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Kinetic Model Development for Bioremediation of Petroleum Contaminated Soil Using Palm Bunch and Wood Ash

Z. R. Yelebe, R. J. Samuel and B. Z. Yelebe
Department of Chemical/Petroleum Engineering, Niger Delta University, Bayelsa State Nigeria

ABSTRACT : *The study of a kinetic model development for bioremediation of 1000g of petroleum (crude oil) contaminated soil to which a mixture of Palm Bunch Ash (PBA) and Wood Ash (WA) was added has been conducted based on Total Petroleum Hydrocarbon (THC) content. Three samples of soil contaminated with 50g, 100g and 150g of petroleum were collected and 0g of PBA or WA (this serves as control), 150g of WA, and 150g of PBA and WA was added to each sample to produce nine samples. Microbiological and physico-chemical properties such as moisture content, pH, organic carbon and total nitrogen of the contaminated soil were investigated at two weeks interval after pollution up to twenty weeks. The results reveal that the percentage reduction in Total Hydrocarbon Content was higher for Palm Bunch Ash and Wood Ash treatment options. The experiment also revealed that bioremediation occurred in all samples including the control samples to which no PBA or WA was added, hence, natural attenuation. After twenty weeks interval, 99.5% THC reduction occurred in the sample that was polluted with 50g of petroleum and treated with 150g of PBA and WA. Thus, a mixture of PBA and WA is a good substitute for NPK fertilizer for bioremediation considering the low costs of PBA and WA, and high percentage reduction in THC.*

KEYWORDS: - *ash, bioremediation, kinetic, petroleum, soil.*

I. INTRODUCTION

Bioremediation is the use of biological organisms or processes to degrade, breakdown, transform, and/or essentially remove contaminants or impairments of quality from soil and water [1]. Advanced countries may have done much in bioremediation, but little is known about the kinetics of bioremediation and how it affects the performance of several available bioremediation options. This is necessary to optimize this remediation technique for communities that are fast losing their arable land to degradation due to the scourge of oil pollution.

Contamination of soils, groundwater, sediments, surface water, and air with hazardous and toxic chemicals is one of the major problems facing the industrialized world today. The national priority list currently contains over 1200 sites, with potential sites numbering over 32 000. The need to remediate these sites has led to the development in new technologies that emphasize the destruction of the pollutants rather than the conventional approach of disposal [1].

A number of different technologies can be applied for the direct remediation of oil-contaminated soils, and among them bioremediation accounts for 5 to 10 percent of all pollution treatment but it may be the most cost effective process for treating lightly or moderately contaminated soils [2]. Since the Gulf War in 1991, numerous remediation investigations have been applied to desert soils in Kuwait contaminated by oil. For example, investigations have been made on: treating both lightly and heavily oil contaminated soils using windrow soil pile systems; the use of land farming, windrow composting piles and static bio-venting piles; and the role of white rot fungi on remediating oil-contaminated soil in the Gulf area [2].

Bioremediation, defined as the use of microorganisms for the degradation or removal of environmental pollutants, is an established and feasible technique currently being used by the United States Environmental Protection Agency for the removal of contamination from soil [3]. Bioremediation techniques, especially with natural (not engineered) microbial populations, enjoy increased public acceptance and support because of their environmentally friendly strategies. Knowledge in the field of bioremediation is growing rapidly, but there are still large gaps in our understanding of the complex processes involved [3]. However, in soil bioremediation bacteria are mainly applied because they are distinguished by high frequency, fast growth and a wide spectrum of the utilized petroleum products [4].

Pollutants are persistent chemical compounds that are toxic (poisonous) to plants and animals or have the potential to cause birth defects (teratogenicity) or cancer (carcinogenicity) in humans [5]. The use of microorganisms are to alter and breakdown petroleum hydrocarbons into carbon dioxide, water and partially oxidized biologically inert products so that land will be good for farming [6].

