Comparative Study of Degradation Kinetics of Crude oil Contaminated Mangrove and Clay Soils

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ABSTRACT

A comparative study of the potential of bioremediation in the removal of hydrocarbon contaminants from a mangrove and clay soils, powered by indigenous microbes as bioremediators was evaluated and compared in a 35-days laboratory scale experiment by fitting the bioremediation data obtained for each soil to a first order kinetic model. The research aim was a comparative evaluation of the rates of degradation of crude oil contaminant in mangrove and clay soils when biostimulated with inorganic fertilizer.

The experimental pots containing mangrove and clay soils were contaminated with the 7% w/w of Bonny light crude oil and biostimulated with 100g inorganic fertilizer (NPK) per kilogram of soil and was maintained at a pH of 6.5 and 50% of the soil's Water Holding Capacity (WHC). Remediation was done in the open laboratory for 35days under atmospheric conditions. The percentage decrease in Total Petroleum Hydrocarbon (TPH) was the response parameter and the crude contaminated soils showed a decrease in TPH over time. The soil nutrient, moisture content and soil pH were the important soil factors known to affect the rate of contaminants degradation were considered.

Results show a regular trend in pH and moisture changes in the soils. The degradation rate of crude oil contaminant in each soil varied, but all soils were able to achieve over 70% crude oil removal within 21days of experimentation. There seems to be a correlation between soil texture and the rate of biodegradation. The results also showed that first-order kinetics could be used to describe biodegradation of crude oil in soil and kinetic constants for the two soils were 0.0511/day for the mangrove soil and 0.0337/day for the clay soil. The total petroleum hydrocarbon in the experimental pots decreased to 1.9% and 0.93% in the clayey and mangrove soils respectively.

Keywords: Mangrove Soil, Clay Soil, Kinetics, Nutrients, Bio stimulation, Soil Matrix.

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1. INTRODUCTION

Records shows that oil spill incidents have occurred in various parts of the World's aquatic and terrestrial environments and most of this spills are associated with negligence and sabotage, corrosion of pipes, and oil tanker's accidents [1, 2, 3]. As crude oil derived products continue to be a major source of energy for homes and industries, their entrance into the environments either by accident or negligence comes with adverse effect on humans, plants and animal health since the contaminants are carcinogenic [4, 5, 6]. Investigations and studies by different authors have elucidated the fate and effects of spilled crude oil in mangrove and clay soils [7, 8] and proved that most constituents of crude oil are tractable.

Although the phenomena underlying petroleum hydrocarbon degradation is in public view, and the conditions limiting the rate of degradation of contaminants in soil have also been identified, the lack of information on biodegradation of petroleum hydrocarbons in different soil media is a major challenge in predicting and transferring the rate of contaminant degradation from one site to another [9, 10, 11]. Even when accurate laboratory measurement of rates has been done, such rates rarely find

utilization in the fields because of the inability to transfer the degradation rate coefficient from the laboratory to the field and from one site to another due to soil heterogeneities and site specific condition. The texture of the soil is a fundamental physical property that plays a definitive role in the determination of the soils characteristics [10]. The rate of biodegradation of crude oil contaminant is known to be a function of the soil texture and source.

Studies shows that, soils with different texture can influence biodegradation of petroleum hydrocarbons in different ways. For instance the increase in sand content of soil was reported to be favourable to aerobic biodegradation by allowing adequate aeration of the soil [12, 13, 14] and the rate is faster in sandy soils than in clayey soils. In contrast, [15, 16] determined higher rate of degradation in clayey loam than sandy soils and loamy soils.

The texture of the soil is an important soil's physical property that determines the rate of contaminant degradation [17, 18]. Soil's textural property is a consequence of the relative proportion of the three constituent's particles (sand, clay and silt) held together by organic matter, coagulated inorganic materials and microorganisms [11].

The soil texture and several other soil's parameters such as nutrients, microorganism, pH and water holding capacity have been identified as some of the various factors that may limit the rate of petroleum hydrocarbon degradation.

1.1. Remediation Technologies

The potential of remediation techniques in the removal of contaminants from the environments is well documented in literature [19, 9, 20, 21]. Most of these techniques are limited to sandy and loamy soil with little attention paid to the utterly moderate to heavy clay soils [22]. Most researchers considered In-situ bioremediation to be effective only in more permeable soils such as loamy soils. Several soil remediation technologies have also been developed for sites contaminated with crude oil. This includes such technologies as electrokinetics separation [23], phytoremediation [24] Bioventing [25], Land farming [26, 27], biostimulation [28] etc.

