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# Kinetic Model for Crude Oil Degradation Using Moringa Extract

**C. P. Ukpaka**

Department Of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology,
Nkpolu, P.M.B. 5080, Port Harcourt, Nigeria.
*chukwuemeka24@yahoo.com*

**I. E Udeh**

Department of Chemical/Petroleum Engineering,
Niger Delta University Wilberforce Island, Bayelsa State, Nigeria.

**Abstract :** *Crude oil spillage on land is a major undeniable challenge we face in the Niger Delta, this is as a result of the oil exploration and exploitation activity done by the big oil multinationals and also those done by indigenous private firms, the petroleum could find its way to the soil via occurrences including pipeline leakages and explosions, corrosion of underground pipes transporting crude oil and petroleum product and also it could come purely in form of untreated industrial waste. As a result of the foregoing this research work was conducted using Moringa leave extract, and the component of interest included phosphates, potassium and nitrogen which are the major stimulators of bioremediation, this components were found to be abundant in the Moringa Oleifera leave extract. The application of Moringa leave extract was found to be useful in the enhancing of crude oil polluted lands, and by so doing it facilitates the rehabilitation of the contaminated soil as well as reinstating the soil constituents for agricultural purposes. This is a new research investigation which show high efficiency in bioremediation program the maximum specific rate and the rate constants as well as they overall order of the bioremediation reaction were determined, using the principle of the rate laws as well as they Monod's equation from which the line waver burke plot was obtained. Therefore the experiment as well as the theoretical model developed can be used to monitor, predict and simulate the rate of degradation of hydrocarbons present in a polluted soil undergoing bioremediation under the influence of Moringa Oleifera leave extract.*

**Keywords :** *kinetics, moringa extract, model, crde oil, degradation, oleifera leave*

## 1. INTRODUCTION

Moringa is the sole genus in the family of plants moringaceae Moringa oleifera. is one of the 14 species of family Moringaceae, native to India, Africa, Arabia, Southeast Asia, South America, and the Pacific and Caribbean Islands, it ranges in size from tiny herbs to massive trees. It iss the most widely cultivated species in the family moringaceae Because M. oleifera has been naturalized in many tropic and sub-tropic regions worldwide, the plant is referred to by a number of names such as horseradish tree, drumstick tree, ben oil tree, miracle tree, and "Mother's Best Friend", the Moringa tree was introduced to Africa from India at the turn ofthe twentieth century where it was to be used as a health supplement. The Moringa plant has been consumed by humans throughout the century in diverse culinary ways. Almost all parts of the plant are used culturally for its nutritional value, purported medicinal properties and for taste and flavor as a vegetable and seed. The leaves of M. oleifera can be eaten fresh, cooked, or stored as a dried powder for many months reportedly without any major loss of its nutritional value. Epidemiological studies have indicated that Moringa oleifera leaves are a good source of nutrition and exhibit anti-tumor, anti-inflammatory, anti-ulcer, anti-atherosclerotic and anti-convulsant activities. The investigation of the different parts of the plant is multidisciplinary, including but not limited to nutrition, ethnobotany, medicine, analytical chemistry, chemical engineering and anthropology. Moringa oleifera leaves and seed powder has also been used in various chemical engineering processes such as water purification and decoagulation. This study is aimed at investigating the activity of moringa leaf extract as an activator of the moringa leave bagasse in cleaning up crude oil polluted soils (Ukpaka,and Farrow, 2009, Prince, 1999; Ogoni, 2001; Amadi, et al; 1993& Octave and Levenspiel, 2004).

Moringa is a tree ranging in height from 5-12 m with an open umbrella-shaped crown, straight trunk (10-30 cm thick) and a corky, whitish bark. The plant (depending on climate) has leaflets 1-2 cm in diameter and 1.5-2.5 cm in length. The tree produces a tuberous tap root which explains its tolerance to drought conditions. Originally considered a tree of hot semi-arid regions (annual rainfall 250-1500 mm), Moringa is adaptable to a wide range of environmental conditions from hot and dry to hot, humid, wet conditions. The tree is tolerant to light frosts, but does not survive as a perennial under freezing conditions. Moringa grows more rapidly, reaching higher heights, when found in well-drained soils with ample water, but tolerates bot sandy soils, heavier clay soils and water limited conditions (Ukpaka and Oboho, 2006; Meisam et al 2010; Siron, 1993; Murphyt and Brouwer, 1995; &Amadi and Antal, 1991). The tree can be established in slightly alkaline soils up to pH 9 as well as acidic soils as low as pH 4.5 and is well suited for a wide range of adverse environments that would not be suitable for other fruit, nut and tree crops. Moringa can be found in the wild or cultivated and sold as a supplement on the health market In India and different parts of Africa, it is cultivated on a large scale in nurseries or orchards. Cultivation entails collection of seeds from the tree, development of plantlets in the greenhouse for 2 to 3 months and transplantation ofmature stems (1-1.5 m long) to the main fields. The leaves, seeds, flowers, pods (fruit), bark and roots are all seen as a vegetable and each part is uniquely harvested and utilized. For example, fresh leaves arepicked, shade dried, ground to a powder, and then stored for later as a food flavoring or additive. Dried or fresh leaves are also used in foods such as soups and porridges (Bertrand et al, 1993), curry gravy and in noodles, rice or wheat. Farmers have added the leaves to animal feed to maintain a healthy livestock while utilizing the manure and vegetable compost for crop growth (Ukpaka, 2006a); applications include the use of Moringa powder as a fish food in aquacultural systems and the Moringa leaves as a protein supplement for animals, such as cows.With the leaves being rich in nutrients, pregnant women and lactating mothers use the powdered leaves to enhance their child's or children's nourishment, especially in developing countries suffering from malnutrition. The seeds contain much of the plant's edible oil which is used as a cooking oil for frying and as a salad oil for dressing (Ukpaka, 2006b; Lendlem, 2002;; Magnusson, 1998; Luizer, 1992; Van Hamme, 2000 &Wami, 1997).

