultural farm land; it was polluted with petroleum product and mixed properly to achieve proper contamination. Five replicates were setup which included two (2) controls, one containing soil alone and the other containing soil and petroleum (polluted) while the other three (3) included polluted soil containing biochar. The replicates containing polluted soil with biochar were kept moist by exposure to atmospheric condition for remediation processes to take place leading to the eventual removal of these petroleum hydrocarbons. The bioremediation experiments were carried out after every two weeks for a period of six weeks under laboratory conditions. The results for pH showed that at the unpolluted stage the soil sample was neutral, but at pollution its pH level was 6.5, the biochar itself was having a pH of 7.4. When applied to the biochar amended soil the pH level at 42 days increased to 7.2 which was close to its natural state. It was observed that the hydrocarbon utilizing bacteria (HUB) was constantly increasing ranging from 5.1×10^4 at unamended contaminated level to 3.36×10^6 (14 days), 4.51×10^7 (28 days) and 2.95×10^8 (42 days) due to its high content in the material. The results showed that the soil amendment with biochar enhanced the petroleum hydrocarbon biodegradation in comparison with the unamended contaminated soil. Therefore, the maize husk biochar proved to be adequate as potential agent for bioremediation processes of soils contaminated with petroleum hydrocarbons.**

Keywords: **Bioremediation, Maize Husk Biochar, Petroleum Hydrocarbon**

I. INTRODUCTION

BIOCHAR is a product of incomplete combustion of biomass in the absence of oxygen (i.e. pyrolysis process). Biochar application to soils can improve soil quality and offer ancillary (accessory; adjuvant; auxiliary) benefit [1], [2], [3]. Biochar as an organic product; formed through heating of biomass or other organic waste matter, to above 250^0C in the absence (or limited) oxygen. Biochar is a fine-grained highly porous charcoal substance that is distinguished from other charcoal in its intended use as a soil amendment material, produced under the condition that optimizes certain characteristics deemed useful in agriculture. The particular heat treatment of the organic biomass used to produce Biochar contributes to its large surface area and its characteristic ability to persist in soils with very little biological decay [4]. Biochar serves as a catalyst that enhances plant uptake of nutrients and water. Compared to other soil amendments, the high surface area and porosity of Biochar enables it to absorb or retain nutrients and water and also provides a habitat for beneficial microorganism to flourish [5], [4].

Different biochars created at different temperature had varying responses to metals although high pyrolysis temperature and an animal-derived Biochar tend to be most effective [6]. Optimizing feedstock and pyrolysis factor and matching them to specific environmental contaminants need to be further tested, the success of field trial and the economic feasibility of large-scale applications also need to be considered [7], [6]. With Biochar addition, the increase of the availability of soil organic matter, the water holding capacity, and the bioavailable nutrition elements can significantly enhance the microbial activities and thereby the soil aggregate formation and stability [8]. The formation of complexes of Biochar with minerals, as the result of interactions between the oxidized carboxylic acid group at the surface of Biochar particles, should be responsible for the improved soil aggregates stability [5]. Crude oil is an extremely complex mixture of aliphatic and aromatic hydrocarbons, including volatile components of gasoline, petrol, kerosene, lubricating oil and solid asphaltene residues. The remediation processes leading to the eventual removal of these petroleum hydrocarbons from the environment involve the trio of physical, chemical and biological alternatives [9]. As a result of this limitation, great deals of literature have reported that bioremediation methods are alternatives and/or supplements to these methods. This is because of their cost effectiveness, environmental friendliness, simplicity of technology and conservation of soil texture and characteristics, however, the method requires longer treatment time [10].

Biochar is the product of thermal degradation of organic materials in the absence of air (pyrolysis) [11]. The use of biochar as an amendment for the remediation of contaminated soil has been found to be effective for three basic reasons: (1) it adsorbs and holds metals and organic compounds thereby removing the material form 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[5], as well as other ecosystem services and sequester carbon (C) to mitigate climate change [12], [13].