The various technologies come with drawbacks that application to the soil will result in the alteration of the properties of the soil. There are also complex and needs the services of trained technicians to operate [29, 30]. Bioremediation through the technology of biostimulation is believed to be appropriate efficient and versatile alternative remediation technology for crude oil contaminated soil environment as it provides a complete transformation of organic compound [17, 31].

It has found application in almost every ecosystem including mangrove and clay soils environments. But the changing site environmental conditions, the variation in soil texture with each soil having a different bioremediation potential, the operating conditions of the remedial technology and their impact on the rates of hydrocarbon biodegradation is a challenge to every bioremediation practitioners [9]. Other challenges like predicting the efficiency of bioremediation for any particular soil and transferring such rates to another site is hampered by heterogeneity arising from soil texture, the complex environmental and operating conditions that exerts a lot of influence on soil biological activities are site specific. The rate of biodegradation in soil because of biological activities and soil type is important in determining the type of microbial population present in such soils.

1.2. Mangrove Soils

Mangroves (soil) are transitional coastal ecosystems that lie between aquatic and land-dwelling environments. This is typical of land environment that are in the tropic and bordering the seas [32]. Because most mangrove forests remains the center of crude oil production in most oil producing regions of the world, the mangrove soil is susceptible to crude oil environmental pollution. Petroleum hydrocarbon pollution of mangrove swamps has greatly endangered the mangrove ecosystem and affected the soil adversely [33]. Although mangrove soils have the ability to tolerate a wide range of physical changes in their environment, but despite this resilience, they are highly vulnerable to oil toxicity and the impacts from cleanup activities [34]. Additionally, the bioremediation problems of mangrove soil became more aggravated because of the expensive treatment and disposal methods employed [33, 8].

1.3. Clay Soils

On the other hand the entrance of crude oil contaminant on clay soil environments also alters the physical and chemical properties of the   soil causing a reduction in the geotechnical properties of the soil and upsetting the microbial biomass which affects the rate of degradation of the crude in such soil [35]. The degree of alteration depends on the soil texture, the specific composition and the quantity of the crude oil spilled. Clay soils are electro-chemically active, possess many physical and chemical properties that may limit the use of bioremediation [22] and are maximally affected when impacted by hydrocarbon contaminants [36]. Also the high water-holding capacity, low air-filled porosity associated with clay soils may often lead to anoxic conditions. The anaerobic condition often poses a problem as the metabolic pathways that dominate hydrocarbon degradation are aerobic [20, 37, 22]

Crude oil contamination of clay soils results in relatively low optimum moisture content leading to a decrease in degradation rate. The rates of biodegradation in soils are a function of the structural constituents of those soils. Results suggest that high clay

content inversely affects the biodegradation. This may be a result of reduced aeration characteristics of high clay levels. The accidental discharge of petroleum hydrocarbon contaminants into the soil and aquatic ecosystems has resulted in a long term threat to all forms of life in the clay and mangrove soil environment [38].

1.4. Bioremediation/Biostimulation

Bioremediation relies on the advantage offered by living organisms, free enzymes, and cellular components to initiate or accelerate the rate of intrinsic degradation of organic compounds under different environmental conditions [39, 40]. Bioremediation application results in a safe and low cost method to remove the total petroleum hydrocarbons from the soil using microorganisms. The peculiarities and heterogeneity of the mangrove and clay soil environments, make bioremediation the most appropriate approach for their cleanups. The bioremediation strategy is dependent on optimizing the environmental factors which affects the microbial growth and biodegradation of pollutant [41]. Mohajeri et al. investigated the concentration of pollutant on the rate of remediation and concluded that pollutant concentrations play a critical role in biotransformation processes [42]. Other researchers [43, 44] demonstrated that the bioavailability of petroleum hydrocarbons to microbes to be one of the factors affecting bioremediation. Also nutrients content of the soil is an important aspect of biodegradation that must be considered [45].

The addition of inorganic or organic nutrients (biostimulation) is an effective approach to enhance the bioremediation process [46]. The efficiency of biostimulation will depend on contact between the added nutrients, the soil bacteria consortia, and the crude oil contaminant [47]. Contamination of a zone with hydrocarbons leads to a rapid depletion of the available pools of major inorganic nutrients, such as nitrogen (N) and phosphorus (P). The biostimulating process will introduce additional nutrients into the polluted environment to increase the numbers of indigenous microorganisms present. Subsequently, the addition of nutrients to aid contaminants degradation is dedicated mostly to the addition of compounds that has phosphorus and nitrogen as primary constituents. This comes handy in the form of inorganic fertilizer or organic manures and it has become the standard industrial practice aimed at enhancing the rate of contaminant removal from the environment [48, 44]. A C:N:P ratio of 120:10:1 will provide an optimum for nutrient's enhanced biodegradation [49]. Nitrogen and Phosphorus may be required to bring the C:N:P ratio close to that of the bacterial biomass and this may be added in form of organic or inorganic fertilizer. The remediation of crude oil contaminated soils may be done successfully under a laboratory environment but the translation of the laboratory result to a field scale practice are ingrained with difficulties especially in soil of high clay content [50].

