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Modeling Palm Bunch Ash Enhanced Bioremediation of Crude-Oil Contaminated Soil

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Abstract- The rate of Bioremediation of crude oil contaminated soil ex-situ to which Palm Bunch Ash (PBA) was added has been studied in this work, based on Total Petroleum Hydrocarbon content.

Four samples each were contaminated with 100 g, 200 g and 300 g respectively of crude oil and 0 g, 100 g, 200 g and 500 g of Palm Bunch Ash were added respectively to the four samples to produce twelve test samples. The samples were analysed for TPH content at two-week intervals after pollution for eight weeks, and the experimental data fit to four models to obtain the model that best fits the data.

Results reveal that PBA enhanced bioremediation follows the logistic growth curve for microbial population growth with the yield coefficient (ratio of microbial population increase per unit substrate consumed) being constant.

PBA enhances the rate of bioremediation especially at low levels of crude oil contamination, because at higher levels of crude oil contamination, the contaminant itself fosters microbial growth at a faster rate than increased addition of PBA.

Keywords- *bioremediation; palm bunch ash; total petroleum hydrocarbon; crude oil contamination; modelling.*

I. INTRODUCTION

Conventional methods for the removal, reduction, or mitigation of toxic substances introduced into soil or ground water via anthropogenic activities and processes include: pump and treat systems, soil vapour extraction, incineration, and containment. The use of each of these conventional methods of treating contaminated soil suffers from recognizable drawbacks and may involve some level of risk [1].

The emerging science and technology of bioremediation offers an alternative method to detoxify contaminants. Bioremediation has been demonstrated and is being used as an effective means of mitigating hydrocarbons, halogenated organic solvents, halogenated organic compounds etc. It is a natural process which relies on bacteria, fungi, and plants to alter contaminants as these organisms carry out their normal life functions. During bioremediation, microbes utilize chemical contaminants in the soils as an energy source and through oxidation-reduction reactions, metabolize the target contaminant into viable energy for microbes, releasing by-products that are typically in less toxic form than the parent contaminant [2,3,4]. Bioremediation of crude oil-contaminated soil can be carried out naturally (natural attenuation), or by the use of nutrients (organic or inorganic fertilizers); by the use of chemicals; or through mechanical means. All the above methods of bioremediation have their advantages and disadvantages [5]. Bioremediation studies on the effects of lipophilic fertilizers coupled with bio surfactants have shown that they are more effective on the saturated fraction than on the aromatic fraction of crude oil [6].

Studies carried out by Ihekweazu [7] in Nigeria confirmed that oil-degrading micro-organisms are abundant and not limited to oil producing areas as reported by Bossert [8]. In his study he observed that after an initial low count of micro-organisms at the higher levels of oil pollution, microbial numbers increased substantially and later reverted to the previous number.

Ayotamuno et al [9] studied bioremediation of crude oil polluted agricultural soil at Port Harcourt, Nigeria. They concluded that bioremediation should be applied during the dry season by applying nitrogenous-based fertilizers (preferably NPK type) between 75 and 200g per 0.16m^2.

Tanee and Kinako [10] conducted comparative studies of biostimulation and phytoremediation in the mitigation of crude oil toxicity in tropical soil of the Niger-Delta area of Nigeria. They applied remediation treatments after one week of pollution. They applied NPK fertilizer, poultry dung, and seed of *Vigna unguiculata* (phytoremediation) with control. They concluded that the use of NPK fertilizer and phytoremediation were good remedial treatment options in the mitigation of crude oil toxicity.

Palm Bunch Ash (PBA) is obtained from the empty fruit bunch of *Elaeis Guineensis* palm tree species. Although the empty fruit bunches are normally thrown away, they have been found to be a source of sodium and potassium compounds when processed to get the ash [11]. Taiwo and

Oshinowo[12] have also reported that Palm Bunch Ash contains mainly Potassium Carbonate and Potassium Hydroxide. Palm Bunch Ash has also been recognised as a 100 % organic fertilizer and the best and cheapest source of potassium oxide [13,14].

Rate of bioremediation vary with the soil, kind of environment, compound to be degraded, its concentration in the environment and microbial population ecology. A wide variety of non-linear models have been developed for the description of patterns of biodegradation of organic compounds that would occur in a host of different environmental circumstances including.