Some important uses of moringa oleifera leave seed and its extracts is detailed below as: Most of the parts of the plant possess antimicrobial activity. They are well known for their pharmacological actions too and are used for the traditional treatment of diabetes mellitus hepatotoxicity, rheumatism, venomous bites and also for cardiac stimulation; Grinded moringa seeds have been used for water clarification in order to remove suspended matter and other physically combined impurities in water; researches have been done on its food preservation ability, generally moringa oleifera has a good antibacterial activity thus they can serve as good food preservatives under certain conditions, moringa leaf tea has been found to cure stress related illnesses such as hypertension, high blood pressure; moringa leaf is a good source/ reservoir of nutrients generally for both plants animals and certain microbes;moringa oleifera leaf and seed can be eaten in the raw form as a source of food; moringa can also used for tired blood (anemia) anthrithis and other joint pains, diarrhea, epilepsy, and stomach pain thyroid disorders etc; it can also be used as an aphrodisiac; it can also be used as an additive in haircare products and moringa is also used to reduce swellings in the body (Ukpaka, 2011).

Moringa oleifera as pointed out earlier has been subject to a number of researches , many research work has been done on its medicinal, nutritional, water purification and even its ability to extract heavy metals from solutions in which they are dissolved, but little to no attention has been given to investigating its bioremediation activity in crude oil soiled environment thus the aim of this research work is to investigate the activities of moringa oleifera in remediation of crude oil soiled environment (Ukpaka, 2006).

In the Niger Delta region of Nigeria the activities of oil exploration and exploitation companies has led to a high level of pollution of the soil that constitute valuable farmlands with crude oil and its process effluents this has led to loss of arable lands and heavy economic losses it has also damaged the flora and the fauna of the region, also the constant pipeline explosions and leakages in waterways and creeks has rendered the marine and aquatic life of the region at a high risk thus there is a need to proffer solutions to all these industrial inefficiencies and challenges if we hope to sustain an industrialised society and good economic returns in the Niger Delta region of Nigeria.

Aims and objectives of the study is as stated such as: to study the activity of moringa leave extract as a bio-stimulator in the bioremediation of crude oil soiled environment,to relate the kinetics of the bioremediation work to the Monod's equation, to come up with models to predict the rate of

bioremediation with Moringa leaf extract as a bio-stimulator, To study the effect of P.H and nutrients in the inhibition of bioremediation reactions and to proffer viable solution to the problems of oil spillage on the lands of the Niger Delta.This study would investigate the constituents of the species moringa oleifera leave extractalso this paper would also study they action of moringa leaf as an activator bioremediation of crude oil polluted soil environment we would also investigate the active components of the moringa leave extract in the biodegradation process and relate the process to the Monod's equation in order to help us ascertain the kinetics of the bioremediation process. This exploration of the micro-organism present in the soil sample used is beyond the scope of this work this work is specifically concerned with the bioremediation process and not the micro-organism responsible for the bioremediation.

## 2. MATERIAL AND METHODS

### 2.1 Development of the Model To Relate Reduction in Concentration and Time

[Crude oil + soil + Moringa leaf extract]mixed+ Micro-organisms $\longrightarrow$

Microbes + CO2+ New biomass (1)

Can be simplified into the following

A + E $\longrightarrow$ E + P (2)

We can also represent the rate equation of the bioremediation having an nth order and a rate constant k as

$$\int_{C0}^{C} \frac{dC}{dt} = -KC^n \quad (3)$$

Equation (3) can be rearranged to obtain

$$\int_{c0}^{c} \frac{dC}{C^n} = \int_0^t -kdt \quad (4)$$

Integrating equation (4) and taking its limits

$$\frac{C^{1-n}}{1-n} - \frac{Co^{1-n}}{1-n} = -kt \quad (5)$$

$$\frac{C^{1-n} - Co^{1-n}}{1-n} = -kt \quad (6)$$

Equation (6) can ten be written as

$$C^{1-n} = Co^{1-n} - (1-n)kt \quad (7)$$

The above equation can be used to predict the concentration of crude oil present in the soil at any time t as the remediation proceeds

In order to obtain the K and n of the reaction we make use of the fractional conversion method. As stated in chemical reaction engineering by octave and levienspiel

$$T_F = \frac{F^{1-n}-1}{K(n-1)} Co^{1-n} \quad (8)$$

Where, Tf = time needed for fractional conversion, F = fractional conversion

K= rate constant of reaction, n = order of the reaction

Next we take the logarithm of both sides of the equation to obtain

$$logT_F = log(\frac{F^{1-n}-1}{K(n-1)}) + (n-1)logCo \quad (8i)$$

In order to obtain the value of n we plot a graph of logTf versus log Co in which

Slope = (n-1) (9)

From which the value of n can be obtained.

