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Research article

EVALUATING THE EFFECT OF CONDUCTIVITY ON CRUDE OIL DEGRADATION IN SALT WATER POND

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Abstract

Conductivity is one of the major factor identified that influence crude oil degradation upon the salt water pond system. The model developed in this research work revealed that increase or decrease in conductivity influence the degradation rate of crude oil upon the action of microorganism. The developed model was simulated with respect to time to monitor and predict the effect of conductivity on microbial population as well as substrate concentration. The result obtained revealed increase as well as decrease in microbial growth rate with increase in substrate degradation in one case and in the case decrease in microbial growth rate with decrease in substrate degradation; the process was attributed to the effect of conductivity on the salt water pond system. Finally, from the findings in this research it is revealed that conductivity is a factor that influences biodegradation and the effectiveness of bioremediation process.

Keywords: Evaluation, Conductivity, crude Oil, Degradation, Salt water, pond

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1. Introduction

The presence of the organizations such as the green algae is of significant importance to the pond as they form the bases of food chain within the pond. Biodegradation could be defined as the breakdown of chemicals compounds due to metabolic actions of micro-organisms. These microbial activities help in improving the rate of degradation in ponds and in other terrestrial and marine environment. Microbial activities in a crude oil contaminated pond are often limited by more than one compound. Although the concentration of petroleum hydrocarbons can influence the

microbial activities, the degradation ability of the microbial activity depends on the above mentioned physiochemical and biological parameter in this case conductivity was considered on the study.

Often, the pond readily assimilates the crude oil pollutants and other wastes without significant deterioration of some quality criteria. The extent of this is referred to as its assimilative capacity. However, the water quality is deteriorating day by day due to these dissolved materials and organic matters discharge into it. This study gives a theoretical and an experimental perspective of biodegradation of petroleum hydrocarbon pollutants in a pond. However, the investigation is target to derive a kinetic model that can predict the rate of biodegradation inhibition due to the changes in the concentration of conductivity is as presented in the study, caused by the crude oil pollutants. Water governs the evolution and function of the universe on the earth hence water is said to be the mother of all living world. Majority of water available on the earth is saline in nature; only small quantity is fresh water. Freshwater has become a scare commodity due to over exploitation and pollution around the earth as reported by Gupta and Shukle (2006); Patil and Tijare (2001); Singh and Mathur (2005). Accurate and reliable information on the water resource system will therefore be a vital aid to strategic management of water resources (Gupta and Deshpande, 2004).

Water quality evaluation of a pond is based on physicochemical parameters. The study on the physiochemical analysis of water is of great significance in removing the constraints in the pond. Temperature is one of the most important ecological factors which controls the physiological behavior and industrialization of the organisms Ade and Vankhede (2001). Higher conductivity was reported to help inhibit protease activities in a pond (Ukpaka and Davis, 2010). The solubility and availability of nutrients is affected by oxygen content of water and therefore the productivity of ponds (Wetzel, 2000). The concentration of dissolved oxygen in the water determines how much oxygen is available to support fish respiration and how easy it is for fish to extract that essential gas from the water. The nitrifying bacteria in the pond use copious quantities of oxygen to convert toxic ammonia to harmless nitrate. Those little bacteria are fierce competitors for dissolved oxygen. But even the nitrifying bacteria are affected if dissolved oxygen levels drop too low. They slow their detoxification efforts — resulting in an ammonia buildup,(Water Quality — Ponds by Stephen M. Meyer). Phosphorus stimulates the growth of microscopic plant while nitrogen promotes overgrowth of aquatic vegetation which degrades water quality. Potassium promotes productivity of aquatic animals such as fish (Wurts, 2000). Organic matter promotes the growth of microorganism Ukpaka, (, 2010). Organic matter also stimulates the growth of decomposers such as bacteria and fungi. A seasonal variation in physiochemical parameters of reservoir was also carried out by Biggs et al; (2005). Abd-Ellah, (2003) investigated the physical limnology and determined the water storage in Abd-Ellah,(2003) studied the level of some heavy metals (Fe, Zn, Mn, Pb, Cu and Cd) in the water and the effects on some organs of fishes. A hydro-biological study conducted in nine different ponds of a rural area showed that the concentrations of chemical Parameters are within the permissible levels of drinking water quality standard of WHO and ISI. The study reveals that rural ponds are very useful as they can be very good sources of water for drinking, domestic use and fishery and should be conserved at any cost (.Gupta, and Deshpande, 2004).

The present study is aimed at determining through principal component analysis of the conductivity of the environment as the most important variables affecting crude oil and bacterial degradation in ponds. The developed models would be of help in the future to predict the point at which the microbial activities in the ponds are influence as a result of increase or decrease in conductivity in polluted pond environment. This is when the assimilative capacity of the pond is exceeded and there is no more biodegradation of the complex hydrocarbons in the pond and thus the pond would become unsafe for both plants and animals. An assimilative capacity study (ACS) develops specific scientific modeling to support and assist municipalities and other legislative authorities in predicting the impacts of pollutants in a pond (Ukpaka, 2011).