This work seeks to develop a model for rate of bioremediation of polluted soils under selected treatments, including addition of (PBA) as nutrients to enhance growth of indigenous bacteria.

A. Model Development

Oyoh and Osoka [15] developed models which they fit to experimental data from NPK fertilizer enhanced bioremediation; these models will be used in this work:

● if the microbial growth rate is exponential and its yield is constant we have:

$$S = S_0 + \frac{X_0}{Y_G}\left[1 - e^{\mu t}\right] \quad (1)$$

● if microbial growth rate is exponential but its yield is not constant we have:

$$S = S_0\left(e^{\mu t}\right)^{\frac{1}{Y_G}} \quad (2)$$

● if microbial growth rate has inhibition (logistic growth curve) with its yield being constant we have:

$$S = S_0 + \frac{X_0}{Y_G}\left[1 - \frac{e^{\mu t}}{1 - \gamma X_0\left(1 - e^{\mu t}\right)}\right] \quad (3)$$

● if microbial growth rate has inhibition (logistic growth curve) and its yield is not constant we have:

$$S = S_0\left(\frac{e^{\mu t}}{1 - \gamma X_0(1 - e^{\mu t})}\right)^{\frac{1}{Y_G}} \quad (4)$$

The above equations were fit to the experimental data in order to obtain the appropriate rate model for the degradation of the substrate through bioremediation.

Where: S is Substrate concentration {TPH (mg/g soil)}, S_0 is the initial substrate concentration (initial TPH), Xo is the initial microbial concentration, Y_G is the yield coefficient, μ is the specific growth rate of the microbes, γ is the inverse of the maximum microbial concentration and t is time (weeks).

II. MATERIALS AND METHODS

A. Materials and Apparatus:

The following materials and apparatus were used for the experiments;

a. Materials:

Palm Bunch Ash (PBA), Distilled water, Crude oil, Soil, Chloroform.

b. Apparatus:

Electronic weighing balance (LT 502),
Sieve (mesh size: 0.3 mm),
Jenway 6305 UV-VIS Spectrophotometer (AAS),
Stove, Sample bottles,
Gallenkamp Prime oven (ove-104-488x/71100-902),
Spatula, Buckets.

B. Experimental

a. Preparation of Palm Bunch Ash:

Palm Bunch Ash collected from Adapalm (Ohaji-Egbema L.G.A., Nigeria) was crushed, sieved and dried for ninety minutes in an oven at a temperature of 200 ^{0}C.

b. Preparation of Crude Oil-Contaminated Soil Samples:

Twelve 2.5-litre buckets were labeled A to L and 1500 g of soil was weighed and added to each of the twelve buckets. Crude oil was weighed and added to each of the soil samples as follows: 100 g to samples A,D,G,J, 200 g to samples B,E,H,K and 300 g to C,F,J,L.

The contents of the bucket were properly mixed after the addition of the oil and kept in a room, away from sunlight, rain and direct climatic influence. Eleven days after contaminating samples, the samples were tilled for about 2 minutes each to allow for aeration.

C. Analysis of Soil samples:

Two weeks after pollution, each set of soil samples were collected in sample bottles for analysis of the TPH content before addition of the ash as follows:

● 2 g of each sample was taken and put into sample bottles labeled A to L.
● 40 ml of chloroform was measured and added to each sample and the sample was tightly closed and thoroughly shaken for 2 minutes for proper mixing of contents.
● The mixtures in the bottles were left to stand for 2 days to allow for complete extraction of the crude oil by the chloroform.
● On the 4th day, each of the samples was decanted; the clear liquid was transferred to fresh sample bottles and the volume made up to 50 ml using chloroform.
● The UV-VIS spectrophotometer was standardized using chloroform for the blank, with wavelength set at 290 nm.

● The absorbance of sample A was measured immediately after completion of the last step and the digital readout of the instrument was recorded.
● The last two steps were repeated for each sample.

D. Addition of PBA:

PBA was then added to the samples as follows: 0 g to samples A,B,C; 100 g to samples D,E,F; 200 g to samples G,H,J, and 500 g to samples J,K,L. Each sample was tilled for 2 minutes every 24 hours and analysed every two weeks for eight weeks to determine the TPH content following the steps enumerated above.