Bioremediation works best on natural carbon-containing substances called hydrocarbon or on chemicals resembling natural substances. Bacteria that metabolize naturally occurring hydrocarbons, such as certain petroleum products are widespread in the environment. Certain bacteria that biodegrade gasoline, for example found in almost all soils are; the gasoline-metabolizing bacteria may be isolated from the bacteria employed in bioremediation include members of the genera pseudomonas, Flavobacterium, Arthrobacter, and Azotobacter. Some toxic substances that have been successfully bio-remediated include the solvent toluene, the moth repellant naphthalene (mothballs), the herbicide 2, 4-dichlorophenoxyacetic acid (2, 4-D), and the fungicide and wood preservative pentachlorophenol [5].

Palm bunch ash is obtained from 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 [7]. Report also has it that Palm Bunch Ash contains mainly Potassium Carbonate and Potassium Hydroxide. Palm Bunch Ash has also been recognized as a 100% organic fertilizer and the best and cheapest source of potassium oxide [8].

Wood ash has been used in agricultural soil applications as it recycles nutrients back to the land. Wood ash has some value as a fertilizer, but does not contain nitrogen. Because of the presence of calcium carbonate it acts as a liming agent and will de-acidify the soil increasing its pH [9].

In this paper two bioremediation options, palm bunch ash, and wood ash, including control will be studied to treat petroleum contaminated soils. The treatment will involve using wood ash only, and using palm bunch ash together with wood ash.

II. MODELING THE RATE OF BIODEGRADATION

The Microbial Growth: The mathematical description of the rate of growth of a microbial culture frequently makes use of an exponential growth pattern. Malthus' law gives exponential growth as [10]:

$$\frac{dX}{dt} = \mu X \tag{1}$$

On integration it gives:

$$X = X_0 e^{\mu t} \tag{2}$$

This growth, however, cannot be sustained indefinitely and for one reason or another will lead to a stationary phase. Pearl and Reed [10] modified the exponential growth equation by adding a further term to account for 'inhibition' at high biomass concentration:

$$\frac{dX}{dt} = \mu X - \mu\gamma X^2 \tag{3}$$

On integration it gives:

$$X = \frac{X_0 e^{\mu t}}{1 - \gamma X_0 (1 - e^{\mu t})} \tag{4}$$

This is logistic equation

2.1 Substrate Degradation and Yield Coefficient

When the yield is considered constant we have:

$$Y = \frac{\Delta X}{-\Delta S} \tag{5}$$

A material balance for the consumption of substrate gives

$$\frac{dS}{dt} = \frac{1}{Y_G}\frac{dX}{dt} + mX \tag{6}$$

Substrate consumed for growth is usually much larger than that consumed for maintenance, such that equation (6) can be simplified thus:

$$\frac{dS}{dt} = \frac{1}{Y_G}\frac{dX}{dt} \tag{7}$$

2.2 Modification of Yield Coefficient

For the purpose of this study, a new definition is proposed for the yield coefficient at times when it is not a constant quantity. In this definition averages of mass of product obtained (change in biomass concentration) and average of reactant consumed (change in substrate concentration) are used instead. The use of averages will normalize the variation of yield with time, so we have:

$$Y_m = \frac{\Delta X / X}{-\Delta S / S} \quad (8)$$

Equation (13) will take the form:

$$\frac{1}{S}\frac{dS}{dt} = \frac{1}{Y_{mG}}\frac{1}{X}\frac{dX}{dt} \quad (9)$$

It can be written as:

$$\frac{d(\ln S)}{dt} = \frac{1}{Y_{mG}}\frac{d(\ln X)}{dt} \quad (10)$$

On Integration it gives.

$$S = S_0\left(\frac{X}{X_0}\right)^{\frac{1}{Y_{mG}}} \quad (11)$$

Equations (7) and (11) can be applied for either exponential growth model or logistic model to obtain:

<u>Exponential Growth With Constant Yield</u>

$$S = S_0 + \frac{X_0}{Y_G}\left[1 - e^{\mu t}\right] \quad (12)$$

<u>Exponential Growth With Varying Yield</u>

$$S = S_0\left(e^{\mu t}\right)^{\frac{1}{Y_G}} \quad (13)$$

<u>Logistic Model With Constant Yield</u>

$$S = S_0 + \frac{X_0}{Y_G}\left[1 - \frac{e^{\mu t}}{1 - \gamma X_0\left(1 - e^{\mu t}\right)}\right] \quad (14)$$