The aims and objectives of the study is as shown below: to assess the water quality of a pond through analysis of conductivity as well to compare the result with national standard limit, to determine the conductivity changes in the pond as a result of contaminants, to determine the influence of the contaminants upon biodegradation in the pond and to develop models that would predict and monitor the conductivity parameter upon influence of biodegradation to aid faster remediation in the future. The research work will cover the following areas stated below which involves theoretical or mathematical formulation/simulation and experimental data generated from the field/laboratory data: Development of model to predict and monitor the rate of change of the conductivity concentration, experimental analysis to monitor the microbial growth rate, development of model to predict and monitor the inhibiting factor (conductivity) on biodegradation of contaminants in the pond system, identification, isolation and characterization of possible micro-organism capable of degrading the contaminants. Testing of the model in terms of microbial and substrate kinetics and testing of the model in terms of microbial and substrate kinetics

As stocking and oil spill rate into the pond increases, aeration and water exchange can prevent low concentration of dissolved oxygen and excessive concentration of hydrocarbons. 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 this is because the oil spill might be so great that ii spite of adequate concentration of DO in the water, it still becomes aerobic and hydrogen-sulphides (H2S) and other reduced substances are produced by microorganisms in the bottom of the pond. Deterioration of environmental conditions on the bottom can then lead to slow growth, diseases and mortality of microorganisms. This study unlike others will help us to develop models that will bring about easier understanding of the physiochemical parameters upon the influence of biodegradation and the point at which the assimilative capacity of the pond is reached when biodegradation can no longer occurs due to the influence of the contaminants on the physiochemical parameters of the pond. This study also has an advantage over others as it compares the influence of conductivity on crude oil contaminants on a salt water pond.

2. Materials and Methods

2.1 Determination of Conductivity using Conductivity meter:

Plug the temperature and conductivity probes into the unit, det the display to read in °C and ms/cm respectively by use of the mode key pad., immerse the probes in the liquid to be measured and the display will read directly in °C and ms/cm.

2.2 Determination of Total Dissolved Solids using Conductivity meter:

Plug the temperature and conductivity probes into the unit, set the display to read in °C and mg/I respectively by use of the MODE keypad and immerse the probes in the liquid to be measured and the display will be directly in °C and mg/I.

2.3 Water Analysis Procedure:

Enumeration of Total Heterotrophic Bacteria.

Aerobic plate count was done by employing serial dilution procedure by Ofunne (1999) to enumerate aerobic bacterial in the water samples. The ten-fold serial dilution was used to obtain 10^{-1} dilution of the samples. Aliquots (0.lml) of the original samples and 10^{-1} were plated in duplicates onto the surfaces of dried sterile nutrient agar plates. All inoculated plates were incubated at 37°C for 24hrs. after incubation, the number of colonies that developed were counted and recorded, and taken as the population of bacterial in the colony forming unit per milliliter (CFU ML^{-1}) of water.

Estimation of Total coliform/faecal coliform bacteria.

Coliform bacterial in water were estimated by using the most probable number (mpn) technique described by Collins and lyne (1980). Approximate volumes of undiluted water samples were inoculated into test of Mac Conkey broth medium. All inoculated media were incubated at 37°C (total coliform bacteria) and at 44.5°C (faecal coliform bacteria) for 24-48 hrs. After incubation, the number of tubes showing positive results were used to estimate the coliform bacteria using a statistical tables and recorded in mpn index $100ml^{-1}$ (coliforms $100ml^{-1}$)

2.4 The formulation of the model

The substrate kinetics

The reaction in the reactor can be described as follows:

$[\text{Crude oil} + \text{water}]_{\text{mixed}} + \text{microorganism} \quad (\text{gas} + \text{heat}) + \text{new microbes}$

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

$$-\gamma = \frac{dC}{dT} = -K.C \qquad (1)$$

Equation 1 can be expressed mathematically as follows

Step 1: Rearranging equation (1) to determine the coefficient of function K or the proportional constant given

$$\frac{dC}{C} = -K.dt \quad (2)$$

Integrating equation (2) we have

$$\int_{Co}^{C} \frac{dC}{C} = -K\int_{0}^{T} dt \quad (3)$$

Simplifying equation (3)

$$[In]_{Co}^{C} = -K[T]_{o}^{t} \quad (4)$$

$$InC - InC_o = -K(t - 0) \quad (5)$$

$$In\left(\frac{C}{C_o}\right) = -Kt \quad (6)$$

Making K the proportionality constant, the subject of the equation, we have

$$K = -\frac{1}{T} In\left(\frac{C}{C_0}\right) \quad (7)$$

From equation (1), the rate of degradation of the crude oil upon the action of the microbial and the physiochemical parameter can be established as given

$$\frac{dC}{dt} = -K.C$$

Application of the Laplace transform to equation (1) yields the following expression as shown below