Table 1: Quantities of Crude oil contamination and Ash in Soil samples A to L.

Quantity Of Oil (g)	100	200	300
Quantity of Ash			
0 g	**A**	**B**	**C**
100 g	**D**	**E**	**F**
200 g	**G**	**H**	**I**
500 g	**J**	**K**	**L**

III. RESULTS AND DISCUSSION

A. Analysis of results

The experimental data was fit to the models using the curve fitting tool box of Matlab 7.0 and only the model equation 3 (the logistic growth curve with constant yield) gave good fit results. The results are given below in figures 1, 2, 3 & 4, and in table 2.

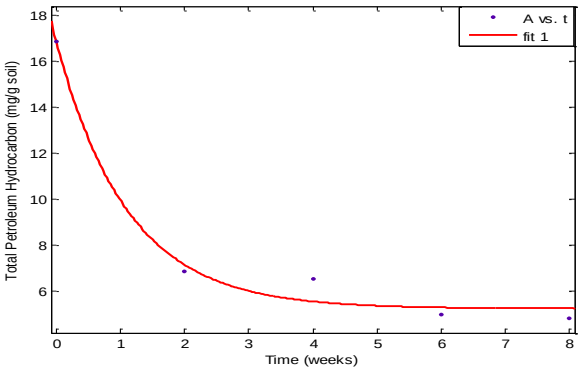

Fig. 1: Total Petroleum Hydrocarbon versus time for sample A

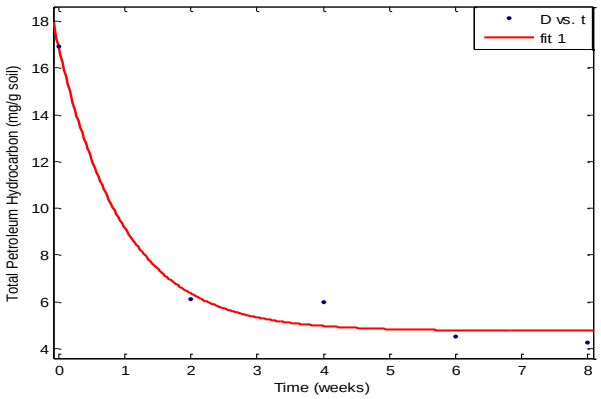

Fig. 2: Total Petroleum Hydrocarbon versus time for sample D

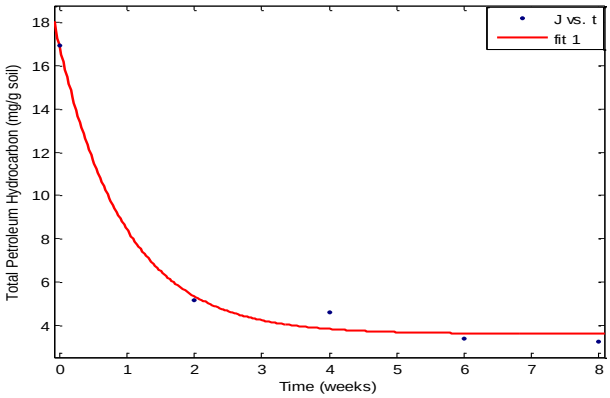

Fig. 3: Total Petroleum Hydrocarbon versus time for sample J

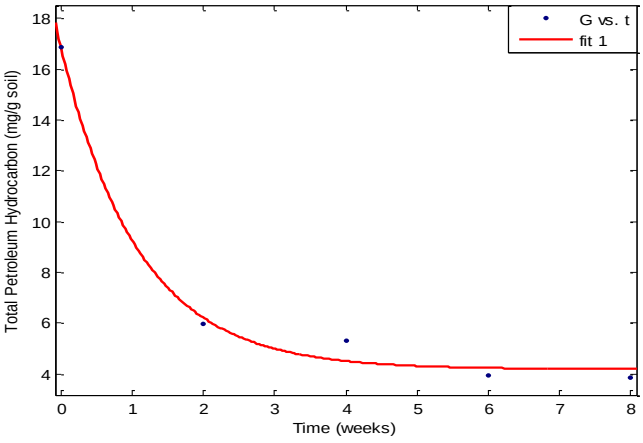

Fig. 4: Total Petroleum Hydrocarbon versus time for sample G

Table 2: Parameter values and Numerical fit results for all samples

Sample No	So (mg/g)	Xo/Y_G	μ	γXo	R^2	RMSE	SSE
A	16.859	4369	0.9041	0.9973	0.9867	0.8226	1.353
B	34.835	5468	1.319	0.9946	0.9979	0.8443	1.426
C	40.142	5854	1.352	0.9941	0.9984	0.8666	1.502
D	16.918	4628	1.017	0.9974	0.9875	0.8384	1.406
E	35.194	6620	1.326	0.9954	0.9980	0.8397	1.410
F	42.656	5387	1.438	0.9930	0.9987	0.8474	1.436
G	16.867	4755	0.9171	0.9973	0.9925	0.6709	0.9002
H	34.994	6239	1.385	0.9951	0.9982	0.8149	1.328
I	40.900	6153	1.442	0.9941	0.9988	0.8026	1.288
J	16.922	4448	1.017	0.9970	0.9938	0.6478	0.8393
K	34.276	5299	1.469	0.9943	0.9986	0.7038	0.9908
L	41.179	5467	1.552	0.9932	0.9992	0.6788	0.9215

B. Discussion of Results

Based on the graphical and numerical fit results for which only eqn. (3) fit the experimental data, we can deduce that the assumptions based on which eqn. (3) was developed are valid for the experimental data, thus:

- The growth of microbes for all samples, with or without addition of PBA, follows the Logistic growth curve.
- The yield coefficient (ratio of change in microbial population to change in substrate concentration) is a constant for each case.

The above is contrary to the observation of Oyoh and Osoka (2007) with fertilizer enhanced Bioremediation, where they observed a difference between the mechanisms of microbial growth for Samples without fertilizer application in comparison to those to which fertilizer was added. This case agrees only with the mechanism for the sample without fertilizer application in their work.

