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Full Length Research Paper

Investigation into the kinetics of biodegradation of crude oil in different soils

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An experimental study was conducted to examine crude oil degradation in different soil (clay, sandy loamy and swampy soil) of 1, 2, 3, 4 and 5 ml × 10 kg^{-1} pollution. The polluted crude oil and soil samples were obtained from Niger Delta area of Nigeria and microbial analysis were conducted on the samples for the purpose of identification, isolation and characterization of possible microbes with a view to determine the kinetics of the reaction (microbial growth rate). Model equations were developed to simulate the degradation and microbial growth rate kinetics of different soil polluted with crude oil as a function of volume, time, substrate concentration and specific rate. The increase in volume of crude oil applied in the soil samples also induced the microbial activities and the two microbial species discussed in this paper is applicable to the study of the kinetics of biodegradation and the characterization of the product, heat generated and new biomass produced in the system.

Key words: Investigation, kinetics, biodegradation, crude oil, different soil.

INTRODUCTION

Through the years, many experimental and theoretical studies have been done on the kinetics of biodegradation of crude oil (James and David, 1977; Alkinson and Marintuna, 1983; Barelay et al., 1990). The subject is of fundamental importance in the comprehension of any phenomenon involving crude oil degradation. The microbial activities enhance environmental cleanup (Antal and Mgbomo 1973), the release of gases, carbon dioxide, heat and new biomass on surface as it occurs in the bioremediation process (Milkin and Steart, 1974; Ogoni and Gumus, 2001; Ogoni, 2002), characterization of micro-organism (Alkinson and Marintuna, 1983; Sterling et al., 2002; Fingas, 2000; Lee et al., 2002; Lessard and Demarco, 2000; Page et al., 2000; Ukpaka, 2010, 2011), determination of total aerobic heterotrophic bacteria and fungi (Ronald 1992; Ukpaka et al., 2005) and enumeration of hydrocarbon utilizing bacteria and fungi (Antal and Mgbomo 1973); Folsom et al., 1990; Lodaya et al., 1991). The activities of the petroleum industry on the environment have attracted the attention of environmentalists on the effluent discharge into the environment emanating from exploration, production, refining and utilization. Recent investigation carried out by various research groups reveal that due to the high level of petroleum activities in Nigeria, and other parts of the world, there is a high concentration of the petroleum hydrocarbon contaminants, traceable to both upstream and downstream sectors of the economy (Gandy and Gandy, 1988). This has resulted in environmental pollution, which affects the ecological system (Schmidt and Gier, 1990; Parson et al., 1990; Phelps et al., 1990; Bashir et al., 1990; Scow et al., 1990; Kistner and Kornelius, 1990; Deweerd et al., 1991; Schnell et al., 1991; Zheng and Yapa, 2000; Ukpaka, 2011a; Ukpaka and David, 2010).

Although, biodegradation is an important process used in minimizing potentially adverse impacts on environmental system, traditionally, it has not been considered quantitatively in environmental assessments. Efforts to use the kinetic of biodegradation system to judge the qualitative evaluation of microbial activities, its biodegradation properties (for example, “fast” or “slow”) or rigorous quantitative models, to predict the kinetics of biodegradation and microbial activities on the different types of the soil used for this investigation (Wami and Ogoni, 1997; Parsons and Govers, 1990; Ronald, 1992).

However, scientific investigation on the effect of oil pollution in Nigeria only began recently after the shell-BP Bomu 11 blows out in July, 1970. The Texaco blow out in 1980 and the Agip Oyakame pipeline leakage of 1980. The Safram (now elf) Obagi 21 blow of 1970 has all without any doubt resulted in disastrous effects on land. Since after the blow out, studies have been carried out on the effect of crude oil on the soil and aquatic environment with special emphasis in its degradation by micro-organisms, since the recognition of the interaction of micro-organisms and petroleum (Antal and Mgbomo 1973). They have been used greatly in solving the environmental problems.

In this research work, however, investigation was conducted in identification, isolation, characterization of micro-organisms and the determination of the physicochemical properties of the crude oil and the soil samples (sandy loam, swampy soil and clay soil). In this case heat substrate reaction kinetics, microbial growth kinetics and product kinetics modeled equations were developed to study the principle behind the bioremediation process. Bioremediation processes are used to treat contaminated soil, success of such treatment processes lies in degrading the organic contaminants and reducing both the toxicity as well as the migration potential of the hazardous constituents (Irwin, 1975; Alkinson and Marintuna, 1983; Barelay et al., 1990; Digrazia et al., 1990; Dasappa and Loehr, 1991; Miller and Alexander, 1991). The role of microbes in the corrosion of metals is due to the chemical activities (metabolism) associated with microbial growth under favourable condition (James and David, 1977; Goldsmith et al., 1989; Arvin et al., 1991). This microbial activities associated with chemical reaction can accelerate exponentially the rate of degradation. Although these activities may be suppressed by mechanical techniques, biological activities often grow again when favourable conditions are restored (Awwa, 2000; Guan, 2001; Kakporbia, 2001; Ukpaka et al., 2010; Ukpaka, 2009).

In fact, it confirms that no comprehensive and feasible models have been developed on effect of different soil samples in biodegradation kinetics of crude oil in batch reactors. However, it is the purpose of this research work to correlate the biodegradation kinetics system of the different soil samples as a function of timer, volume of crude oil to soil ratio, microbial population, substrate concentration and then determination of Line Weaver Bulk Plot parameters (Vmax or μ_{max} and Ks or Km) since the microbial degradation of crude oil under environmental conditions in soil phase using aerobic, anaerobic and facultative anaerobic condition is influenced by volume of crude oil deposited, the soil texture and structure, the type of micro-organism present and the composition of both the crude oil and the soil (Ukapa, 2010; Antunes-do et al., 2010; Scbastiao and Guides, 2006; Brekke and Solberg, 2005; Jha et al., 2008; Antunes-do and Coasta, 2000; Guo and Wang, 2009).

THE MODEL

Biomass growth rate model

When an organic waste (petroleum hydrocarbon) is discharged into the environment, the organic content of the effluent undergoes biochemical reactions as reported (Irwin, 1975). The rate of biodegradation is influenced by the concentration of the substrates and the product inhibition (James and David, 1977). The biodegradation is generally classified as aerobic, anaerobic and facultative anaerobic process taking place under the same environmental condition, resulting in the production of new biomass, carbon dioxide, water and product.

$$[\text{Soil + crude oil}]_{\text{mixed}} + \text{micro-organism} \xrightarrow{K} \text{gases} + CO_2 = \text{heat release} + \text{new biomass} \quad (1)$$

Where, $[\text{soil + crude oil}]_{\text{mixed}}$ = A, micro-organism = E, product [gas and CO_2] = P heat generated = Q, and other hydrocarbon gases.

Therefore Equation (1) can be written as $A+E \rightarrow P+E$ (2)

The microbial growth rate kinetics can be experienced at the lag, progressive, stationary and decline phase and for dynamic studies, the general conservation equation for a steady state must be modified to give the following unsteady state mass balance;

$$\frac{d}{dt}\left(\text{biomass in the system}\right) = \left(rate\ of\ addition\ of\ micro-organism\ to\ system\right) - \left(rate\ of\ removal\ of\ micro-organism\ from\ system\right) + \left(rate\ of\ production\ within\ system\right) \quad (3)$$

Assuming the rate of addition and removal of micro-organism from the system is equal. Therefore equation (3) becomes;

$$\frac{d}{dt}\left(biomass\,\text{in}\,the sytem\right) = \left(rate\ of\ production within system\right) \quad (4)$$

Since the rate of growth of biomass is proportional to the initial content or number of micro-organism (biomass growth of particular microbial species presented), the time required for the biomass increase was determined by the application of the differential.

$$\frac{d\mu}{dt} = \phi\mu \quad (5)$$

On rearranging Equation (5) yields

$$\frac{d\mu}{dt} - \phi\mu = 0 \quad (6)$$

Where $\frac{d\mu}{dt}$ change in biomass per unit time is, μ is the micro organism and ϕ is the proportionality constant.