The observed effects on soils fertility have been explained mainly by a pH increase in acid soils or improved nutrient retention through cation adsorption [14]. Reference [15] 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 biochar. The effect of biodegradation is a change in petroleum composition. Some part are readily degraded by bacteria, and other compounds are degraded only very slowly due to leak of degrading enzymes/mechanisms by bacteria or because the hydrocarbons were toxic to the bacteria. This causes a difference in degradation for different oils, and thereby creates a different in toxicity between oils [16].

II. MATERIALS AND METHODS

1) Collection of Sample

The soil sample used for the study was collected from the top soil (1m) of an agricultural farm land, Rivers State University, Port Harcourt, Nigeria. The soil sample was dried, homogenized, passed through a 4.75µm (pore size) sieve and was stored in a polythene bag and / kept in the laboratory prior to use. The crude oil was obtained from Nigerian National petroleum corporation, Omoku, Nigeria. It was weathered by exposure to the atmospheric condition from 10.00am to 4.pm for two weeks with occasional stirring after which it was stored for further use. Maize husk used for biochar production was obtained from road side corn dealers, Port Harcourt, Nigeria.

2) Characterization of Soil Sample

The soil sample was characterized for total nitrogen (N), total phosphorus, potassium, chloride ion, moisture content, Cr, Pb, Fe, Cd, HUB and pH according to standard methods. The pH was determined according to the modified method of [17] and total nitrogen was determined by the semi-micro-Kjeldhal method [18]. Available phosphorus was determined by Brays No.1 method [19] and moisture content was determined by the dry weight method. The Hydrocarbon Utilizing Bacteria (HUB) populations was determined by the vapor phase transfer method [20].

3) Preparation of Biochar

The maize husk as the material for biochar preparation was well washed with water several times, cut into small sizes, sundried for two weeks and then over dried at 110^{O}C for 3hrs, the dried sample was used for black carbon (biochar) preparation.

The maize husk biochar was prepared using local pyrolysis formulae for thermal decomposition of the dried sample whereby a cooking pot was filled with the maize husk and then covered air tight after which it was placed on a burning gas cooker for 8hrs after which it was then cooled to room temperature.

4) Soil Phase Experimental Design and Soil Treatment

Soil sample (2kg) was put into 5 different plastic (microcosm) with a volume of about 10L which included two (2) controls, one containing soil alone and the other containing soil and petroleum (polluted) while the other three (3) included polluted soil containing biochar and labeled WM2, WM3, WM4, with each remediation expiring after every two weeks respectively for a total of six weeks. The microcosm containing polluted soil with biochar was kept moist by exposure to atmospheric condition for remediation process to take place.

5) Determination of Microbial (Hydrocarbon Utilizing Bacteria) Count

Quantification of the Hydrocarbon Utilizing Bacteria (HUB) present in the soil samples was determined at the beginning of the experiment (time zero) and after 14, 28 and 42 days of remediation time by the *pour plate* count technique. Soil samples (10 g) was transferred into sterilized Erlenmeyer conical flasks containing 90 ml of sterile 0.9% (m/v) NaCl solution and then shaken in a shaker for 15 min at 150 rpm. Samples (1 mL) were subjected to a serial 10-fold dilution procedure and cultivated in a nutrient agar medium. Three plates were inoculated for each dilution. The plates were incubated at 30 °C for 48 h and the number of colony forming units (CFU) was counted in each sample. The results were expressed as colony-forming units per gram of dry soil (CFU/g dry soil). All microbiological counts and experiments were carried out in triplicate.

III. RESULTS

1) Physicochemical Properties of Samples

The physicochemical properties considered in this analysis includes; Tennesseee (T.N), Hydrocarbon Utilizing Bacteria (HUB), Cadmium(Cd), Lead (Pd), Chromium (Cr), Phosphorus (P), Calcium (K) and Iron (Fe). The results for the physicochemical properties are shown in Tables 1 – 3.