1.5. Remediation Kinetics and Modeling

Efforts made by researchers and remediation practitioners to make basic phenomena fundamental to the science of bioremediation of crude oil contaminants to be completely understood is now yielding results. This includes the environmental conditions that will enhance the rate of degradation, the state and nature of the contaminant and the soil parameters but according to Shewfelt et al. the necessary degradation rates needed for design, prediction and scale-up are hardly known [51]. Information on kinetics for soils contaminated with crude oil is extremely important as it quantifies the rate and extent of remediation. [52]. But the prediction of crude oil biodegradation kinetics is difficult and complicated because of environmental factors, soils heterogeneity and the difference in the composition of crude oil contaminants. [42].

So many researchers have investigated the kinetics of soil bioremediation when contaminated with crude oil [53, 18, 54]. [53] developed a kinetic model for crude oil contaminated soil using palm bunch ashes. W. Namkoong et al [17] analyzed using kinetic models the effects of different mix ratios of compost and sewage sludge on diesel contaminated soils. Hwang et al applied composting technique to study the rate of degradation of a diesel fuel contaminated soil [55]. The results they obtained by assuming a first order rate was in agreement with other known experimental values. In the same way Agarry et al. did kinetic studies on enhanced soil bioremediation of bonny light crude oil amended with crop and organic wastes. The model estimated the degradation rate and half-life of the pollutants relative to the treatment. Their result confirms that the application of crop residues and animal dung wastes (organic wastes) can improve the biodegradation rate of crude oil contaminant in soil [29].

Kinetics modeling of crude oil contaminated soil remediation is very complex due to the number of factors involved [56]. The kinetic studies in a natural environment are often experimental, reflecting only the basic knowledge about the microbial density and its activity in the given environment [57]. But kinetic analysis is the key factor to understanding a biodegradation process. The extent of remediation offered by microbes is best articulated from the bioremediation kinetic model and described by first order kinetic equation [58, 59, 60, 61]. The kinetic information is essential in the estimation of the concentration of the contaminant at any time and permits the prediction of its level in future.

The first-order kinetic equation that describes the rate of total petroleum hydrocarbon reduction in soil is expressed by the following equation:

$$\frac{dC}{dT} = -kC^n = r \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots1.1$$

Where:

T = time (day), C = remaining crude oil concentration (mg/kg) in soil at any time (t) and k = first-order kinetic constant (1/day) and n = 1 for a first order reaction [62].

Although microbial growth on crude oil pollutant mixture is important in bioremediation treatment.

This research relied on a general assumption that the microbial concentration will remains constant over the duration of the process [63, 53] in arriving at a rate equation, therefore the effect of the microbial biomass concentration will be neglected. Integrating equation 1.1 yields the first-order kinetics equation for a non-growth process.

$$C = C_0 e^{-kt} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.1.2$$

C_o = concentration of crude oil at t=0 (g/kg soil)

To estimate the degradation rate constant (k), the first order model equation was linearized by taking the natural log of both sides of equation 1.2 to obtain:

$$In \frac{C_0}{C} = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.3$$

Plotting Ln(C_0/C) versus time (t) to give a straight line plot and the slope of the line will represent the first-order kinetic constant (k). Most researchers have shown that the rate of biodegradation of hydrocarbons in soil obeys the first order kinetics [64, 63].

1.6. Biodegradation half-life time

The biodegradation half-life is the time required for contaminant concentration to reduce to half of their original concentration.

$$t_{1/2} = \frac{In\ 2}{k} = \frac{0.6932}{k} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.4$$

Where $t_{1/2}$ the half-life time and k is the rate constant. The model equation is used to make predictions and gives a knowledge of the concentration of contaminants present at a given time.