Therefore Equation (6) can be written in terms of bacteria and fungi species present in the system.
hence,

$$\frac{d\mu_B}{dt} - \phi_B\mu_B = 0 \quad (7)$$

and

$$\frac{d\mu_F}{dt} - \phi_F\mu_F = 0 \quad (8)$$

where $\frac{d\mu_B}{dt}$ and $\frac{d\mu_F}{dt}$ are changes in biomass per unit time for bacteria and fungi species, ϕ_B and ϕ_F are proportional constant for bacteria and fungi species, μ_B and μ_F are population of microorganism for bacteria and fungi species in the system.

Equation (6) was solved by considering the necessary boundary conditions such as; t = 0, $\mu_{(0)} = \mu_0$.
Therefore application of mathematical approach (Laplace transfer) to Equation (6) yielded

$$S\mu_o - \mu(0) - \phi\mu_{(s)} = 0 \quad (9)$$

Substituting the boundary condition at, t = 0, $\mu(0) = \mu_o$ into equation (9) and rearranging, it becomes

$$\mu_{(s)} = \frac{\mu_o}{S - \phi} \quad (10)$$

Therefore Laplace inverse of equation (10) with respect to time gives

$$\mu_{(t)} = \mu_o e^{\phi t} \quad (11)$$

Therefore the value of ϕ was determined by rearranging Equation (11) thus:

$$\frac{\mu_t}{\mu_0} = e^{\phi t} \quad (12)$$

Simplifying Equation (12), it becomes

$$\ln\frac{\mu_t}{\mu_o} = \phi t \quad (13)$$

$$\therefore \quad \phi = \frac{1}{t} In \frac{\mu_{(t)}}{\mu_o} \quad (14)$$

Where t = time per week.

Considering the initial statement at the progressive phase for one week interval neglecting the effect of temperature and nutrient, the following expressions will be obtained as shown in Table 1, for the determination of various ϕ_B and ϕ_F. Using Equation (14), at t = 1, yields the different values in Table 1.

Where μ is specific rate, μ_{max} is maximum specific rate, [S] is substrate concentration and k_m is the equilibrium constant.

Monod equation model

The Monod equation for microbial kinetic which rates the specific growth rate of the micro-organism and the limiting components. The general form of this equation is presented by Alkinson and Marintuna (1983) as;

$$\mu = \frac{\mu_{\max}[S]}{K_m + [S]} \quad (15)$$

Model for correlation of Monod equation and biomass growth rate

Considering the stage at which the specific rate μ is a function of time (t) or time dependent, therefore equation (15) can be written as:

$$\mu_o e^{\phi t} = \frac{[\mu_o e^{\phi t}]_{\max}[S]}{K_m + [S]} \quad (16)$$

Substituting the values obtained in Table 1 into Equation (12) yields the result in the Table 2.

Table 1. Determination of the various proportionality constants for ϕ_B and ϕ_F.

Oil applied ml x 10 kg^{-1} (volume)	Proportionality constants ϕ_B and ϕ_F					
	$[\phi]_{clay\ soil}$		$[\phi]_{sandy\ loamy}$		$[\phi]_{swamp\ soil}$	
	ϕ_B	ϕ_F	ϕ_B	ϕ_F	ϕ_B	ϕ_F
0	$\frac{3}{4}\mu_{OB}$	$\frac{33}{40}\mu_{OF}$	$\frac{16}{25}\mu_{OB}$	$\frac{57}{100}\mu_{OF}$	$\frac{3}{5}\mu_{OB}$	$\frac{9}{50}\mu_{OF}$
1	$\frac{39}{50}\mu_{OB}$	$\frac{33}{50}\mu_{OF}$	$\frac{57}{100}\mu_{OB}$	$\frac{11}{25}\mu_{OF}$	$\frac{83}{100}\mu_{OB}$	$\frac{3}{10}\mu_{OF}$
2	$\frac{22}{25}\mu_{OB}$	$\frac{3}{4}\mu_{OF}$	$\frac{21}{25}\mu_{OB}$	$\frac{37}{50}\mu_{OF}$	$\frac{3}{4}\mu_{OB}$	$\frac{9}{25}\mu_{OF}$
3	$\frac{7}{10}\mu_{OB}$	$\frac{83}{100}\mu_{OF}$	$\frac{17}{20}\mu_{OB}$	$\frac{9}{10}\mu_{OF}$	$\frac{22}{25}\mu_{OB}$	$\frac{33}{50}\mu_{OF}$
4	$\frac{73}{100}\mu_{OB}$	$\frac{43}{50}\mu_{OF}$	$\frac{43}{50}\mu_{OB}$	$\frac{14}{25}\mu_{OF}$	$\frac{39}{50}\mu_{OB}$	$\frac{19}{25}\mu_{OF}$
5	$\frac{34}{50}\mu_{OB}$	$\frac{4}{5}\mu_{OF}$	$\frac{39}{50}\mu_{OB}$	$\frac{1}{2}\mu_{OF}$	$\frac{4}{5}\mu_{OB}$	$\frac{73}{100}\mu_{OF}$

Michael's Menten model

The Michael's Menten equation for substrate kinetic which gives the specific rate of substrate concentration and limiting component; the general form of this equation is presented by Irwin (1975) as:

$$V = \frac{V_{max}[S]}{K_S + [S]} \quad (16a)$$

Enzyme/substrate reaction model (Figure 1), considering the following reaction mechanism;

Where A is substrate, E is enzyme, P is product EA is enzyme-substrate complex, K_1, K_2, K_3 and K_4 are the various equilibrium constants.

$$A+E \xrightarrow{K_1} P + E \quad (17)$$

Rate of reaction model

With the rate equation given as

$$-\gamma_A = \frac{dC_A}{dt} = K \quad (18)$$

Where $K = KC_{EO}C_{AO}$ = constant, integrating (18) between the limits

$C_A = CAO$ at $t = 0$ and $C_A = C_A$ at $t = t$ yields

$$C_A = CAO = -K_t \quad (19)$$

Still considering the reaction given as:

$$A + E \xrightarrow{K_1} P + E$$

With the rate equation given as:

$$-\gamma_A = \frac{dC_A}{dt} = KC_{EO}C_A \quad (20)$$

Where K is kinetic rate constant, C_{Eo} is initial concentration of the enzyme, C_A is concentration of the substrate, r_A is rate of reaction, $\frac{dC_A}{dt}$ is the rate of change of substrate concentration per unit time. Since one of the characteristics of enzyme or catalyst is that, their concentration is constant in any reacting system

Thus,

$$-\gamma_A = \frac{dC_A}{dt} = KC_A \quad (21)$$

Where $K = KC_{EO}$ = constant, integrating Equation (21) at $C_A = C_{Ao}$ and at $t = t$ yields

$$\ln C_A - \ln C_{AO} = -Kt \quad (22)$$

Substrate concentration model

Let us consider the saturation kinetics

$$A+E \underset{K_3}{\overset{K_2}{\rightleftarrows}} EA \xrightarrow{K_e} P + E$$

Table 2. Equations that led to the determination of specific growth, maximum specific growth rate and equilibrium constants for different soil samples.