<u>Logistic Model With Varying Yield</u>

$$S = S_0\left(\frac{e^{\mu t}}{1 - \gamma X_0(1 - e^{\mu t})}\right)^{\frac{1}{Y_G}} \quad (15)$$

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

Where: S is Substrate concentration (Total Petroleum Hydrocarbon, TPH (mg/g soil)), S_0 is the initial substrate concentration (initial TPH), X_0 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 (week) [6], [11], [12].

III. MATERIALS AND METHOD

3.1 Study Area

This study was carried out in Niger Delta University, Wilberforce Island, Amassoma, Bayelsa State, South-South Nigeria. Land in this area is mostly used for agriculture, mixed cropping being apparently the most common method of agriculture. Lands are also used for settlement and other activities.

3.2 Field Sampling

Soil samples were collected by digging with spade to at least 30cm depth. This was done before the commencement of treatment to enable the comparison on efficiency of treatment options. The soil samples were collected at one point.

3.2.1 *Materials*: Palm Bunch Ash (PBA), Wood Ash (WA), Distilled water, Crude oil, Soil, Chloroform.

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

3.2.3 *Preparation of Palm Bunch Ash and Wood Ash*: Palm Bunch Ash and Wood Ash collected from Awegbene (Sagbama L.G.A., Nigeria) was crushed, sieved and dried for ninety minutes in an oven at a temperature of 200^{O}C.

3.2.4 Preparation of petroleum (crude oil) contaminated Soil samples: Crude oil was collected from Ogboinbiri flow station located at Southern-Ijaw L.G.A of Bayelsa State Nigeria. Nine 2.5-litre buckets were labeled A to I and 1000g of soil was weighed and added to each of the nine buckets. Crude oil was weighed and added to each of the soil samples as follows: 50g to samples A,D,G, 100g to samples B,E,H, and 150g to C,F,I.

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. Ten days after the pollution of the soil samples, the samples were tilled for about five minutes each to allow aeration.

3.2.5 Addition of Palm bunch ash and Wood ash: PBA and WA was added to the samples as follows: 0g (i.e. no PBA or WA) to samples A, B, C; 150g (only WA) to samples D, E, F; 150g (PBA + WA) to G, H, I; as shown in Table 1. Each sample was tilled for 5minutes every 24 hours and analyzed every two weeks for twenty weeks.

3.2.6

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

Quantity Of Crude Oil	50g	100g	150g
Quantity of Ash			
0g (no ash)	A	B	C
150g of WA	D	E	F
150g of PBA + WA	G	H	I

IV. RESULTS AND DISCUSSION

Samples A, D and G were selected for analysis based on the experimental results and fitted with model equations. The samples were chosen due to low petroleum contaminant (50g) and the potency of the treatment method. The results from experiment fitted with model equations are presented below.

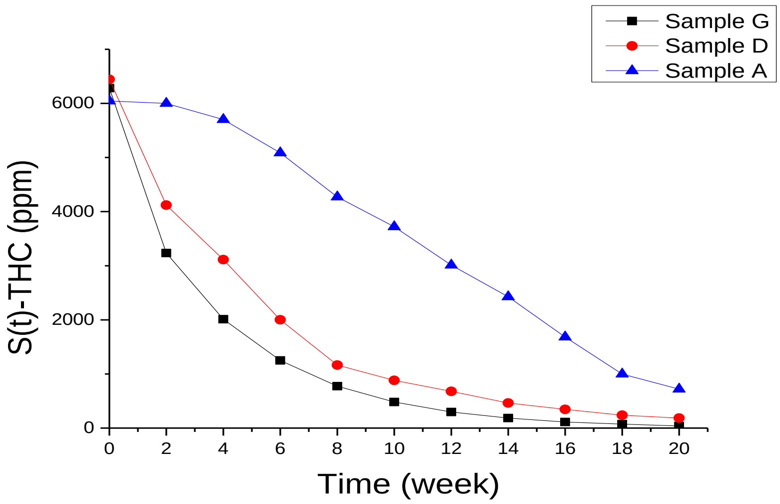

Fig. 1: THC versus time (fitted using Exp. Growth equation with constant yield)