To calculate the degree of degradation we apply the following equation:

$$\%(D) = \frac{THC_0 - THC_i}{THC_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots.1.5$$

Where THC_o and THC_i represents the initial and residual TPH

2. MATERIALS AND METHODS

2.1. Collection of samples

The acquisition of soil samples for the bioremediation study was done using a hand auger, shovel and machete. The un-impacted soil samples were collected from two locations in Bayelsa State, Nigeria in early July 2018. The grass vegetation was pull down with a machete and shovel and the soil was collected by digging down to a depth of approximately 30cm. The NPK fertilizer (20:20:20 was for the study purchased from a chemical store in Swali Market, Yenagoa, Nigeria.

2.2. Crude Oil

The Bonny light crude oil used in the experiments was obtained from a Shell location in Ughelli, Delta State Nigeria The crude oil was a light crude blend equivalent to the Brent crude.

2.3. Soil Sample Characterization

The bulked soil samples were air dried in the open, homogenized by grinding, and sifted by passing through a 2-mm (#10) sieve to remove stones and other particles unintentionally taken from the field prior to physicochemical parameters analysis. The soil sample classification and characterization for physicochemical parameters was done in the Soil Laboratory of the Department of Civil Engineering, Niger Delta University according to standard methods of soil analysis. The physical and chemical properties of the soils are summarized in Table 2.1. The soil samples were kept in polythene bags away from contamination prior to use.

The analysis of the soil samples showed clay soil to be distinctively different from the mangrove soil in its high clay content. The mangrove soil is a silty-loam texture and separates from the clay soil in colour being dark grey in appearance. Textural analysis of

the soil samples shows that the textural content of the clayey soil is clay and that of mangrove soil to be silty loam with a pH value of 6.68 for the mangrove soil and 7.21 for clay soil as summarized in table 2.1. Other physicochemical parameters measured included the organic carbon content of 28.30g/kg and 37g/kg for the clay and mangrove soils respectively

Table 2-1: Baseline Textural Characteristic of Soil Samples

Particle Size Distribution	Clay Soil (%)	Mangrove Soil (%)
Clay	56.58	30.90
Silt	23.69	52.37
Sand	19.73	16.73
Texture	**Clayey**	**Silty Loam**

Table 2-2: Soils Physicochemical Analysis

S/No	Experiment	Clayey	Mangrove
1	Soil pH	7.21	5.68
2	Organic Carbon	4.86	3.63
3	Nitrogen (N)	0.24	0.27
4	Phosphorus (P)	0.62	0.12
5	Potassium (K)	6.72	0.31
6	Total Petroleum Hydrocarbon	7% w/w	7% w/w
7	C:N Ratio	20.25	13.44

2.4. Bioremediation Process

The laboratory studies of the hydrocarbon biodegradation in the soils were based on small-scale version of in-situ field experimentation. Even when the study was laboratory based, it was carried out in the open at atmospheric temperature under shade. The experimentations were performed optimally at temperature of $27^0C – 30^0C$, C to N ratio of 10:1, pH = 6.5 and Soil moisture content of 50% Water Holding Capacity of the soils.

Literature have it that the maximum percentage of crude oil present in disturbed and undisturbed contaminated soil samples should be within 10% w/w for experimentation [65]. The soil was therefore spiked with a 70g/kg soil of Bonny light crude-oil on the experimental mixing tray containing one (1) kilogram each of air-dried mangrove and clay soils previously obtained under field conditions, this was followed by tumbling for uniform sorption of the contaminant. The Crude oil or TPH content of the contaminated soil was determined and adjusted to 7% by diluting with clean soil. The soil samples was sprayed in a tray pan and left in the open for the evaporation of the lighter component of the oil. The degree of contamination of soil with crude oil equals 7% w/w or 70,000 ppm. The experiment was conducted in triplicate with one control for each soil.

Results of the soil physicochemical analysis indicated that the soils were limited by nutrient needed to achieve a C:N ratio of 10:1 for efficient biodegradation as the C:N ratio of the soil samples were 20.25 for the clay soil while it was 13.44 for the mangrove soil. The lower concentration of nitrogen and phosphorus in sample is incapable of enhancing the natural degradation of sample contaminant. Since the C: N ratio is a critical factor in bioremediation and considering the above results, an amount of inorganic fertilizer NPK (20:10:10) nutrient was needed to adjust the C:N ratio and thoroughly mixed for optimum remediation. The soils were amended with 100g of NPK fertilizer each. The moisture content was adjusted to 50% of the soil water holding capacity by the addition of clean water and incubated in the open at atmospheric condition. The content of each plastic bucket was thoroughly mixed every week for proper aeration, and the moisture content and soil pH were maintained at 50% water holding capacity and 6.5 respectively. The pH was adjusted by adding calcium carbonate or ammonium sulphate as the case may be.