Table 1 Physicochemical Properties of Sample at 14 Days

PROPERTIES	UNPOLLUTED (Control)	POLLUTED (Control)	Maize Husk Biochar (Control)	Remediation with Maize Husk Biochar
pH	7	6.5	7.4	6.8
Cl^- (ppm)	20	20	180	30
$NaCl^-$ (ppm)	33	33	297	49.5
T.N (%)	0.17	2.36	4.7	1.53
P (mg/kg)	0.043	0.196	1.209	0.148
K (mg/kg)	1.03	1.42	3.153	1.190
HUB(cfu/ml)	6.8×10^2	5.1×10^4	2.86×10^3	3.36×10^6
Cr (mg/g)	5.08710	12.35568	1.03812	9.63019
Fe (mg/kg)	3.10010	4.513840	1.03810	3.71520
Pb (mg/kg)	7.63599	9.58261	0.03891	8.20316
Cd (mg/kg)	0.31854	1.054	0.01356	0.71883

The physicochemical properties of the soil, the material and the remediating stage (14 days) of the samples are shown in Table 1 above which considered how much the biochar material has affected the soil at a polluted stage. At 14 days the polluted soil sample with biochar has shown some reduction in the amount of heavy metals present.

Table 2 Physicochemical Properties of Sample at 28 days

PROPERTIES	UNPOLLUTED (Control)	POLLUTED (Control)	Maize Husk Biochar (Control)	Remediation with Maize Husk Biochar
pH	7	6.5	7.4	7
Cl^- (ppm)	20	20	180	20
$NaCl^-$ (ppm)	33	33	297	33
T.N (%)	0.17	2.36	4.7	2.08
P (mg/kg)	0.043	0.196	1.209	0.396
K (mg/kg)	1.03	1.42	3.153	1.433
HUB(cfu/ml)	6.8×10^2	5.1×10^4	2.86×10^3	4.51×10^7
Cr (mg/g)	5.08710	12.35568	1.03812	6.02631
Fe (mg/kg)	3.10010	4.513840	1.03810	2.03810
Pb (mg/kg)	7.63599	9.58261	0.03891	5.62981
Cd (mg/kg)	0.31854	1.054	0.01356	0.42267

Table 2 shows a further reduction in the heavy metals of the material at 28 days remediation time, a careful consideration shows that at this stage the material has bonded strongly with the soil to reduce most of the carbon bond chain that held carbon to soil replacing them with its physicochemical properties.

Table 3 Physicochemical Properties of Sample at 42 days

PROPERTIES	UNPOLLUTED (Control)	POLLUTED (Control)	Maize Husk Biochar (Control)	Remediation with Maize Husk Biochar
pH	7	6.5	7.4	7.2
Cl^- (ppm)	20	20	180	90
$NaCl^-$ (ppm)	33	33	297	148
T.N (%)	0.17	2.36	4.7	2.68
P (mg/kg)	0.043	0.196	1.209	0.569
K (mg/kg)	1.03	1.42	3.153	1.964
HUB(cfu/ml)	6.8×10^2	5.1×10^4	2.86×10^3	2.95×10^8
Cr (mg/g)	5.08710	12.35568	1.03812	2.13925
Fe (mg/kg)	3.10010	4.513840	1.03810	1.15831
Pb (mg/kg)	7.63599	9.58261	0.03891	2.37813
Cd (mg/kg)	0.31854	1.054	0.01356	0.05984

The result after 42 days of remediation shows greatly a decrease in the amount of heavy metals. HUB was constantly increasing, this is because of its high content in the material. HUB is required so as to reduce the carbon content, bacterial necessary for self-remediation was reduced to the state of pollution, maize husk biochar when applied to the soil started restoring these bacterial. This increase in HUB and the decrease in other physicochemical properties are shown in Table 4 for the polluted soil sample and the samples with biochar. The physicochemical properties of the biochar itself and the properties of the unpolluted soil sample are not considered in the table. This is in order to show the actual rate of reduction and addition of these properties.