Oil applied ml x $10kg^{-1}$	Specific rate equations					
	Clay soil		Sandy loamy soil		Swampy soil	
	Bacterial (μ_B)	Fungi (μ_F)	Bacterial (μ_B)	Fungi (μ_F)	Bacterial (μ_B)	Fungi (μ_F)
0	$\left[\mu_o e^{(In\,3/4)t}\right] = \frac{\left[\mu_0 e^{(In\,3/4)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,16/25)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,57/100)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/5)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$
1	$\left[\mu_o e^{(In\,39/50)t}\right] = \frac{\left[\mu_0 e^{(In\,39/50)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,57/100)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,1/25)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,83/100)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,7/10)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$
2	$\left[\mu_o e^{(In\,22/25)t}\right] = \frac{\left[\mu_0 e^{(In\,22/25)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/4)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,21/25)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,37/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/4)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,23/25)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$
3	$\left[\mu_o e^{(In\,7/10)t}\right] = \frac{\left[\mu_0 e^{(In\,7/10)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,83/100)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,17/20)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,93/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,22/25)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$
4	$\left[\mu_o e^{(In\,73/100)t}\right] = \frac{\left[\mu_0 e^{(In\,73/100)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,43/50)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,43/50)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,14/25)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,39/50)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,19/25)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$
5	$\left[\mu_o e^{(In\,34/50)t}\right] = \frac{\left[\mu_0 e^{(In\,34/50)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,3/5)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,39/50)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,1/2)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$	$\mu = \frac{\left[\mu_0 e^{(In\,4/5)t}\right]_{max}[S]_B}{K_{mB}+[S]_B}$	$\mu = \frac{\left[\mu_0 e^{(In\,73/100)t}\right]_{max}[S]_F}{K_{mF}+[S]_F}$

where $\mu = \mu_0 e^{In\phi t}$

Recalling the Michael's – Menten equation for such reaction gives

$$-\gamma_A = \frac{K_2 C_A}{K_m + C_A} \qquad (23)$$

Where $K_m = K_2 / K_1$

Substituting Equation (21) into Equation (23) and integrating between the limits yields:

$$\frac{In\, C_A / C_{AO}}{C_A - C_{AO}} = \frac{K_2 t}{K_m (C_{AO} - C_A)} - \frac{1}{K_m} \qquad (24)$$

Hence,

$$In\frac{C_A / C_{AO}}{(C_A - C_{AO})} \quad Vs \quad \frac{t}{(C_{AO} - C_A)}$$

Product kinetic model

The rate at which crude oil is being used up to produce hydrocarbon gases, CO_2, H_2O, heat and biomass is given as:

$$\frac{dC_{CO2}}{dt} = -\gamma_{CO2} \qquad (25)$$

$$\frac{dC_{H_2O}}{dt} = -\gamma_{H_2O} \qquad (26)$$

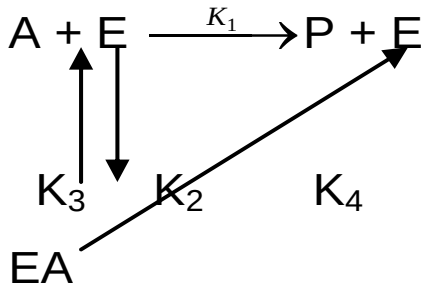

Figure 1. The enzyme-substrate reaction mechanisms.

$$\frac{dC_{Heat}}{dt} = -\gamma_{Heat} \quad (27)$$

$$\frac{dC_b}{dt} = -\gamma_{biomass} \quad (28)$$

The rate law for Equations (25), (26), (27) and (28) is given as:

$$-\gamma_{CO_2} = \frac{V_{\max(CO_2)} C_{CO2}}{K_{CO2} + C_{CO2}} \quad (29)$$

$$-\gamma_{H_2O} = \frac{V_{\max(H_2O)} C_{H_2O}}{K_{H_2O} + C_{H_2O}} \quad (30)$$

Therefore the overall rate of the product produce can be expressed as:

$$\frac{dC}{dt} = \frac{dC_{CO2}}{dt} + \frac{dC_{H_2O}}{dt} + \frac{dQ_{Heat}}{dt} + \frac{dC_{biomass}}{dt} \quad (31)$$

$$-\gamma_{overall} = (-\gamma_{CO2}) + (-\gamma_{H2O}) + (-\gamma_{Heat}) + (-\gamma_{biomass}) \quad (32)$$

where $-\gamma_{overall}$ is the overall rate of reaction, $-\gamma_{CO2}$ is the rate of production of carbon dioxide, $-\gamma_{H2O}$ is the rate of production of water, $-\gamma_{Heat}$ is the rate of heat generated during the reaction, $-\gamma_{biomass}$ is the rate of production of biomass in the system, $\frac{dc}{dt}$ is the change in substrate concentrate of the reaction system per unit time, $\frac{dc_{CO_2}}{dt}$ is the change in carbon dioxide concentration per unit time, $\frac{dc_{H_2O}}{dt}$ is the change in water concentration per unit time, $\frac{dQ_{Heat}}{dt}$ is the change in quantity of heat generated per unit time and $\frac{dc_{biomass}}{dt}$ is the change in biomass built up per unit time

Relating in terms of Michael's Menten equation yields

$$\gamma_{overall} = \frac{V_{\max(CO_2)}}{K_{CO_2} + C_{CO_2}} + \frac{V_{\max(H_2O)} C_{H_2O}}{K_{H_2O} + C_{H_2O}} \quad (33)$$

Where ($-\gamma_{Heat}$) and ($-\gamma_{biomass}$) is negligible

Model for the determination of fractional conversion

Substituting equation (25) into equation (29) and then rearranging and integrating yields

$$t = \int_{C_{CO_2}}^{C_{CO_2}} \frac{dC_{CO_2}}{-\gamma_{CO_2}} \quad (34)$$

$$t = \int_{C_{CO_2}}^{C_{CO_2(0)}} \frac{K_{CO_2} + C_{CO_2}}{V_{\max(CO_2)} C_{CO_2}} dC_{O_2} \quad (35)$$

Writing equation (35) in terms of fractional conversion yields

$$C_{CO2} = C_{CO2(0)} (1 - x) \quad (36)$$

Therefore substituting Equation (36) into Equation (35) yields

$$t = \frac{K_{CO_2}}{V_{\max(co_2)}} In \frac{1}{1-x} + \frac{C_{CO_2}}{V_{\max} C_{O_2}} \quad (37)$$

Similarly for H_2O: $t = \frac{K_{H_2O}}{V_{\max(H_2O)}} In \frac{1}{1-x} + \frac{C_{H_2O}}{V_{\max} C_{H_2O}}$ (38)

$$CH_U : t = \frac{K_{CH_U}}{V_{\max(CH_U)}} In \frac{1}{1-x} + \frac{C_{CH_U}}{V_{\max} C_{CH_U}} \quad (39)$$

Where X = fractional conversion, K_{H2O}, K_{CO2}, K_{CH4} are equilibrium constants for water, carbon dioxide and methane respectively. V_{max} (H_2O), $V_{max(CO2)}$, $V_{max(CH4)}$, are maximum specific rate values for water, carbon dioxide and methane respectively.

Heat kinetic model

Since the instantaneous microbial heat generated rate Q_{gr} is given as

$$Q_{gr} = U\text{reactor}\beta\mu \, 1/Y_A \quad (40)$$

Where Q_{gr} is heat generated during the reaction process, $V_{reactor}$ is the reactor volume, β is a constant, μ is the microbial growth rate, Y_A is yield factor of component A, therefore Equation (40) can be rearranged and written as:

$$\mu = \frac{Q_{gr} Y_A}{V_{reactor}} \beta \quad (41)$$

Recalling the Monod equation

$$\mu = \frac{\mu_{\max} S}{K_m + S} \quad (42)$$

Therefore substituting Equation (42) into Equation (41) yields

$$\frac{Q_{gr} Y_A}{V_{reactor} \beta} = \frac{\mu_{\max} [S]}{K_m + [S]} \quad (43)$$

where $-\gamma_{Heat} = \mu$ and $\gamma = \mu = V$

Hence

$$Q_{gr} = \left[\frac{\mu_{\max} [S]}{K_m + [S]}\right]\left[\frac{V_{reactor} \beta}{Y_A}\right] \quad (44)$$

Similarly,

$$-\gamma_{biomass} = \frac{\mu_{\max (biomass)} \, C_{biomass}}{K_{biomass} + C_{biomass}} \quad (45)$$

Where μ is specific rate of microbes, μ_{max} is maximum specific growth rate of microbes, [S] is substrate concentration, $V_{reactor}$ is volume reactor, Y_A is yield factor, is yield factor, Y_A $C_{biomass}$ is biomass concentration

MATERIALS AND METHODS

Sample collection

Soil samples were collected without bias, the surface soil of about 0 to 10 cm depth. Each soil sample was collected from six different locations and then mixed together to obtain a gross representation of each sample. The cap of the sterile tube is used to collect soil sample from each location for microbial study of the unpolluted soil. And they are then stored in a refrigerator before analysis is carried out on it, which is by preparing a solution of 14g of nutrient agar and 500ml of distilled water with a pelt of 7.4 in a conical flask. Sample location: Middle Belt-soil in Kaima, clay texture mangrove – swampy – Eagle Island and coast plain Terrac-sandy soil.