2.5. Analytical Methods

Biodegradation activities of microbes in the soil were evaluated by directly monitoring the loss of the target compounds through the evaluation of Total Petroleum Hydrocarbon (TPH) [66]. The total petroleum hydrocarbon (TPH) fraction of the soil was evaluated as chloroform-extractable material. Ten grams of the crude oil impacted soil sample was taken from the experimental

buckets and the total petroleum hydrocarbon (TPH) was extracted (liquid-liquid extraction) from it with 40 ml of chloroform. The TPH fraction extracted was then allowed to dry by evaporating the chloroform solvent. Degradation of TPH was measured gravimetrically using spectrophotometer and comparing the results with a prepared standard plot.

The variation in total petroleum hydrocarbons (TPH) in the soils was monitored by withdrawing samples at the initial stage of the experiment and subsequently at 7-day intervals for 35days to determine the residual Total Petroleum Hydrocarbon (TPH).

2.6. Kinetics Evaluation of Soils

A comparative study of the potential of bioremediation in a mangrove and clay soils, powered by indigenous microbes was evaluated and compared by fitting the bioremediation data obtained for each soil treatment to a first order kinetic model. Venosa and Holder have opined that a first order kinetics can be used with accuracy to describe the biodegradation of petroleum hydrocarbons in soils [67]. The results obtained are in agreement with previous results by other researchers [68, 69] the first order equation assumption was validated using the experimental results as shown in figures 3.1 to 3.3.

2.7. Analysis of Biodegradation Data

We integrated the combined balance in ΔTPH and rate law to plot degradation rate data in terms of change in TPH versus Time (days). The evaluation was done using biodegradation rate constants, from the First Order Kinetics Model, which was achieved through the linear function of Microsoft Excel Statistical tool pack. Most researchers [61, 70] believes that record number of compounds follows a first order rate law and that a first-order kinetics is said to be valid if a linear relationship is achieved upon plotting the natural logarithm of (TPH_o/TPH) versus time (t in days) to give a straight line of slope k.

Concentration of total petroleum hydrocarbon (TPH) left in the soil at regular intervals of seven days was calculated and their natural logarithm plotted against time as shown in figure 3-1 and 3-2 in order to analyse the kinetics for the biodegradation process. From figures 3.1 to 3.3 it could be observed that the biodegradation process followed a first order kinetics and the plotting of the decreasing TPH concentration in soil against time gave was linear with rate constants of 0, 0571/day for the mangrove soil and 0.0335/day for the clayey soil. The observed correlation pattern was comparable to other works reported by other researchers such as [69]. S. Hutchins et al. [69] reported that first-order rate constant ranged from 0.016 to a high of 0.38/day depending on compounds of hydrocarbon. E. Hwang, et al [55] found that the first-order kinetic rate constant of diesel oil was 0.099/day. In this work correlation analysis of R^2 for the crude oil biodegradation kinetics process was found to be 0.906 and 0.943 for the mangrove and clayey soil respectively which proved the correlation positive and linear for the decrease in concentration as a function of time.

3. RESULTS AND DISCUSSION

3.1. Bioremediation Studies

The biodegradation of crude oil in two soils (clay and mangrove) was studied over a period of 35 days. All the experiments were conducted under optimal conditions (Atmospheric temperature of between $28^{o}C$ – $30^{o}C$, C:N ratio of 10:1, soil moisture content of 50% of soil water holding capacity and pH of 6.5). Since pH moisture and nutrient were employed at optimal levels, the variations in the rate of degradation of the two soils were not dependent on these parameters but rather by the differences in the soil microbial remediators and soil textures. The initial TPH concentration of each soil was maintained at 7000mg/kg soil. The experiment was conducted in triplicate for each soil with one control. The indigenous microbes resident in each soil degraded the petroleum hydrocarbon contaminant in soil effectively as presented in tables 3.1 and 3.2. The rate of degradation of crude oil contaminant in the two soils was exponential resulting in a first order model as envisaged. All through the 35days of experimentation between 70% - 90% TPH reduction was observed in the experiments.