2) Comparison of Physicochemical Properties of Sample with the Control

Table 4 Comparison of Physicochemical Properties of Sample with the Control

PROPERTIES	POLLUTED Sample	Soil + Oil+ Biochar (14 days)	Soil+ Oil+ Biochar (28 days)	Soil+ Oil+ Biochar (14 days)
Ph	6.5	6.8	7	7.2
Cl^- (ppm)	20	30	20	90
$NaCl^-$ (ppm)	33	49.5	33	148
T.N (%)	2.36	1.53	2.08	2.68
P (mg/kg)	0.196	0.148	0.396	0.569
K (mg/kg)	1.42	1.190	1.433	1.964
HUB(cfu/ml)	5.1×10^4	3.36×10^6	4.51×10^7	2.95×10^8
Cr (mg/g)	12.35568	9.63019	6.02631	2.13925
Fe (mg/kg)	4.513840	3.71520	2.03810	1.15831
Pb (mg/kg)	9.58261	8.20316	5.62981	2.37813
Cd (mg/kg)	1.054	0.71883	0.42267	0.05984

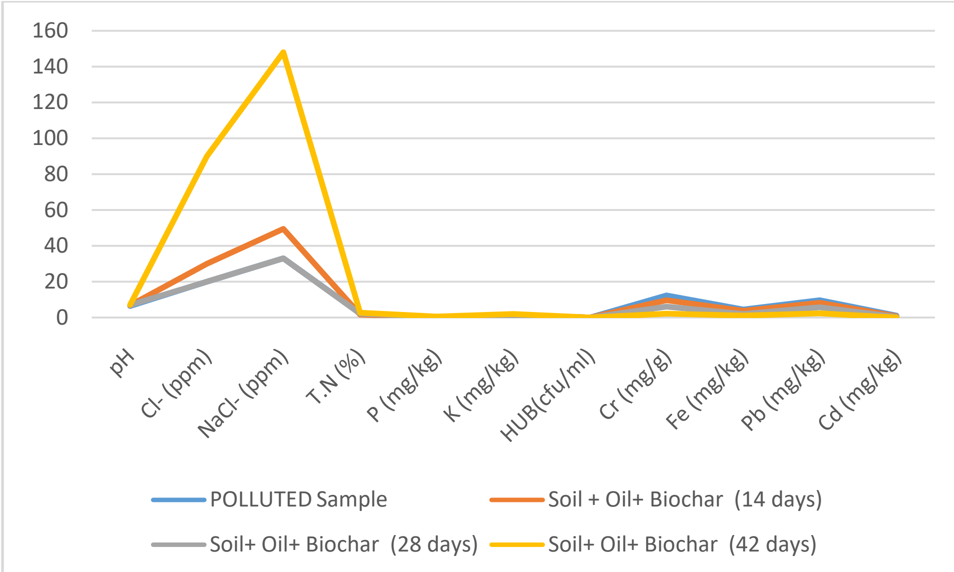

Fig. 1 Graph showing the Rate of increase/decrease in Physicochemical Properties of Soil

IV. CONCLUSION

Biochar which is a result of the pyrolysis of organic matter has been studied over the years with different approach and with different intentions; this study focuses on the use of biochar as an environmental remediating material. This study confirms that biochar produced through the pyrolysis of maize husk is effective in its use for biodegradation of soil microcosm polluted with crude oil or any other environment affected by crude oil spill.

Biochar usually has a neutralizing effect for its application to acid soils due to its potential to increase a soil pH. The results for pH showed that at the unpolluted stage the soil sample was neutral, but at pollution its pH level was 6.5, the biochar itself was having a pH of 7.4. When applied to the biochar amended soil the pH level at 42 days increased to 7.2 which was close to its natural state. It was observed that the hydrocarbon utilizing bacteria (HUB) was constantly increasing ranging from 5.1×10^4 at unamended contaminated level to 3.36×10^6 (14 days), 4.51×10^7(28 days) and 2.95×10^8 (42 days) due to its high content in the material. The results showed that the soil amendment with biochar enhanced the petroleum hydrocarbon biodegradation in comparison with the unamended contaminated soil. Therefore, the maize husk biochar proved to be adequate as potential agent for bioremediation processes of soils contaminated with petroleum hydrocarbons.

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