Determination of total aerobic heterotrophic bacteria and fungi

The variable plate count method, using a surface spreading technique was used to determine the number of soil aerobic bacteria and fungi. Serial dilution was prepared using soil suspension, which is obtained by adding one gram (1 g) of soil sample obtained from the centre of soil cores into 100 m of sterile distilled water. The suspension was shaken vigorously and allowed to settle before 1 ml is used for serial dilution. The 1 ml dilution is plated on triplicate agar supplement at 28°C for 24 h (1day) (Atlas 1981).

Aerobic fungi was determined also by surface spreading technique, using serial dilution, 1 ml of each dilution was plated on malt extract agar into which 100 μg/l of streptomycin and 15 mg of penicillin G has been incorporated in plates triplicate were incubated at 25°C for 72 h (3days) (Atlas 1981).

Enumeration of hydrocarbon utilizing bacteria and fungi

It involves the viable count method using surface spreading technique. Serial dilution of the soil samples was prepared form 10^{-1} to 10^{-15}. One ml of soil dilution was plated in triplicate with agar and 50 μg/l of nystatin to inhibit fungi for bacteria count. After then the polluted soil is put in the Petri dishes, the plates was wrapped with masking tape and made airtight. This is aimed at supplying hydrocarbon as the sole source of carbon energy for growth of the utilizer through vapor phase transfer. The plates were incubated at 37°C for seven days before enumeration.

RESULTS AND DISCUSSION

Biodegradation of Nigeria crude oil in different soil were studied to determine the microbial and substrate kinetics and the Monod's constants (V_{max}, μ_{max} K_S and K_m) for both species used during the investigation. Also the microbial numbers of the micro-organism (Bacteria and fungi) per week activities are shown in Tables 3, 4, and 5 for the different soil types (clay soil, sandy soil and swampy soil). The initial microbial number used for this investigation is $5cfug^{-1}$ for the different experimental set-up.

Similarly, the experimental results obtained from the

Table 3. Microbial number (x $10^5 kg^{-1}$) in top 10cm of polluted soil; clay soil (Bacteria and fungi).

Oil applied ml x 10 kg^{-1}	Total microbial number introduced = 5cfug^{-1} for each of the species (microorganism)													
	1st week		2nd week		3rd week		4th week		5th week		6th week		7th week	
	Ba_1	Fu_1	Ba_2	Fu_2	Ba_3	Fu_3	Ba_4	Fu_4	Ba_5	Fu_5	Ba_6	Fu_6	Ba_7	Fu_7
0	9	7	12	6	10	9	14	10	20	16	15	16	13	12
1	11	10	14	15	12	17	16	20	28	23	22	16	14	6
2	16	14	18	12	14	16	19	23	32	27	29	22	18	10
3	19	16	20	10	16	12	23	18	50	27	32	20	24	5
4	21	24	24	20	19	23	26	37	64	51	36	69	28	30
5	25	24	27	30	20	46	29	60	83	74	40	38	32	21

Table 4. Microbial number (x $10^5 kg^{-1}$) in top 10cm of polluted soil, farm land soil (sandy, loamy) bacterial and fungi.

Oil applied ml x 10 kg^{-1}	Total microbial number introduced = 5 cfug^{-1} for each of the specie (microorganism)													
	1st week		2nd week		3rd week		4th week		5th week		6th week		7th week	
	Ba_1	Fu_1	Ba_2	Fu_2	Ba_3	Fu_3	Ba_4	Fu_4	Ba_5	Fu_5	Ba_6	Fu_6	Ba_7	Fu_7
0	11	8	17	14	18	16	20	20	30	26	20	39	14	10
1	16	14	28	32	36	40	48	60	100	65	80	68	78	47
2	22	14	26	22	38	30	80	71	96	83	70	64	40	25
3	23	20	27	22	51	47	78	61	125	117	92	77	40	38
4	25	20	29	36	70	68	91	135	173	206	82	104	50	70
5	25	25	32	50	88	90	101	200	250	310	83	112	50	80

Table 5. Microbial number (x 10^5 kg^{-1}) in top 10 cm of polluted soil, swamp soil (Bacterial and fungi).

Oil applied ml x 10 kg^{-1}	Total microbial number introduced = 5cfug^{-1} for each of the species (microorganism)													
	1st week		2nd week		3rd week		4th week		5th week		6th week		7th week	
	Ba_1	Fu_1	Ba_2	Fu_2	Ba_3	Fu_3	Ba_4	Fu_4	Ba_5	Fu_5	Ba_6	Fu_6	Ba_7	Fu_7
0	3	5	5	11	6	19	7	28	8	53	7	24	6	10
1	5	8	6	27	8	44	9	63	11	108	12	63	11	41
2	6	11	8	30	10	34	14	40	16	53	17	23	15	17
3	7	16	8	24	12	27	14	30	18	35	24	10	20	5
4	7	23	9	16	12	21	14	23	19	23	28	9	25	4
5	8	30	10	22	12	30	16	30	19	17	32	8	28	8

investigations for the consumption rate of substrate concentration on the different types of soil used is shown in Table 4.

Where A_{sa}, A_{sw} A_{cl} = 0ml x $10kg^{-1}$ (Zero pollution)
B_{sa}, B_{sw} B_{cl} = 1 ml × 10 kg^{-1} (1 ml pollution)
C_{sa}, C_{sw} C_{cl} = 2 ml × 10 kg^{-1} (2 ml pollution)
D_{sa}, D_{sw} D_{cl} = 0 ml × 10 kg^{-1} (3 ml pollution)
E_{sa}, E_{sw} E_{cl} = 0 ml × 10 kg^{-1} (4 ml pollution)
F_{sa}, F_{sw} F_{cl} = 5 ml × 10 kg^{-1} (5 ml pollution)

Also, the computational result that led to the determination of specific rate (V) for the different soil types is shown in Table 7.

Microbial kinetic characteristics

The results obtained from the investigation shows lag phase, progressive phase, stationary phase and death or decline phase was used in the determination of the microbial number (μ) cfu/kg at each phase. It was observed that for the lag phase, there was a decrease in the initial microbial number and increase in biomass at

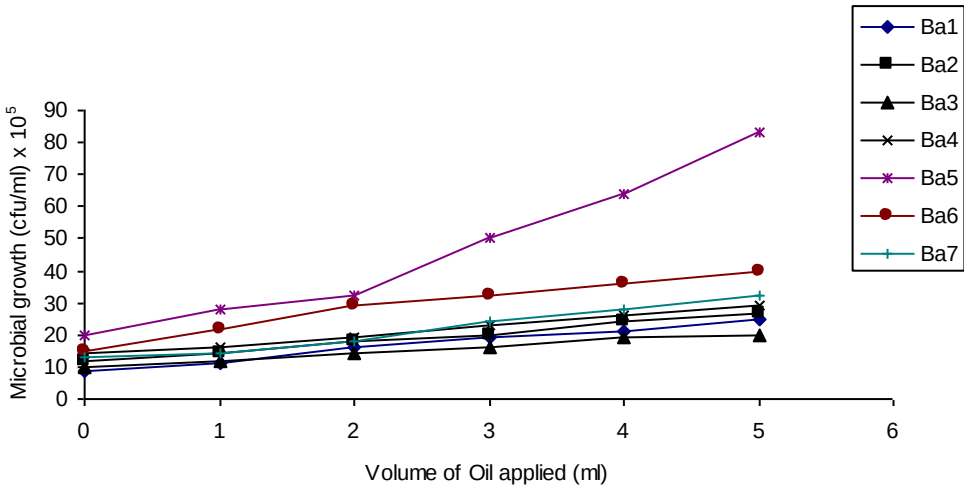

Figure 2. Microbial growth vs volume of oil applied for clay soil (bacteria sp).