3.1.2 Measurement of Physical and Chemical Properties

Table 3-1: Mangrove Soil TPH Data

S/No	Day	TPH	TPH/(TPH)$_i$	LN(TPH/TPHo)
1	0	0.07	1	0
2	7	0.0601	0.858571	-0.152485401
3	14	0.0461	0.658571	-0.417682292
4	21	0.0391	0.558571	-0.582372775
5	28	0.0173	0.247143	-1.397788741
6	35	0.0093	0.132857	-2.018480842

Table 3-2: Clay Soil TPH Data

S/No	Day	TPH	TPH/TPHI	LN(TPH/TPHo)
1	0	0.07	1	0
2	7	0.049	0.7	-0.356674944
3	14	0.043	0.614286	-0.487295126
4	21	0.041	0.585714	-0.534923175
5	28	0.028	0.4	-0.916290732
6	35	0.019	0.271429	-1.304056263

3.2. Removal of total petroleum hydrocarbons in Mangrove and Clay Soils

The biodegradation of crude oil contaminant in clay and mangrove soils, studied with initial TPH concentration of 70,000ppm or 7000mg/kg soil had a rapid reduction in TPH within the first week of remediation in the clay soil while it was slow but steady in the mangrove soil. Remediation progressed until the 35th day culminating in the total removal of 72.9% TPH in the clay soil as against 86.7% in the mangrove soil. The graphs of the kinetic pattern for total hydrocarbon using the least square function of Micro Soft Excel were seen to be exponential resulting in a first order model. The bioremediation profile for the soils is presented in figure 3-1 to figure 3-3.

The degradation rate of petroleum hydrocarbon in the soils (mangrove and clayey) were compared by considering their rate constants. From the plot we observed that the rates of hydrocarbon degradation biodegradation in mangrove soil was better pronounced than in clay soil as observed in a higher first-order degradation rate constant (k value) of 0.057/day than the clay soil of 0.0337/day. It appeared that the differential in the crude oil biodegradation rate observed arose from the impact of soil textures (soil sand, clay content, and silt) as other environmental parameters were same and held at their optimal levels in the experimental pots. So remediation studies have shown that there is a close interaction between soil particle size, contamination and the functionality of microorganisms on crude oil biodegradation in soil. A cursory look at the particle size distribution on table 2.1 shows that the clayey soil had 56.5% clay content as against 30.9% for the mangrove soil. Clay particles generally have negative impact on the degradability of hydrocarbon in soil. The primary reason underlying the variation in rate may have resulted from the high clay particle contents of the clayey soil.
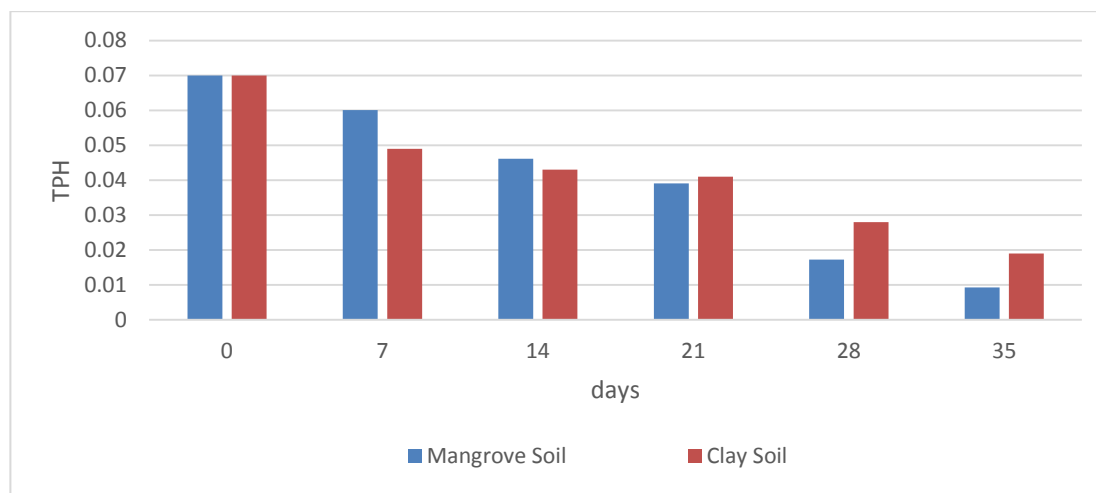

Figure 3-1:Biodegradation Profile of TPH with respect to time

Kogbara et al showed that there is a decrease in percent THC reduction as soils clay content increases [10]. M. Eyvazi [15] obtained a similar result and concluded that it was due to reduced aeration and porosity which is a function of soil clay contents. Sandy soils have a higher percentage of macro pores than the clayey soils which produces more of the micro pores and as such the clay soils are more susceptible to water logging and hinder the microbial degradation of hydrocarbons [71] which may have affected the k value of the clay soil. It has also been established that moderate clay content of soil can retain nutrient in soil and desolve them when necessary encouraging the growth of microorganism. In this study due to the reasonable levels of clays, it is believed that the presence of soil clay stimulated the microorganism's activity and thus the biodegradation rate of organic contaminant in the first week of experiment.