Fig. 1 shows that bioremediation took place and the total hydrocarbon content decreased. The initial values of total hydrocarbon content contaminated with the same gram of crude oil are almost the same before the time of treatment. During treatment it was observed that the reduction in THC was higher for those in which wood ash and palm bunch ash was used together followed by the single wood ash addition and the controls. This is due to the fact that wood ash and palm bunch ash serves as organic fertilizer which enhances the growth of microorganisms that degrade the crude oil in the soil at a faster rate.

Fig. 1 also shows that sample A which is the control with 50g of crude oil also degraded. This is to show that bioremediation occurs naturally without addition of nutrients to the soil (natural attenuation) though, this takes longer time. Sample D also showed high reduction in THC revealing that the addition of wood ash alone increases the rate of bioremediation. Sample G showed the highest reduction in THC revealing that the combination of PBA and WA is more effective than the use of PBA or WA alone.

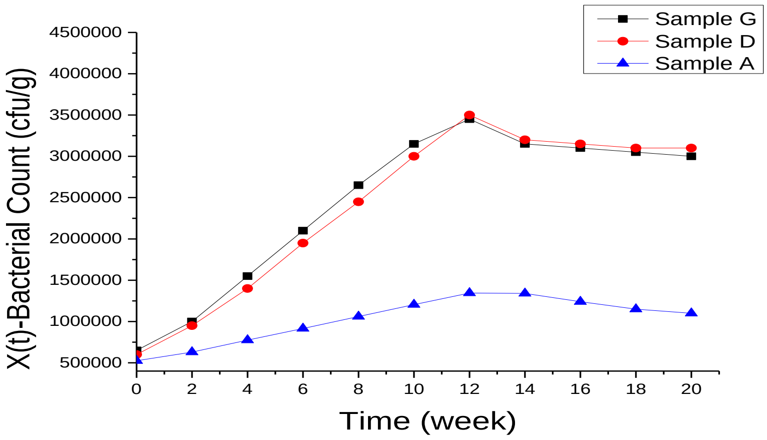

Fig. 2: Bacterial count versus time (fitted using Exp. Growth equation)

Fig. 2 shows an accelerated growth of microbes. The acceleration of growth of microbe during the bioremediation process is indicative of the ability of indigenous microorganisms to adapt to the presence of the contaminants and bring about their transformation to reduce levels of contamination in the soil. Maximum growth of microbes occurred at the twelfth week.

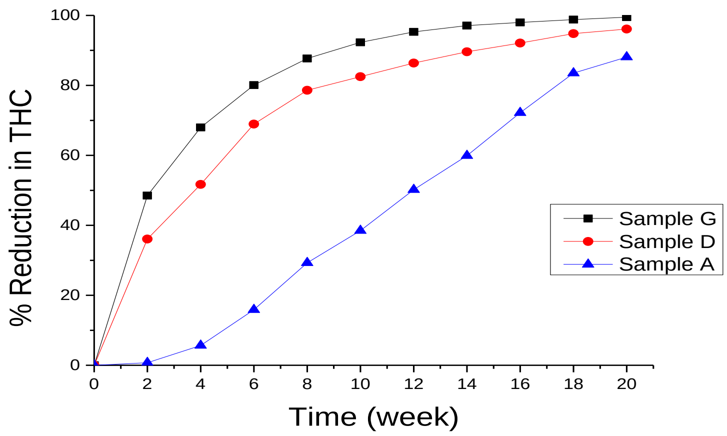

Fig. 3: Percentage Reduction in THC versus time for Samples A, D and G

Fig. 3 shows that Sample G recorded higher percentage reduction in THC as about 99.5% reduction is observed in six weeks of treatment. This suggests a possibility of complete treatment and restoration of quality of contaminated soil in the next few weeks. Sample A with no ash added takes a longer recovery period and percentage reduction at the end of the treated period shows 86%. While the percentage reduction for Sample D at the end of the treated period is 95%.