To obtain the value of k we substitute the vaiue of n and the other known values we are left with only k as the unknown from which we can solve to obtain the value of k

We can further develop a model that relates specific rate of the bioremediation reaction, the initial concentration of the Moringa oleifera extract and the rate constant by means of the monod's equation

$$V = \frac{V_{max}[S]}{K+[S]} \quad (10)$$

Where S = initial concentration of Moringa leaf extract [M],K =specific rate constant of the bioremediation reaction stimulated by Moringa Oleifera extract

Vmax= maximum attainable rate of crude disappearance

Equation (10) can be re-written as :

$$V = \frac{V_{max}[M]}{K+[M]} \quad (11)$$

Model of the pH as an inhibitor or activator

The monods equation for the mechanism of inhibition is stated as

$$V = \frac{V_{max}[M]}{K+[M]} \times I \quad (12)$$

In a situation where the pH is an activator that is the increment in pH favours the bioremediation reaction the inhibitor is represented as

$$\text{I} = P^H \quad (13)$$

Therefore,

Equation (12) becomes

$$V = \frac{V_{max}[M]}{K+[M]} \times P^H \quad (14)$$

This only holds if an increase in the pH favours the bioremediation reaction.

In a situation where an increase in pH acts as an inhibitor to the bioremediation reaction the inhibition is represented as

$$\text{I} = \frac{1}{P^H} \quad (15)$$

Equation (12) theoretically becomes

$$V = \frac{V_{max}[M]}{K+[M]} \times \frac{1}{P^H} \quad (16)$$

Equation (16) is only valid in a bioremediation reaction in which the increment in the pH inhibits .

Equation (7) can also be related to equation (11) this can help us establish the concentration of the crude oil in the soil undergoing bioremediation at any time T knowing the initial concentration of Moringa introduced into the soil.

Defining equation (11) in terms of michealis menten terms it becomes

$$C = \frac{C_{max}[M]}{K+[M]} \quad (17)$$

But from equation (7)

$$C^{1-n} = Co^{1-n} - (1-n)kt$$

Therefore equation (17) becomes

$$Co^{1-n} - (1-n)kt = \frac{[Co^{1-n} - (1-n)kt]_{max} \times [M]}{K+[M]} \quad (18)$$

The above equation can be written in terms of the line waver burke plot just like

The monod's equation is expressed as

$$\frac{1}{V} = \frac{K}{V_{max}[S]} + \frac{1}{V_{max}} \quad (19)$$

Thus we see that we can express equation (19) in the line waver burke plot

$$\frac{1}{Co^{1-n}-Kt(1-n)} = \frac{K}{[Co^{1-n}-Kt(1-n)]_{max}[S]} + \frac{1}{Co^{1-n}-Kt(1-n)_{max}} \quad (20)$$

We can also obtain the specific bioremediation rate constant and the maximum rate of bioremediation by plotting the line weaver burke plot of

$$\frac{1}{V} = \frac{K}{V_{max}[Co]} + \frac{1}{V_{max}} \quad ; \text{-V=kCn} \quad (21)$$

Where ,-V= rate of reaction, K= specific rate of bioremediation, C=concentration of crude present in the soil , K= rate constant of reaction

To obtain the values of k and –Vmax we plot a graph of $\frac{1}{V}$ vs $\frac{1}{Co}$ having an intercept of $\frac{1}{V_{max}}$ also, K can be obtained from slope given as $\frac{K}{V_{max}[Co]}$.

The work is concerned with the investigation of the kinetics of crude oil degradation using moringa extract. Before we can attempt to study the action of this leaf extract on crude oil polluted soil environment it is necessary to find out the characteristic constituents of the Moringa leaf extract and the composition of certain important elements/compounds that aid biodegradation that are present in the Moringa oleifera leaf extract and also find out if and microorganism that can thrive in the media of the Moringa oleifera leaf extract.

There are certain microorganisms that are actually responsible for the bioremediation process and these microbes secrete enzymes that help them to break down this crude oil in the soil into consumable substances. The response of these microorganisms to Moringa oleifera leaf extract is of utmost importance to this work. If the Moringa oleifera aids the growth of the microbes this in turn will help influence the bioremediation process

### 2.2 The Moringa Leaf Sample Collection Extract Preparation

The moringa oleifera leave was gotten from agudama epie community in yenagoa local government area of bayelsa state nigeria.

A juice extractor was used to extract the Moringa juice from the Moringa leaf immediately they were harvested and then the Moringa juice/ extract and the left over chaff were refrigerated immediately.

Two different kinds of analysis were carried out on the Moringa oleifera juice extract namely

1. microbial analysis; to find out if the extract can support micro-organisms.
2. Chemical analysis; to find out the presence and composition of certain chemical species in the extract.

### 2.3 Determination of total petroleum hydrocarbon (TPH)

Reagents

1. Hydrochloric acid
2. Tetra-chloromethane Apparatus

*1. Buck Model HC-404 System*

Weigh out 5g of oven dried soil, after which acidify soil with HCl to minimize contaminants and kill microbes. Pipette in 60ml of CCl4 and combine it with the soil to extract the TPH materials, after which filter solution containing the extract from the suspension. Transfer filtrate into cuvette and place into the Buck Model HC-404 with standard 10mm IR Quartz Cuvette instruments, cell holder the ppm of TPH present in sample will be displayed in the visual display unit of the instrument.

## 3. RESULTS AND DISCUSSION

Based on the experiment conducted it was observed that the rate of disappearance of the TPH increased as the amount of the bio-stimulant Moringa Oleifera leave extract increased notice that reactor H its concentration reaches d lowest value by a lot of margin and in reactor C, its TPH reduced but it isn't as much as it is in reactor H, this is as a result of the fact that the Moringa Oleifera contains in it certain nutrients in the form of phosphates and nitrates that are very important in bioremediation process because the help to supply nutrients to the soil and in so doing the microbes responsible for the bioremediation feed on this nutrient and as they do that the reproduce and thus their population

increases as the population increases more microbes become available to breakdown the crude oil in the soil thus the crude oil present in the soil experiences a continual decrease. Thus an increase in the quantity of Moringa Oleifera brings about an increment in the nutrients supplied to the soil this in turn stimulates the bioremediation.The results of the crude iol degradation is illustrated in table 1 and figure 1 for various reactor studied as well as upon the influence of moringa extract.