The reason why the rate was slower although steady in silty-loam soil was gleaned from the work of Amellal et al who pointed out that the performance of biodegradation processes of PHCs in silty soils to be generally slower than sandy or clayey soils [72]. Other researcher that carried out similar works and came out with comparable results includes: [68, 54, 73].

This study found significant disappearance of the petroleum hydrocarbons from the extractable fraction after 35days experimentation with half-lives of 20.5 days for the clay soil and 12.16 days for mangrove soil. The half-lives found are comparable to work by other authors including [22, 29] who used weathered diesel for their experiments.

The plots shows that the first-order kinetic can be applied with accuracy to describe the bioremediation process of crude oil contaminated mangrove or clay soils. The first-order rate constants obtained was consistent and comparable with other published data by other authors in previous studies concerning the degradation of hydrocarbon in soil. Hutchins and co. concluded that the first-order rate constant for hydrocarbons ranged from 0.016/day to as high as 0.38/day depending on the constituents of the crude oil in question. Hwang, et al. discovered that the k-value for the degradation of diesel oil contaminated soil was 0.099/day. Antizar-Ladislao et al. showed that the first-order kinetic constant at $38^{o}C$ was 0.013/day for hydrocarbon contaminated soil [18].
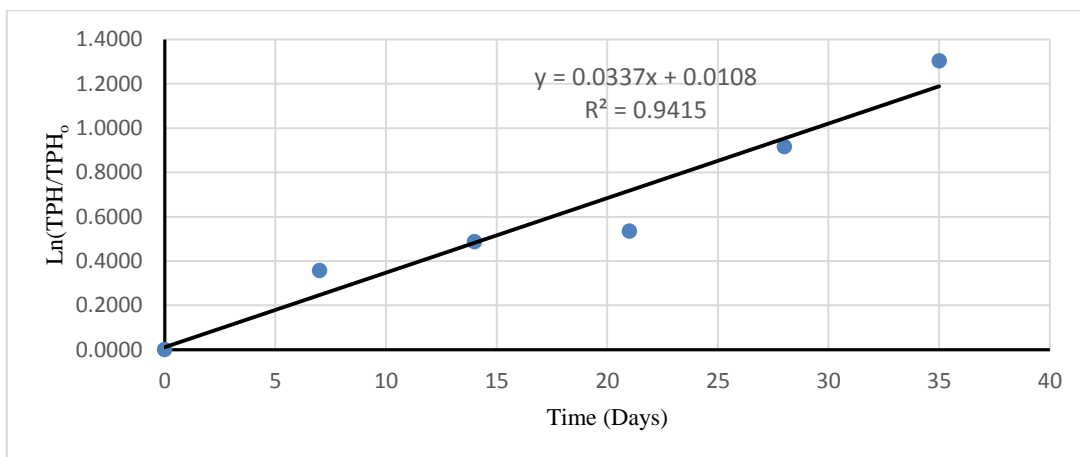

Figure 3-2: Plot of Ln(TPH/(TPH)$_i$) versus Time (Days) for Clay Soil
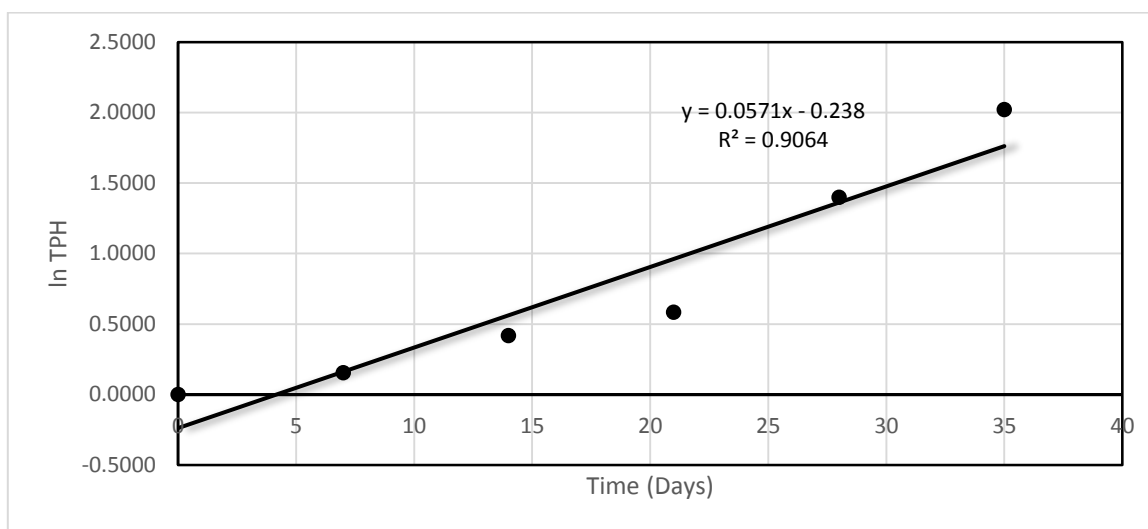