4.1 Analysis of Some Physico-Chemical Properties of the Polluted Soil

pH: soil pH [in water (1:2; soil to water ratio)] was determined using air-dry soil samples (passed through a 2mm sieve). The pH values were determined using a Philip's digital pH meter [13]. The soil suspension was not stirred during the measurement.

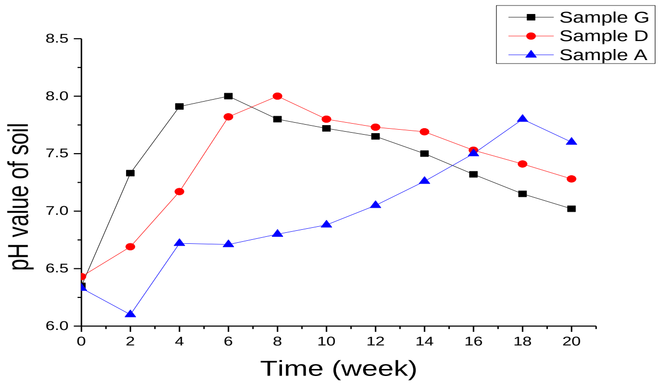

Fig. 4: pH versus time for Samples A, D and G

Fig. 4 shows the pH value for the samples. Sample A shows a slight decrease in the second week of treatment and followed by an increase in the fourth week. The decrease in pH value can be due to local decomposition of organic residue to acid or CO_2 evolution, while the increase in the pH value may be a result of bicarbonate accumulation during biodegradation of petroleum compounds by microorganisms. Samples D and G that ashes were added show greater increase in pH because palm bunch ash contains Potassium Carbonate and Potassium hydroxide and while wood ash contains Calcium Carbonate which when added to water turns basic (alkaline) which increases the pH value.

4.1.1 *Moisture Content*: The procedure is as follows [14]:

$$\text{Moisture content (\%)} = \frac{(w1 - w2) \times 100}{w1}$$

w1 = weight (g) of sample before drying
w2 = Weigh (g) of sample before after drying.

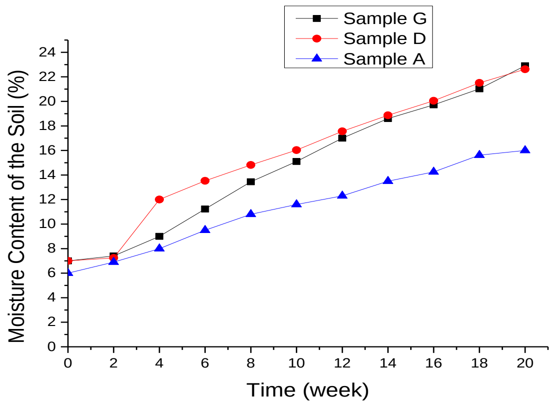

Fig. 5: Moisture Content versus time for Samples A, D and G

Fig. 5 shows that there was increase in the moisture contents of the soil for all the samples including the controls. The increase in moisture content indicates that the microorganisms degraded hydrocarbons in the soil and water which is one of the two products of degradation, the other being carbon dioxide was produced. A little increment in moisture content of the soil was observed in week 2 for Sample D and G due to the addition of ashes that absorbed water into itself but above week 2 there was significance increase.