**Table1.***Concentration of TPH of the samples as recorded on a 2 day interval for 16 days*

| Reactor Time(days) | $A_w$C (ppm) | $D_d$C (ppm) | $H_w$12 (ppm) | $F_d$12 (ppm) | $B_w$9 (ppm) | $U_d$9 (ppm) | $C_w$6 (ppm) | $G_d$6 (ppm) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.062 | 0.06 | 0.059 | 0.058 | 0.057 | 0.063 | 0.059 | 0.062 |
| 2 | 0.061 | 0.06 | 0.054 | 0.057 | 0.051 | 0.057 | 0.056 | 0.06 |
| 4 | 0.060 | 0.059 | 0.047 | 0.049 | 0.049 | 0.051 | 0.05 | 0.058 |
| 6 | 0.061 | 0.06 | 0.041 | 0.045 | 0.048 | 0.046 | 0.049 | 0.054 |
| 8 | 0.059 | 0.06 | 0.039 | 0.04 | 0.047 | 0.045 | 0.049 | 0.053 |
| 10 | 0.060 | 0.059 | 0.031 | 0.039 | 0.044 | 0.044 | 0.048 | 0.053 |
| 12 | 0.058 | 0.06 | 0.028 | 0.038 | 0.043 | 0.043 | 0.048 | 0.052 |
| 14 | 0.058 | 0.059 | 0.027 | 0.037 | 0.039 | 0.041 | 0.047 | 0.051 |
| 16 | 0.057 | 0.059 | 0.025 | 0.035 | 0.038 | 0.041 | 0.045 | 0.05 |

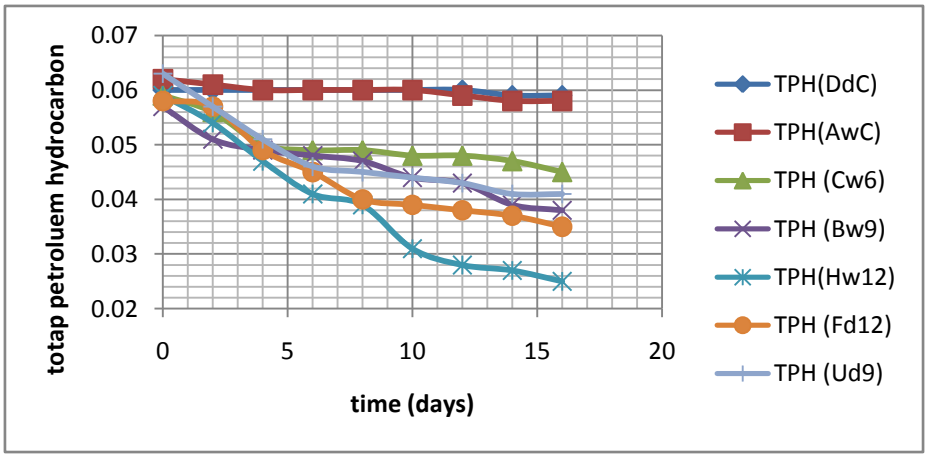


**Fig1.** *Graph of ppm of TPH versus time showing the reduction rate of the TPH for reactors (U,F,H,B,C,A,D)*

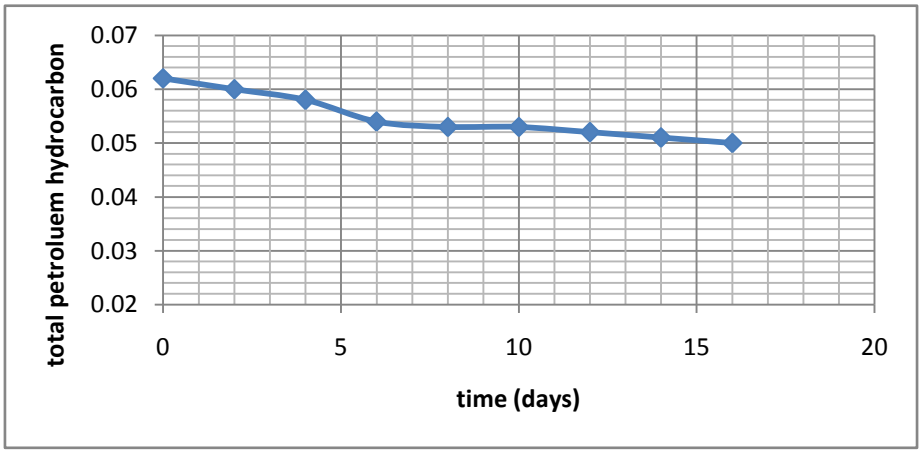


**Fig2.** *Graph of ppm of TPH versus time showing the reduction rate of the TPH for reactor G*

Furthermore notice that the crude oil in the control reactors A and C never experienced any appreciable decrease in their concentration over the 16 day period, even though some of the crude present in these reactors disappeared its quantity and its rate of disappearance becomes negligible when compared to that of the reactors that were stimulated this is simply because naturally bioremediation occurs in the environment but this natural bioremediation is slow and it may take hundreds of years before a soil polluted with crude oil and that was left to nature to remedy will return to a TPH free state. Thus the natural process of bioremediation was stimulated that is its speed was increased by the Moringa oleifera leave extract. Figure 2 illustrate the degradation of hydrocarbon upon the influence of time.