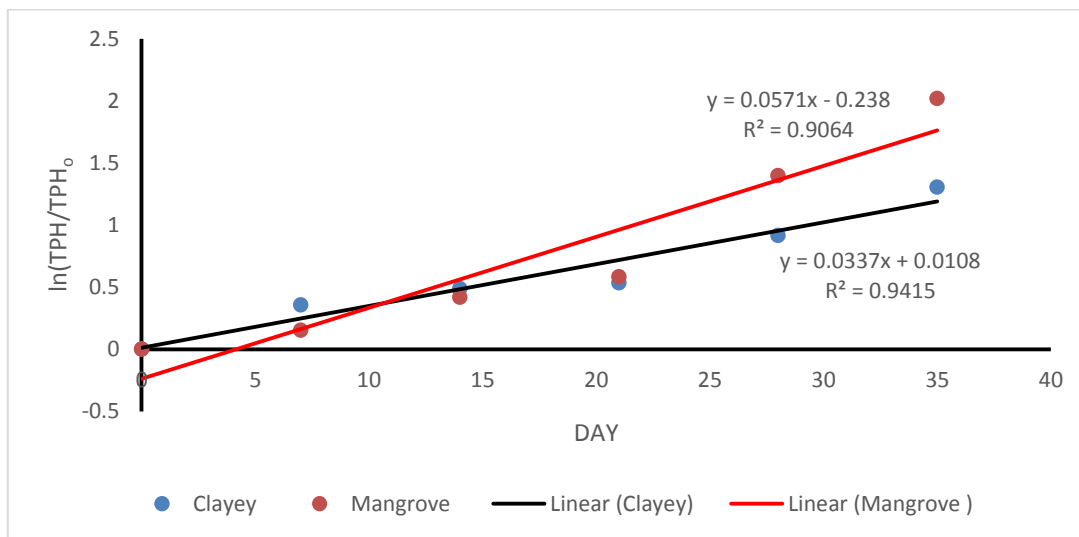**Figure 3-3:Plot of Ln (TPH) versus Time (Days) for Mangrove Soil**

Figure 3-4: Combined Plot for Clay and Mangrove Soils

Table 3-3: First Order Biodegradation Kinetic Constants and Half for soils

S/No	Soil Texture	Oil (w/w)	Kinetic equation	R^2	$t_{1/2}$ (days)
1	Mangrove	7000mg	Y=0.0571X-0.228	0.9064	12.14
2	Clayey	7000mg	Y=0.0337X+ 0.0108	0.9415	20.57

4. CONCLUSION

Experimental studies of crude oil degradation performed using small scale laboratory in-situ systems was employed on two different soil textures and the result obtained was utilized in the analysis of the extent of degradation of crude oil present in a contaminated soil in order to determine the best and suitable treatment approach for use in field scale bioremediation applications. In the study a significant removal of hydrocarbon from contaminated soils was achieved when compared to the un-amended soils, proving the establish fact that bioremediation, with the addition of amendments, to be a viable choice for the remediation of oil-contaminated soils. The biodegradation of crude oil was high in the soils amended with inorganic fertilizer when compared to the controls.

The study also show that biostimulation with inorganic fertilizer in the attempt to remove crude oil contaminant from a clayey and a mangrove soil was more effective in the mangrove soil as revealed by the kinetic constant. A correlation relating degradation rate to soil texture, or size distribution of mineral particles is essential in rate equation formulation and subsequent strategy to decontaminate the soil from pollutants.

This study suggests that oil contaminated coarser soils to be easily treatable by applying bioremediation through biostimulation than finer soils and it is essential that further investigation be carried out. The results so obtained equally suggest that higher sand than clay content of soil favours faster crude oil degradation in soil.

A kinetic formulation of a correlation equation of particle size distribution and their interactive effect on the rate of TPH reduction is essential and will give remediation consultants a simple, fast and effective tool to estimate the biodegradation rate constant for soils allowing reasonable predictions for contaminated lands when the soil texture is known.

Conflict of Interest

We declare that there is no conflict of interest concerning this publication.

4.1. References

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