4.1.2 *Total Nitrogen:* This was measured using the Kjeldahl method [13], [15]:

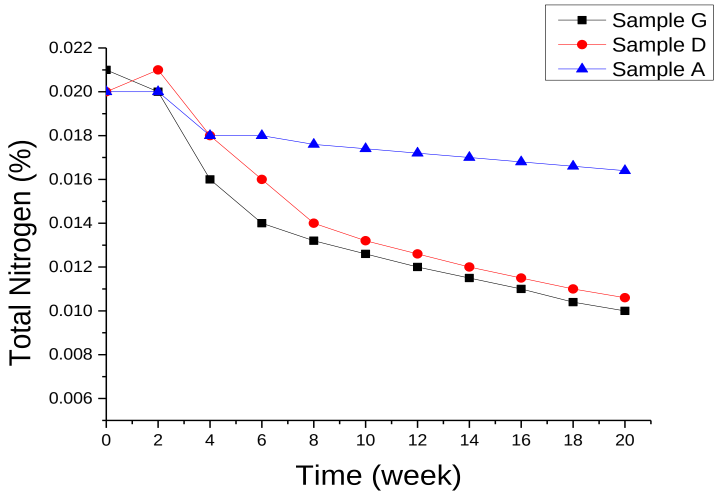

Fig. 6: Total Nitrogen versus time for Samples A, D and G

Fig. 6 shows a decrease in Total Nitrogen. This is contrary to the observation of Oyoh and Osoka[6] with NPK fertilizer which they reported an increase. This can be attributed to the fact that wood ash contains Calcium Carbonate and palm bunch ash contains basically Potassium, as against NPK fertilizer which contains Nitrogen, Potassium and Phosphorus. Nitrogen reduction as total hydrocarbon content reduced indicates that Nitrogen concentration can be used as fertilizers to the microbes that degrade the crude oil. The microbes make use of Nitrate and Phosphate in the degradation process.

4.1.3 Organic Carbon: The wet oxidation method of Walkley and Black [16] was used in determining the organic carbon content.

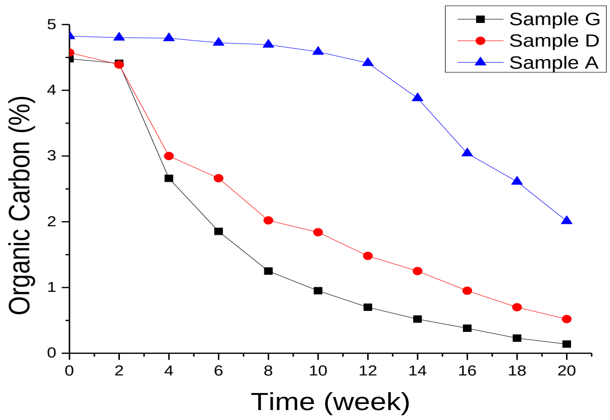

Fig. 7: Organic Carbon versus time for Samples A, D and G

Fig. 7 shows that Organic Carbon decreased. This reduction is due to the fact that hydrocarbon with its major constituent carbon and hydrogen are broken down by microorganisms to form CO_2 and H_2O and therefore the CO_2 escape leaving a reduced Carbon content in the soil.

V. CONCLUSION

This study showed that bioremediation can occur naturally with or without addition of nutrients to the soil (natural attenuation). Addition of nutrients palm bunch ash and wood ash in this case, increases the rate of bioremediation. This increase is more found for low crude oil contaminations than it is at high crude oil contaminations.

Consideration of bioremediation for remediation of a site contaminated with crude oil requires a detailed site, soil, and waste characterization that must be conducted in order to evaluate the potential application of the technology at the site and to demonstrate the feasibility of the approach.

The microbial growth rate follows the exponential growth curve for all treatment options

$$X = X_0 e^{\mu t}$$

The Palm Bunch Ash and Wood Ash enhanced Bioremediation follows the exponential growth curve when yield is considered constant

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

The study also showed that some physico-chemical properties such as pH and moisture content of the contaminated soil increased while total nitrogen, phosphorus and organic carbon reduced during bioremediation.

The study also revealed that bioremediation occurred in all samples including the control samples to which no PBA or WA was added. After twenty weeks interval 99.5% THC reduction occurred in the sample which was polluted with 50g of petroleum and treated with 150g of PBA and WA, whereas other samples showed lower percentage reduction in THC. Thus, a mixture of PBA and WA is a good substitute for NPK fertilizer for bioremediation considering the low costs of PBA and WA, and high percentage reduction in THC.

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