This may be explained by the fact that they used optimum loading of fertilizer and the fact that PBA contains basically Potassium, as against fertilizer which contains Nitrogen, Phosphorus and Potassium.

From the numerical fit results, that is, the values of Xo/Y_G, μ, γXo obtained we can deduce that:

- With the initial microbial population (Xo) assumed constant for all samples, then variations in Xo/Y_G are only attributable to variations in Y_G. The ratio increases with decrease in Y_G and vice versa. The yield coefficient (Y_G) is a measure of the extent to which substrate consumption results in microbial population growth. The yield coefficient tends to increase with increase in level of crude oil contamination, but decreases for a while with increase in quantity of PBA added before increasing.
- The specific growth rate (μ) increases with increase in amount of PBA added and also increases with increase in level of crude oil contamination. Increase in specific growth rate with level of contamination was more prominent when 500g of PBA was added, where it increased from 1.017 (Sample J) to 1.552 (Sample L).
- Thus the microbes grow faster in highly crude oil contaminated soil and crude oil contamination tends to foster microbial growth more than addition of PBA. As an example, Samples B and C differ by 100g increase in crude oil contamination and this increases specific growth rate by 0.033, while Samples B and E which differ by additional 100g PBA have only 0.007 increases in specific growth rate. The trend follows all through the work.
- γXo is the ratio of the initial microbial concentration to the final, thus the lower its value, the higher is the value of the final microbial population. γXo reduces steadily with increase in level of crude oil contamination, but with increase in amount of PBA, it tends to first increase and finally reduces.

IV. CONCLUSION

PBA enhanced Bioremediation follows the logistic growth curve for microbial population growth with the yield coefficient (ratio of microbial population increase per unit substrate consumed) being constant for each case, based on the model below:

$$S = S_0 + \frac{X_0}{Y_G}\left[1 - \frac{e^{\mu t}}{1 - \gamma X_0\left(1 - e^{\mu t}\right)}\right]$$

PBA enhances the rate of Bioremediation especially at low levels of crude oil contamination, because at higher levels of crude oil contamination, the contaminant itself fosters microbial growth at a faster rate than increased addition of PBA.

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