### 3.1 Obtaining the Order(N) and the Specific Reaction Rate Constant (K) of the Reaction.

From the graphs given we can attempt to deduce the order and rate constant of the equation by using the formula presented in equation (8) and (8i) stated as

$$T_F = \frac{F^{1-n} - 1}{K(n-1)} Co^{1-n}$$

and

$$logT_F = log(\frac{F^{1-n} - 1}{K(n-1)}) + (n-1)logCo$$

to obtain the n and k of all the batch reactors
using F = 0.8 where f stands for fractional conversion
Reactor C6w

**Table2.***Showing logTf vs logCo for reactor C*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.059 | 0.0472 | 5.8 days | 0.763 | -1.229 |
| 0.058 | 0.0464 | 12.4 days | 1.073 | -1.3365 |
| 0.057 | 0.0456 | 14. 5days | 1.161 | -1.4441 |

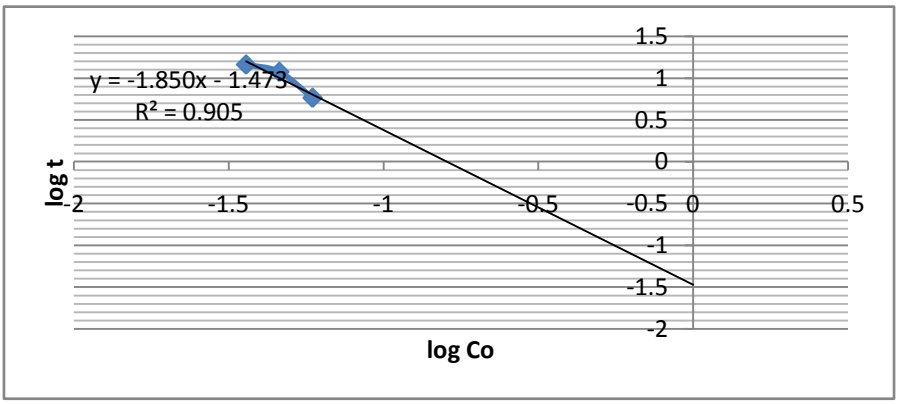


**Fig3.** *graph of logTf vs logCo for reactor C*

Reactor Bw9

**Table3.** *showing logTf vs logCo for reactor B*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.057 | 0.0456 | 8.7 days | 0.9395 | -1.2441 |
| 0.046 | 0.0346 | 10.7 days | 1.0294 | -1.3372 |
| 0.037 | 0.0296 | 12.8 days | 1.1072 | -1.4317 |

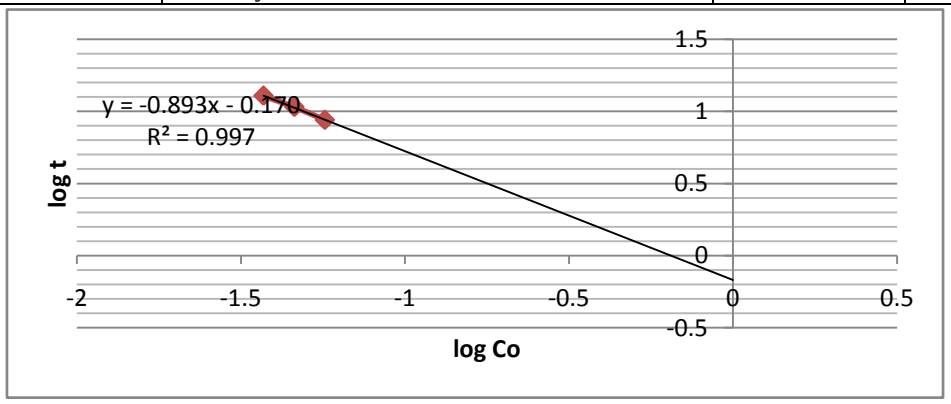


**Fig4.** *graph of logTf vs logCo for reactor B*

From slope n and k is obtained from equation (8) and (9)
K= 0.3176 and n= 1.8937
Reactor Hw12

**Table 4.** *Showing logTf vs logCo for reactor H*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.059 | 0.0472 | 3.9 days | 0.5910 | -1.2291 |
| 0.047 | 0.0372 | 4.6 days | 0.6622 | -1.3279 |
| 0.032 | 0.0250 | 5.6 days | 0.7481 | -1.4948 |

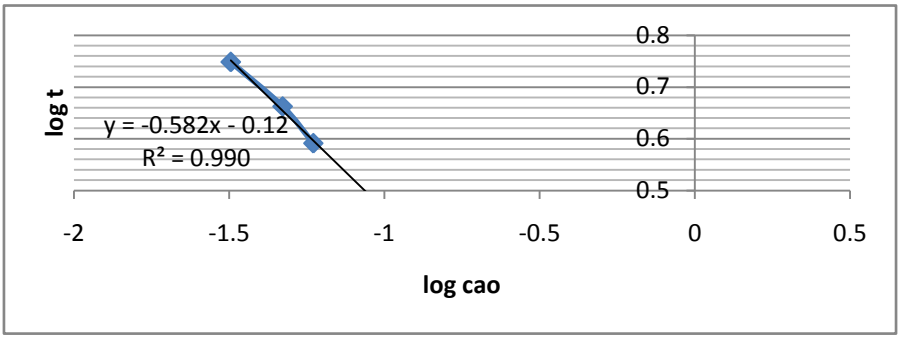


**Fig5.** *graph of logTf vs logCo for reactor H*

From slope n and k is obtained from equation (8) and (9)

n= 1.5829 k= 0.3254

Reactor Fd12

**Table5.** *showing logTf vs logCo for reactor F*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.058 | 0.0404 | 4.81 | 0.6821 | -1.2365 |
| 0.048 | 0.044 | 5.5 | 0.7345 | -1.3596 |
| 0.033 | 0.0424 | 6.053 | 0.782 | -1.4757 |