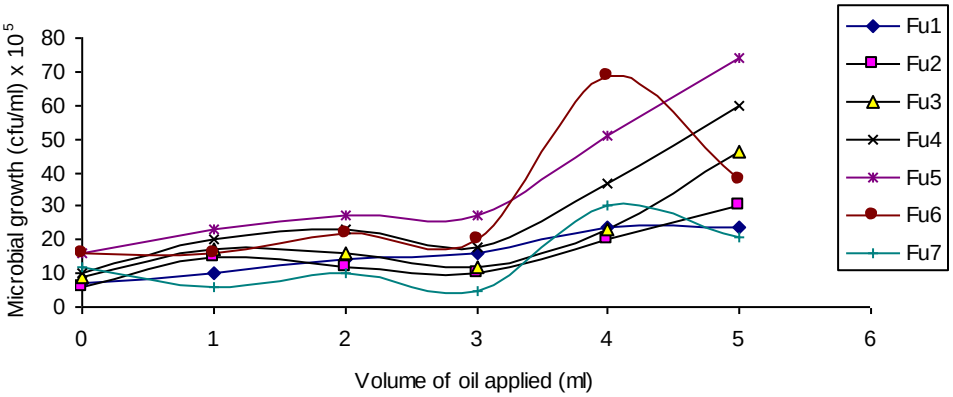

Figure 3. Microbial growth vs volume of oil applied for sandy loamy (fungi sp).

the progressive phase as shown in Tables 3, 4 and 5 for the different soil samples.

As shown in Tables 1, 2 and 3, it was discovered, from analysis, that growth rate of bacteria and fungi species at the progressive phase increased linearly until the whole substrate concentration was reduced to the minimum level when the process became stagnant (stationary phase). Similarly, the decay rate increases as the substrate consumption decreases. Results obtained as reflected in this paper indicates that the growth rate of the bacteria and fungi species increased with increase in time until the stationary phase was attained. Similarly, the decay rate of the bacteria and fungi species increased with increase in time until the whole substrate concentration was reduced to the minimum level.

In modeling, the rate of microbial growth of bacteria and fungi species in degrading crude oil was influenced by the degree of environmental factors such as temperature. (20 to 38°C), pH (sandy-loamy = 6.9, swampy soil = 9.7 and clay soil = 7.1) and electrical conductivity (sandy-loamy = 120 × 10^{-6}mol/cm, swampy soil = 498 × 10^{-6} mol/cm and clay soil = 260 × 10^{-6} mol/cm).

Effect of volume of crude oil applied on the biodegradation process

The effect of the increase in volume of crude oil applied on the soil samples to accompanying biodegradation are shown in Figures 2, 3, 4, 5, 6 and 7 for crude oil concentration of 1, 2, 4 and 5 ml. The substrate concentration at which the comparison for sandy loamy is 1 < l < 3 < 5 < 4 ml, clay is 1 < 2 < 3 < 4 < 5 ml only at 28 and 35 days that 5 < 4 ml for clay and sandy loamy soil. The higher the volume of crude oil concentration, the higher the microbial growth rate and the higher the estimated degradation period.

At 1 ml, volume of crude oil applied to the different soil samples yields substrate concentration of the following order $S_{sa} < S_{cL} < S_{sw}$ (S is the substrate concentration of

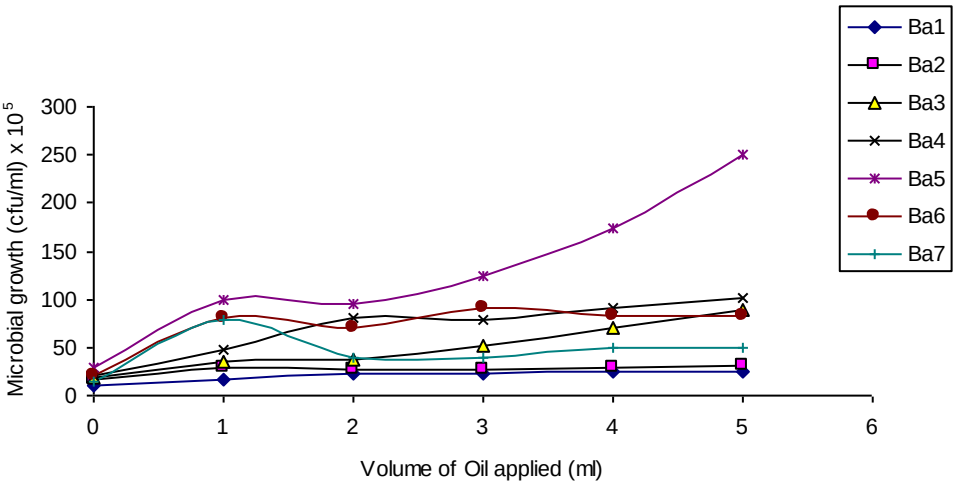

Figure 4. Microbial growth vs volume of oil applied for sandy loamy soil (bacteria sp.).

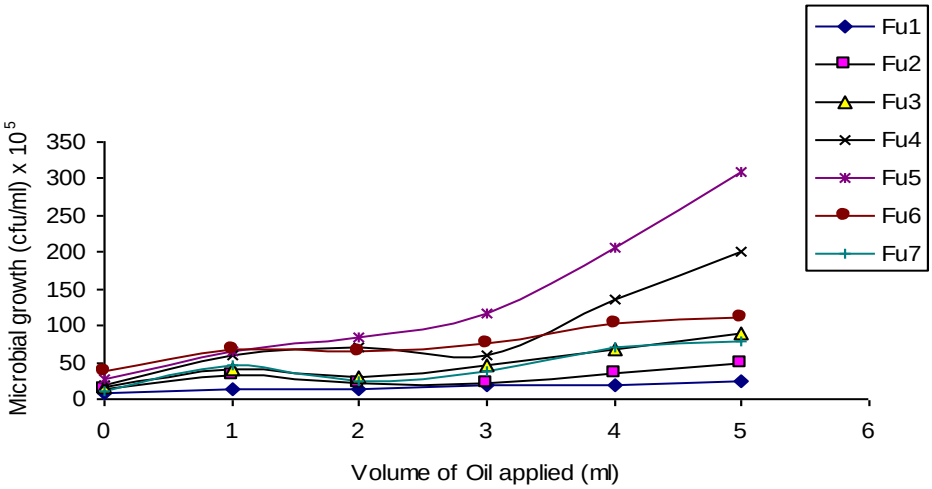

Figure 5. Microbial growth vs volume of oil applied for sandy loamy soil (fungi sp.).

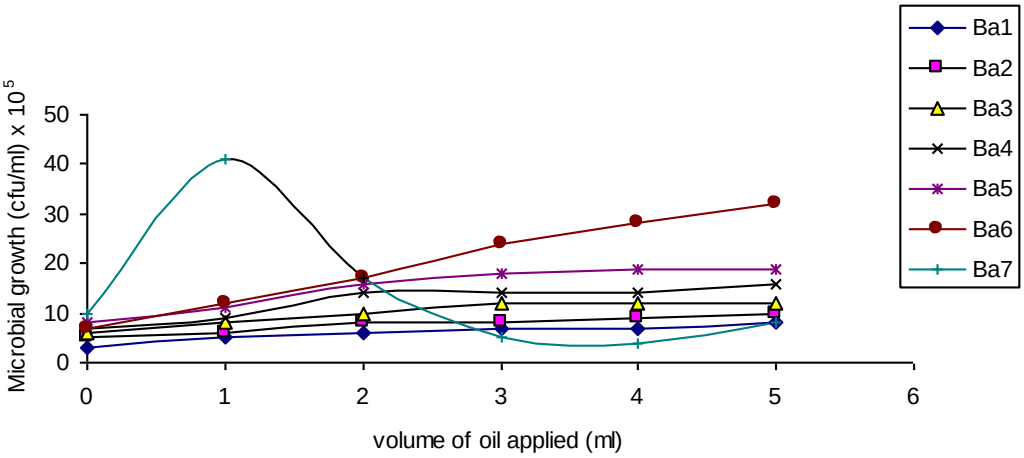

Figure 6. Microbial growth vs volume of oil applied for swampy soil (bacteria sp.).

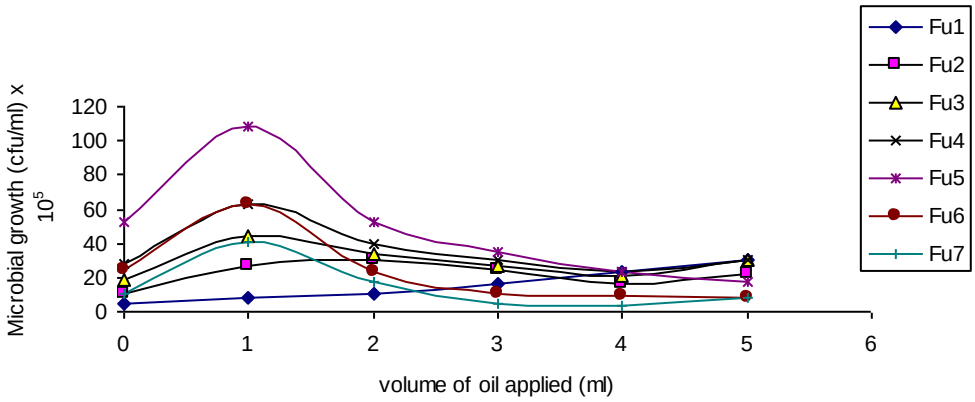

Figure 7. Microbial growth vs volume of oil applied for swampy soil (fungi sp.).

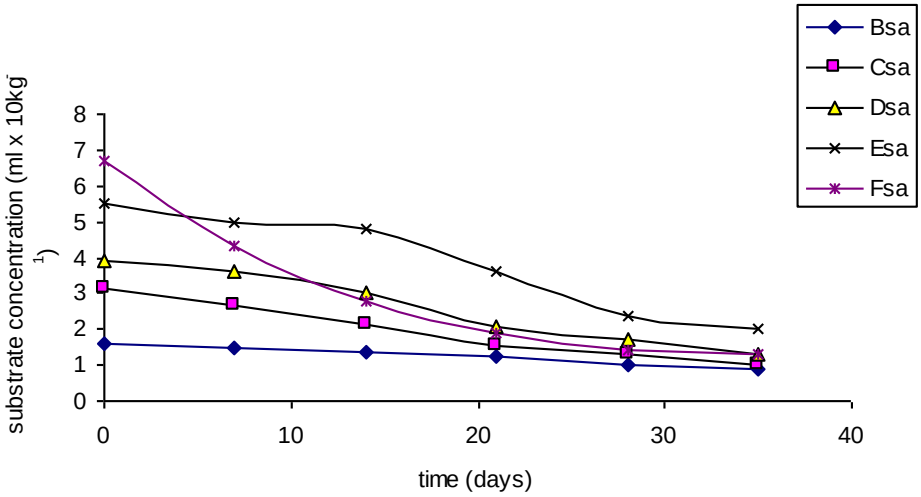

Figure 8. Substrate concentration vs time for sandy loamy soil.

1.45 < 1.92 < 1.98); for 2 ml, $S_{sa} < S_{sw} < S_d$ (2.64 < 3.60 < 3.966); for 3 ml, $S_{sa} = S_{sw} < S_{cL}$ (3.60 = 3.60 < 3.96); for 4 ml, $S_{sa} < S_{sw} < S_{cL}$ (5.00 < 5.08 < 5.70) and 5 ml, $S_{Sq} < S_{cL} < S_{sw}$ (4.32 < 5.46 < 5.76) at 7 days observation. This could be attributed to the physicochemical properties of the sample such as, pH (sandy loamy = 6.9, swampy soil = 9.7, and clay soil = 7.1) and electrical conductivity (sandy loamy = 120 × 10^{-6} mol/cm, swampy soil = 498 × 10^{-6}mol/cm and clay soil = 260 × 10^{-6} mol/cm).

Effect of time on the substrate concentration

Figures 8, 9 and 10 show the variation of the substrate concentration with the time for 1, 2, 3, 4 and 5 ml × 10 kg^{-1}. On the different soil samples, the biodegradation pattern of this reaction is slightly different as most of the substrate concentrations increases. The rate of change in substrate concentration varies with time and is different for different volume of crude oil applied. These results were used for determining the substrate concentration gradient. The investigation result shows that the values for concentration gradient depends on initial substrate concentration, composition of the crude oil, spreading rate, environmental temperature and temperature of the system, mechanical weathering which includes the rate of diffusion of the crude oil, evaporation of the lighter components (gases, and CO_2), microbial activity in the system and absence of microbial inhibitors.

The results of the theoretical model show a clear behaviour similar with those of the experimental values. The behaviour suggests that there is a difference in the substrate concentration gradient, as evaluated by the theoretic model.

Table 6 illustrates the substrate concentration at zero pollution, 1, 2, 3, 4 and 5 ml pollution for sandy loam, swampy and clay environment. Decrease in substrate concentration was experienced with increase in time for

Table 6. Experimentally determining the substrate concentration for the different types of soil.

Time (Day)	Substrate concentration (ml x 10kg^{-1})																	
	Sandy loam						Swampy						Clay					
	A_{sa}	B_{sa}	C_{sa}	D_{sa}	E_{sa}	F_{sa}	A_{sw}	B_{sw}	C_{sw}	D_{sw}	E_{sw}	F_{sw}	A_c	B_{cl}	C_{cl}	D_{cl}	E_{cl}	F_{cl}
0	Tr	1.58	3.16	3.90	5.50	6.72	Tr	2.06	3.65	4.81	5.10	6.10	Tr	1.96	4.16	4.83	5.77	5.96
7	Tr	1.46	2.64	3.60	5.00	4.32	Tr	1.98	3.60	4.71	5.08	5.76	Tr	1.92	3.96	4.50	5.70	5.46
14	Tr	1.36	2.16	3.00	4.80	2.80	Tr	1.92	3.54	4.53	5.00	5.12	Tr	1.86	3.60	4.42	4.90	4.63
21	Tr	1.26	1.56	2.10	3.60	1.92	Tr	1.86	3.48	4.43	4.96	5.00	Tr	1.52	3.48	3.92	4.50	3.93
28	Tr	1.02	1.32	1.72	2.40	1.40	Tr	1.82	3.38	4.09	4.92	4.86	Tr	1.46	3.40	3.73	4.00	3.55
35	Tr	0.90	1.00	1.31	2.00	1.31	Tr	1.79	3.27	4.03	4.80	4.73	Tr	1.38	3.30	3.70	3.93	2.97

Table 7. Computation of 1/S and 1/V for sandy loamy, clay, and swamp.