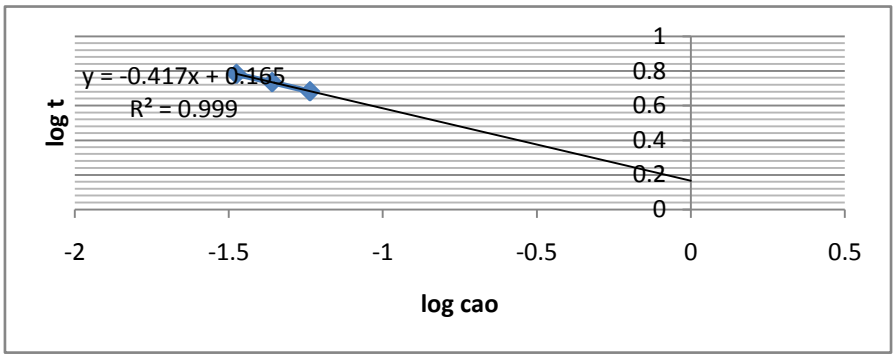


**Fig6.** *Graph of logTf vs logCo for reactor F*

From the graph n can be obtained as 1.4177 and k as 0.1606

Reactor $U_d9$

**Table6.** *Showing logTf vs logCo for reactor U*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.063 | 0.0504 | 4.2 days | 0.6232 | -1.2 |
| 0.054 | 0.0456 | 5.4 days | 0.7323 | -1.2376 |
| 0.044 | 0.0424 | 6.5 days | 0.8129 | -1.3565 |

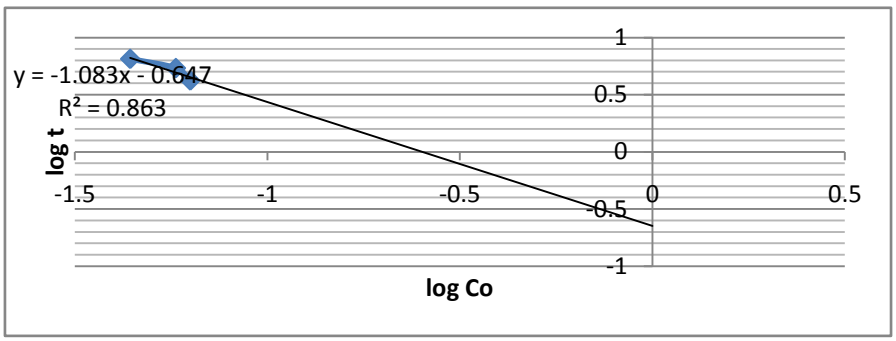


**Fig7.***Graph of logTf vs logCo for reactor U*

From the graph n= 2.0832 and the value of k is obtained from equation 3.8 to be 1.1445

Reactor Gd6

**Table7.** *Showing logTf vs logCo for reactor G*

| Co | 0.8Co | Time needed to decompose from Co to 0.8Co | Log $T_f$ | logCo |
|---|---|---|---|---|
| 0.062 | 0.0496 | 16.4 days | 1.2148 | -1.2076 |
| 0.05 | 0.0400 | 35.6 | 1.3136 | -1.3010 |
| | | | | |

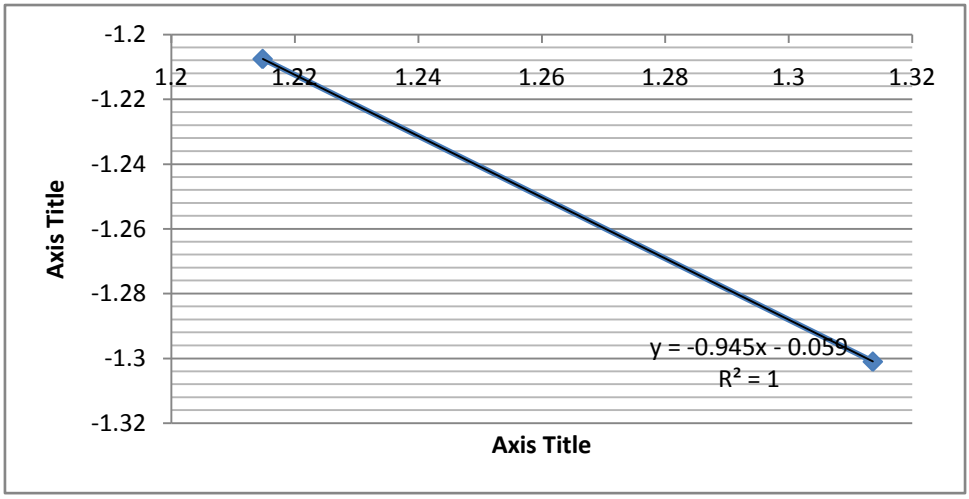


**Fig8.** *Graph of logTf vs logCo for reactor G*

From the graph n=1.9453 and k= 0.20948863

**Table8.** *Table of n and k values*

| Amount of Moringa | Reactor | Order (n) | Rate constant(k) |
|---|---|---|---|
| 12ml | $H_w12$ | 1.5829 | 0. 3254 |
| 12ml | $F_d12$ | 1.4177 | 0.1606 |
| 6ml | $C_w6$ | 2.8501 | 3.8168 |
| 6ml | $G_d6$ | 1.9453 | 0.2098 |
| 9ml | $B_w9$ | 1.8937 | 0.3176 |
| 9ml | $U_d9$ | 2.0832 | 1.1445 |