Time	Sandy loamy Substrate concentration (ml x 10kg^{-1})					Specific rate					Reciprocal substrate					Reciprocal of specific rate				
	S_{Fsa}	S_{Bsa}	S_{Csa}	S_{Dsa}	S_{Esa}	V_{Fsa}	V_{Bsa}	V_{Csa}	V_{Dsa}	V_{Esa}	$1/S_{Fsa}$	$1/S_{Bsa}$	$1/S_{Csa}$	$1/S_{Dsa}$	$1/S_{Esa}$	$1/V_{Fsa}$	$1/V_{Bsa}$	$1/V_{Csa}$	$1/V_{Dsa}$	$1/V_{Esa}$
0	6.72	1.58	3.16	3.90	5.50	0.34	0.02	0.07	0.04	0.07	0.15	0.63	0.32	0.26	0.18	-	-	-	-	-
7	4.32	1.46	2.64	3.60	5.00	0.22	0.01	0.07	0.09	0.03	0.23	0.68	0.38	0.28	0.20	2.94	50.00	14.29	25.00	14.29
14	2.80	1.36	2.16	3.00	4.80	0.13	0.01	0.09	0.13	0.17	0.36	0.74	0.46	0.33	0.21	4.55	100.00	14.29	11.11	33.33
21	1.92	1.26	1.56	2.10	3.60	0.07	0.03	0.03	0.05	0.17	0.52	0.79	0.64	0.48	0.28	7.69	100.00	11.11	7.69	5.88
28	1.40	1.02	1.32	1.72	2.40	0.01	0.02	0.05	0.06	0.06	0.71	0.98	0.76	0.58	0.42	14.29	33.33	33.33	20.00	5.88
35	1.31	0.90	1.00	1.31	2.00						0.76	1.11	1.00	0.76	0.50	100	50.00	20.00	16.67	16.67
	CLAY SOIL																			
	S_{Fsa}	S_{Bsa}	S_{Csa}	S_{Dsa}	S_{Esa}	V_{Fsa}	V_{Bsa}	V_{Csa}	V_{Dsa}	V_{Esa}	$1/S_{Fsa}$	$1/S_{Bsa}$	$1/S_{Csa}$	$1/S_{Dsa}$	$1/S_{Esa}$	$1/V_{Fsa}$	$1/V_{Bsa}$	$1/V_{Csa}$	$1/V_{Dsa}$	$1/V_{Esa}$
0	5.96	1.96	4.16	4.83	5.77	-	-	-	-	-	0.17	0.51	0.24	0.21	0.17	-	-	-	-	-
7	5.46	1.92	3.96	4.50	5.70	0.07	0.01	0.03	0.05	0.01	0.18	0.52	0.25	0.22	0.18	14.27	100.00	33.33	20.00	100.00
14	4.63	1.86	3.60	4.42	4.90	0.12	0.01	0.05	0.01	0.11	0.22	0.54	0.28	0.23	0.20	8.33	100.00	20.00	100.00	9.09
21	3.93	1.52	3.48	3.92	4.50	0.10	0.05	0.02	0.07	0.06	0.25	0.66	0.29	0.26	0.22	10.00	20.00	50.00	14.29	16.67
28	3.55	1.46	3.40	3.73	4.00	0.05	0.01	0.01	0.03	0.07	0.28	0.68	0.29	0.27	0.25	20.00	100.00	100.00	33.33	14.29
35	2.97	1.38	3.30	3.70	3.93	0.08	0.01	.01	0.01	0.01	0.34	0.72	0.30	0.27	0.25	12.5	100.00	100.00	100.00	100.00
	SWAMP																			
	S_{Fsa}	S_{Bsa}	S_{Csa}	S_{Dsa}	S_{Esa}	V_{Fsa}	V_{Bsa}	V_{Csa}	V_{Dsa}	V_{Esa}	$1/S_{Fsa}$	$1/S_{Bsa}$	$1/S_{Csa}$	$1/S_{Dsa}$	$1/S_{Esa}$	$1/V_{Fsa}$	$1/V_{Bsa}$	$1/V_{Csa}$	$1/V_{Dsa}$	$1/V_{Esa}$
0	6.10	2.06	3.65	4.81	5.10	-	-	-	-	-	0.16	0.49	0.27	0.21	0.20	-	-	-	-	-
7	5.76	1.98	3.60	4.71	5.08	0.05	0.01	0.01	0.01	0.01	0.17	0.51	0.28	0.21	0.20	20.0	100.00	100.00	100.00	100.00
14	5.12	1.92	3.54	4.53	5.00	0.09	0.01	0.01	0.03	0.01	0.20	0.52	0.28	0.22	0.20	11.11	100.00	100.00	33.33	100.00
21	5.00	1.86	3.48	4.43	4.96	0.02	0.01	0.01	0.01	0.01	0.20	0.53	0.29	0.23	0.20	50.00	100.00	100.00	100.00	100.00
28	4.80	1.82	3.38	4.09	4.92	0.03	0.01	0.01	0.05	0.01	0.21	0.55	0.30	0.24	0.20	33.33	100.00	100.00	20.00	100.00
35	4.73	1.79	3.27	4.03	4.80	0.01	0.01	0.02	0.01	0.02	0.21	0.56	0.31	0.25	0.20	100.00	100.00	50.00	100.00	50.00

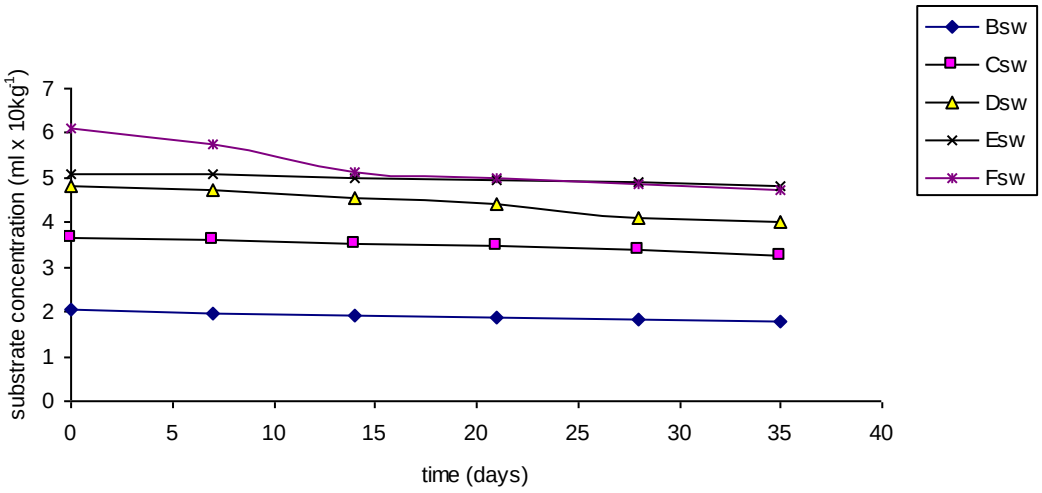

Figure 9. Substrate concentration vs time for swampy soil.

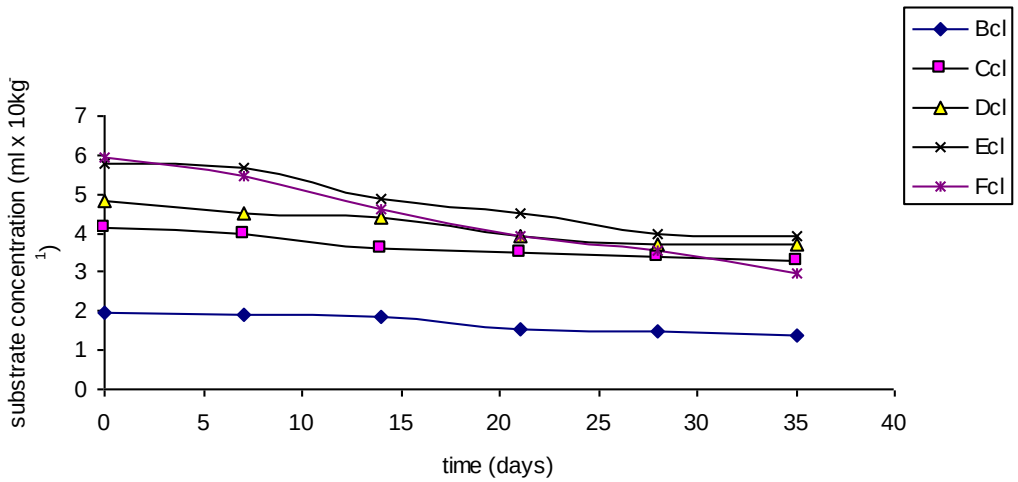

Figure 10. Substrate concentration vs time for clay soil.