Substitute the values of n and k into equation (7) so as to obtain equations of each reactor

$$C^{1-n} = Co^{1-n} - (1-n)kt$$

For reactor $H_w12$

$$C^{1-1.5829} = Co^{1-1.5829} - (1-1.5829).3254t$$

Which can be further written as

$$C^{-0.5829} = Co^{-0.5829} + 0.1894t$$

For reactor $F_d12$

$$C^{-0.4177} = Co^{-0.4177} + 0.06708t$$

For reactor $C_w6$

$$C^{-1.8501} = Co^{-1.8501} + 7.06146t$$

For reactor $G_d6$

$$C^{-0.9453} = Co^{-0.9453} + 0.1983t$$

For reactor $B_w9$

$$C^{-0.8937} = Co^{-0.8937} + 0.2838t$$

For reactor $U_d9$

$$C^{-1.0832} = Co^{-1.0832} + 1.2383t$$

**Table 9.** *Tableof reactor and equations of reaction*

| Reactor | Equation of reaction |
|---|---|
| $H_w12$ | $C^{-0.5829} = Co^{-0.5829} + 0.1894t$ |
| $F_d12$ | $C^{-0.4177} = Co^{-0.4177} + 0.06708t$ |
| $B_w9$ | $C^{-0.8937} = Co^{-0.8937} + 0.2838t$ |
| $U_d9$ | $C^{-1.0832} = Co^{-1.0832} + 1.2383t$ |
| $C_w6$ | $C^{-1.8501} = Co^{-1.8501} + 7.06146t$ |
| $G_d6$ | $C^{-0.9453} = Co^{-0.9453} + 0.1983t$ |

The above sets of equations can be used to predict the concentration of the crude oil present in the soil at any time t for each of the reactors knowing the initial concentration of crude that was present in the soil at the time when they bioremediation reaction was initiated.

The can be written in form of the line waver burke plot as

$$\frac{1}{Co^{-0.5829}+0.1894t} = \frac{K}{[Co^{-0.5829}+0.1894t]_{max}[S]} + \frac{1}{[Co^{-0.5829}+0.1894t]_{max}} \quad (22)$$

for reactor H

$$\frac{1}{Co^{-0.4177}+0.06708t} = \frac{K}{[Co^{-0.4177}+0.06708t]_{max}[S]} + \frac{1}{[Co^{-0.5829}+0.06708t]_{max}} \quad (23)$$

For reactor F

$$\frac{1}{Co^{-0.8937}+0.2838t} = \frac{K}{[Co^{-0.8937}+0.2838t]_{max}[S]} + \frac{1}{[Co^{-0.8937}+0.2838t]_{max}} \quad (24)$$

For reactor B

$$\frac{1}{Co^{-1.0832}+1.2383t} = \frac{K}{[Co^{-1.0832}+1.2383t]_{max}[S]} + \frac{1}{[Co^{-1.0832}+1.2383t]_{max}} \quad (25)$$

For reactor U

$$\frac{1}{Co^{-1.8501}+7.0614t} = \frac{K}{[Co^{-1.8501}+7.0614t]_{max}[S]} + \frac{1}{[Co^{-1.8501}+7.0614t]_{max}} \quad (26)$$

For reactor C

$$\frac{1}{[Co^{-0.9453}+0.1983t]} = \frac{K}{[Co^{-0.9453}+0.1983]t_{max}[S]} + \frac{1}{[Co^{-0.9453}+0.1983t]_{max}} \quad (27)$$

For reactor G

The results presented in table 2, 3, 4, 5, 6 and 7 illustrates the relationship of $\log T_f$ against $\log C_n$ for various day of degradation of crude upon the influence of time for reactor $C_6w$, $B_w9$, $H_w12$, $F_d12$, $U_d9$ and $G_d6$ respertively. The variation on the functional paramaters can be attributed to to variation on the degradation time. The results presented in Figure , 3, 4, 5, 6 and 7 illustrates the relationship of $\log T_f$ against $\log C_n$ for various day of degradation of crude upon the influence of time for reactor $C_6w$, $B_w9$, $H_w12$, $F_d12$, $U_d9$ and $G_d6$ respertively. The variation on the functional paramaters can be attributed to to variation on the degradation time. Relationship of $\log T_f$ against $\log C_n$ shows an increase in both dimensions with equations of best fit established in each cuve as presented in this paper.

It was also observed that of the reactions, the reactors that were operated under wet condition experienced a much higher bioremediation rate than those under dry conditions, this is due to the fact that the water supplied to the micro-organism under wet conditions weren't supplied to those that were operated under dry conditions and water is of paramount importance to both micro and macro life because it is part of the metabolic pathway by which micro-organism feed, produce energy and grow thus as a result of that the moist reactors experienced a faster bioremediation rate than those done under dry conditions.

Thus we can conveniently say that they higher they Moringa oleifera leave extract they faster they bioremediation process this statement only olds to the extent of inhibition of bioremediation caused by excessive supply of nutrirnts to the soil to be bioremediated

## 4. CONCLUSION

Based on the experiments conducted we can clearly observe that the Moringa oleifera stimulated the bioremediation of crude oil in the soil this is largely attributed to the nutrients supplied to the soil by the Moringa oleifera leave extract this further helps the micro-organisms present in the soil to grow as they grow the population of microbes is increased theoretically as a result of this more microbes are available in the soil to consume the crude oil and thus the bioremediation proceeds at a faster rate. Thus we can conclude that the bioremediation was induced by the extract. Furthermore as pointed out in the discussion biostimulants can in some ways act as inibitors this appens wen the biostimulants supply nutrients to the soil in an excess amount in so much that they become toxic to the micro-organism present in the soil and they do this by inhibiting the metabolism of the microbes this then to death and eventual population decrease of the microbes in the soil as as a result of this the bioremediation process is truncated

Furthermore webobserve pH increase favoured they bioremediation reaction this was as a result of the fact that the soil was acidic and increase in the P.H of the soil meant that the soil is tending towards neutrality this favoured the bioremediation because the micro-organisms responsible for bioremediation, example of which include Pseudomonas, Aeromonas, Moraxella, Beijerinckia, flavobacteria, chrobacteria, Nocardia, Corynebacteria, Atinetobacter all perform optimally in an alkaline environment

Finally the models developed can used to monitor, predict and simulate the rate of degradation of hydrocarbons present in a polluted soil undergoing bioremediation under the influence of Moringa oleifera leave extract, As well as to ascertain the amount of Moringa oleifera to be added to the soil to be remediated in order to prevent inhibition of the bioremediation process by excessive nutrient supplied

## REFERENCES

[1] Amadi A, Dickson, A.A and Maate, G.O, (1993) Remediation of Oil Polluted Soils: Effect of Organic and Inorganic Nutrient Supplement on the Performance of Maize water, air, and soil pollution. p 66.

[2] Amadi A. and Antal S.P (1991) "Degradation of Bonny Medium Crude by Microbial Species Isolated from Oshika- Oyakama Oil polluted Area". International journal of Biochemical engineering, vol. 1, no. 2. Pp.1 -10.

[3] Bertrand J.C., Bianchi M, Al-Mallah M., Acquaviva N., Mile G.(1993) Hydrocarbon biodegradation and hydrocarbonoclastic bacterial communities composition grown in seawater as a function of sodium chloride concentration. 3. Exp. Mar. Biol. Ecol. Vol.1, p.125.

[4] Octave and Levienspiel,(2004), Chemical reaction engineering, Wiley India Edition. : Interpretation of Batch Reactor Data. Guess nth order kinetics. Pp 62-63

[5] Lendlem, A. (2002) Biodegradable, Elastic Shape Memory Polymers for Potential Biomedical Application, American Association of Advancement of Science, pg 1673

[6] Luizer, W. D (1992) Material Derived from Biomass/ Biodegradable Materials. Proceedings of the National Academy of Science, vol 89, no. 2, 39-42.

[7] Magnusson K.(1998) Oil handling in the Baltic Sea Area 1996 -2001. SSPA MaritimeConsulting AB, Report 7935-2.

[8] Meisam Tabarabaci, Raha Abdul Rahim, Andre Denis G. Wright, Yoshihito Shirui, NortianiAbdullah, Alawi Sulaiman, Kenji Sakal and Mohr Au Hassan, (2010). Importance of MethanogenicArchaea Population In Anaerobic Waste Water Treatment. Journal of Process Biochemistry,vol 45, no 8, pp. 1214 - 1225.

[9] Murphyt., Moller A, Brouwer H. (1995) In situ treatment of Hamilton harbour sediment. 3. Aquat. Ecosyst. Health, vol. 3, 195.

[10] Ogoni, H.A (2001) Development of Kinetic model for product inhibition in biodegradation of petroleum hydrocarbon, African Journal of Environment Studies, vol 2, no 1. pp.23-25

[11] Prince R.(1999) Crude Oil Biodegradation. Encyclopedia of Environmental Analysis and Remediation, Wiley, New York, USA.

[12] Siron R., Pelletier E., Delille D., Roy S. (1993) Fate and effects of dispersed crude oil under icy conditions simulated in microcosms. Mar. Environ. Res. Vol.3,p. 273.

[13] Ukpaka C.P. (2006). Modeling Degradation Kinetics of petroleum hydrocarbon mixture at specific concentration. Journal of Research in Engineering, vol.3, no.3, pp.47-56

[14] Ukpaka CP, Amadi SA, Umesi N, (2009). Modeling the physical properties of activated sludge biological wastewater treatment system in a plug flow reactor. The Nigeria Journal of Research and Production, A Multidisciplinary Journal, vol.15, no.1, pp. 37-56.

[15] Ukpaka CP, Farrow ST,(2009). Development of model for temperature distribution on fin material during ethanol production, Nigerian Journal of Research and Production, vol.14, no.1, pp. 202-217.

[16] Ukpaka C.P, (2011). Modelling the prediction of biokinetics of dissolved oxygen for wet season degradation of petroleum hydrocarbon in pond system, International Journal of Pharma world Research, 2(3), pp. 1-27.

[17] Ukpaka C. P, (2011). Revaluation of Biokinetic model for the prediction of biochemical oxygen demand in a pond system for wet season degradation of petroleum hydrocarbon, International Journal of Pharma world Research, 2(2), pp. 1-26.

[18] Ukpaka, C. P. (2006a). Factors affecting Biodegradation Reaction of Petroleum hydrocarbon at various concentration. International Journal of Physical Sciences, vol.1, no.1, pp.27-37

[19] Ukpaka, C. P; (2006b). Assessment of drilling cuttings and crude oil discharged into a lake in Niger Delta, Journal of Engineering Science and Technology, vol.1, no.1, pp. 51-57,

[20] Ukpaka, C. P; and Oboho E.O. (2006). Biokenetics for the production of Nitrogen in a natural aquatic ecosystem polluted with crude oil. Journal of Modeling, Simulation and Control (AMSE), vol. 67, no.2, pp.39-58,

[21] Van Hamme J., Odumeru J, Ward O. (2000) Community dynamics of a mixed-bacterial culture growing on petroleum hydrocarbons in batch culture. Can. J. Microbiol. Vol. 46, p. 441.