1, 2, 3, 4 and 5 ml in the different soil environment.

Specific rate (Vor μ) maximum specific rate and (V_{max} or μ_{max}) and dissociation rate constant (K_m or K_s)

The specific rate of degradation was determined only for sandy loam, clay and swampy soil polluted with crude oil. The values of the specific rate for each of the experimental condition were obtained using the procedures outlined in this research investigation, the specific rates were determined by plotting substrate concentration against time (slope of the curve) for sandy loamy, clay and swampy soil mixtures (Nml × 10/kg, where N = 1,2,3,4 and 5).

The values of the maximum specific rate of substrate concentration and Michael's Menten constant is obtained by rearranging the equation obtained. Line-Weaver Bulk plot for the various experimental conditions, the results of the theoretical computed values of the reciprocal of the various values of the specific rate of substrate concentration are presented in Figures 8, 9 and 10. The values of maximum specific rate of substrate concentration and Michael's Menten constants were computed from the plots in Figures 11 and 12 using the equation $\left(\frac{K_D}{V_{max}} = slope\right)$

Conclusion

Models for the simulation of specific growth rate of bacteria and fungi species for 1, 2, 3, 4 and 5 ml × 10 kg^{-1} of different soil samples and degradation kinetic

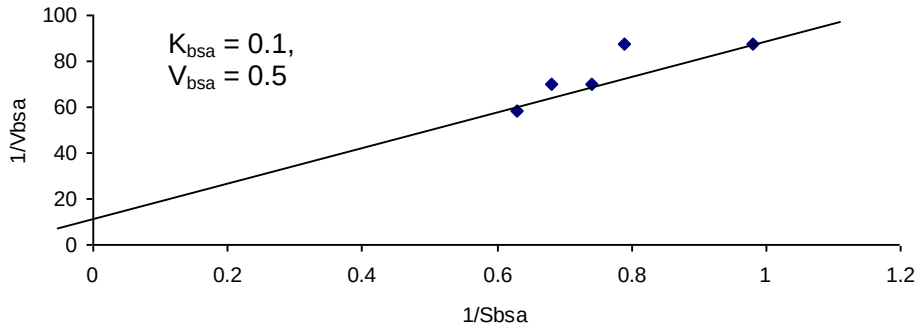

Figure 11. 1/Vbsa vs 1/Sbsa for C_8 degredation on sandy loamy soil.

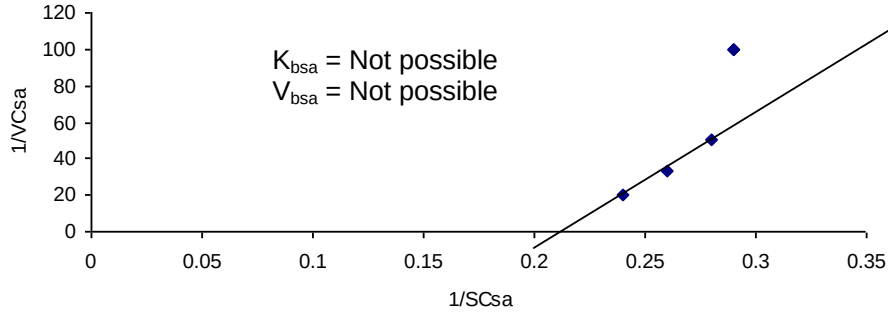

Figure 12. 1/VCsa vs 1/Scsa for C_8 degredation on clay soil.

equations developed and equation for the determination of heat generated during the enzyme – catalysed reaction has been proposed. They are based on the description of the simultaneous microbial growth rate and substrate utilization inside the reactor, on the characterization of the microbes and the substrate concentration.

The proposed models were assessed using data obtained from the experimental investigation. In the present experimental study, investigation into the kinetics of biodegradation of Nigeria crude oil in different soil was examined. The following results were obtained:

1) For the microbial growth rate of the species (bacteria and fungi) was sandy loamy > day > swamp soil.
2) The degradation rate for the process to enhanced environmental clean up was faster in the following order; sandy loamy > clay > swamp soil in bioremediation process.
3) Substrate concentration decreases with increase in microbial activities and time.
4) For the three soil sample and two microbial species, models were developed to predict the microbial growth, substrate concentration specific growth rate, specific rate of degradation, maximum specific growth rate, maximum specific rate of degradation, model for carbon dioxide, water, biomass and gas production.
5) Effect of volume increase of crude oil application on the various soil samples. The developed models were found useful in monitoring and predicting the biodegradation of Nigeria crude oil in different soil.

The bio-production of carbon dioxide and heat evolution on the kinetics of biodegradation of crude oil in different soil samples will appear in the next paper.

NOMENCLATURE

S_{Bsa} = substrate concentration of sandy loamy soil for 1 ml x 10/kg
S_{Dsa} = substrate concentration of sandy loamy soil for 2 ml x 10/kg
S_{Esa} = substrate concentration of sandy loamy soil for 3 ml x 10/kg
S_{Fsa} = substrate concentration of sandy loamy soil for 4 ml x 10/kg
V_{Rsa} = specific rate of sandy loamy soil degradation for 1 ml x 10/kg per week
V_{Csa} = specific rate of sandy loamy soil degradation for 2 ml x 10/kg per week
V_{Dsa} = specific rate of sandy loamy soil degradation for 3 ml x 10/kg per week

V_{Esa} = specific rate of sandy loamy soil degradation for 4 ml x 10/kg per week
V_{Fsa} = specific rate of sandy loamy soil degradation for 5 ml x 10/kg per week
A = substrate concentration (ml/g)
E = enzyme concentration (cfu/g) per week
P = product concentration (ml/g)
Q_{gr} = quantity of heat generated (J/kg.k)
S = substrate concentration (ml/g)
K = kinetic rate constant (dimensionless)
C_{EO} = initial concentration of the enzyme (cfu/g)
C_A = final concentration of the substrate (ml/g)
γY_A = yield factors
$C_{biomass}$ = biomass concentration (cfu/g) per week
$V_{reactor}$ = volume of reactor (m^3)
C_{Co2} = carbon oxide concentration (ml/g)
C_{H2o} = water concentration (ml/g)
$V_{max(H2o)}$ = maximum specific rate of carbon dioxide produced (ml/g)
$V_{max(H2o)}$ = maximum specific rate of water produced (ml/g)
$K_{biomass}$ = equilibrium constant of biomass (dimensionless)
K_{Co2} = equilibrium constant of carbon dioxide (dimensionless)
K_{Ho2} = equilibrium constant of water (dimensionless)
t = time per week
X = fractional conversion (%)
K_S = equilibrium constant for substrate (dimensionless)
K_m = equilibrium constant of carbon dioxide (dimensionless)
V = specific rate of enzyme catalysed reaction (kg/ml)

Greek symbols

ϕ = proportionality constant
ϕ_β = proportionality constant of bacteria
ϕ_F = proportionality constant of fungi
μ_0 = initial inoculate of microorganism (cfu/g)
μ = final biomass concentration (cfu/g)
μ_S = biomass concentration at steady state condition (cfu/g)
μ_t = biomass concentration with respect time (cfu/g) per week
β = constant (dimensionless)
$\gamma_{biomass}$ =rate of production of biomass (cfu/g) per week
γ_{CO2} = rate of production of carbon dioxide (ml/g) per week
γ_{H2O} = rate of production of water (ml/g) per week
γ_{QHeat} = rate of production of heat (J/g.K) per week
γ_{gases} = rate of production of various gases (ml/g) per week
$\mu_{max\ (biomass)}$ = maximum specific rate of biomass (cfu/g) per week

Subscripts

B = Bacteria
F = Fungi
t = time
S = laplace sign
Sa = sandy loamy soil
Cl = clay soil
Sw = swampy soil

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