$$\frac{dC}{dT} = SC_{(s)} - C(0)$$

$$-KC = -KC_{(s)} \quad (8)$$

Substituting equation (8) into equation (1) we have

$$SC_{(s)} - C(0) = -KC_{(s)} \quad (9)$$

Considering the following necessary boundary conditions such as

$$at\ t = 0, C(0) = C_0 \quad (10)$$

Substituting equation (10) into equation (9), we have

$$SC_{(s)} - C_{(0)} = -KC_{(s)} \quad (11)$$

Rearranging equation (11), we have

$$SC_{(s)} + KC_{(s)} = C_{(0)} \quad (12)$$

$$C_{(s)}(S+K)\ \ C_0 \quad (13)$$

Dividing through equation (13) by (S + K) yields,

$$C(s) = \frac{C_0}{S + K} \tag{14}$$

Considering the time domain of equation (1), we can say that

$$C_t = C0\ e^{-Kt} \tag{15}$$

Relating the material model to the Michael-Menten equation which states that the specific rate of reaction, mathematically can be expressed as

$$V = \frac{V_{\max}[S]}{K_S + [S]} = \frac{V_{\max}[H]}{K_H + [H]} \tag{16}$$

Defining equation (15) in terms of Michael's Menten expression we have

$$C_t = \frac{[Ct]_{\max}[S]}{K_s + [S]} = \frac{[C_t]_{\max}[H]}{K_H + [H]} \tag{17}$$

Equation (3.17) can further be written as

$$C_0 e^{-K_t} = \frac{\left[C0e^{-k_t}\right]_{\max}[H]}{K_H + [H]} \tag{18}$$

18 is the developed model to predict rate of change of physiochemical parameters.

Relating equation (18) into lineWave Burk Plot, we have

$$\left[C_0 e^{-kt}\right][K_H + [H] = \left[C_0\, e^{-kt}\right]_{\max}[H] \tag{19}$$

Multiplying equation (19) by ($1/C_oe^{-kt}$), yields

$$\left[C_0 e^{-kt}\right][K_H] + [H]\frac{1}{C_0 e^{-Kt}} = \left[C_0 e^{-Kt}\right]_{\max}[H]\frac{1}{C_0 e^{-Kt}} \tag{20}$$

$$[K_H] + [H] = \left[C_0 e^{-Kt}\right]_{\max}[H]\frac{1}{C_0 e^{-Kt}} \tag{21}$$

Making ($1/C_0e^{-Kt}$) the subject of the equation (21), we have,

$$\frac{[K_H + [H]]}{\left[C_0 e^{-Kt}\right]_{\max}[H]} = \frac{1}{C_0 e^{-Kt}} \tag{22}$$

Therefore, equation (22) can be written as

$$= \frac{1}{C_0 e^{-Kt}} = \frac{[K_H]}{\left[C_0 e^{-Kt}\right]_{\max}} + \frac{[H]}{\left[C_0 e^{-Kt}\right]_{\max}[H]} \tag{23}$$

Equation (22) can be further expressed to give the final solution as shown below

$$\frac{1}{C_0 e^{-Kt}} = \frac{[KH]}{\left[C_0 e^{-Kt}\right]_{\max}[H]} + \frac{1}{\left[C_0 e^{-kt}\right]_{\max}} \tag{24}$$

Equation (24) is the same as the lineWaver Burk Plot method for determining the fundamental parameters of K_H and ($C0e^{-Kt}$). Equation (24) is the same as

$$\frac{1}{V} = \frac{K_s}{V_{max}[H]} + \frac{1}{V_{max}} \quad (25)$$

2.5 The Inhibition Model

Recalling the mathematical expression of Michael-Menten in terms of inhibition, we have

$$V = \frac{V_{max}[H]}{K_H + [H]}.I \quad (26)$$

2.6 Model Conductivity (CON), as an Inhibitor

The mathematical model in terms of change in CON concentration can be defined as

$$\frac{dCON}{dt} = \gamma.CON \quad (27)$$

$$\frac{dCON}{dt} = -\gamma.CON$$

Using the same boundary conditions as stated above for pH. The general solution for equation (27) can be written as

For decrease in CON

$$(CON)_t = (CON)_o e^{\gamma T} \quad (28)$$

For increase in CON

$$(CON)_t = (CON)_o e^{-\gamma T} \quad (29)$$

Where,

$$\gamma = \frac{1}{T} In\left(\frac{CON}{(CON)_o}\right) \text{ For increase in CON} \quad (30)$$

$$\gamma = -\frac{1}{T} In\left(\frac{CON}{(CON)_o}\right) \text{For decrease in CON} \quad (31)$$

Relating the general equation in equation (28), (29), (30) and (31) into equation (26) we have

In terms of Michael-Menten model for increase in CON concentration

$$V = \frac{V_{max}[H]}{K_H + [H]}.(CON)_o.e^{-\gamma T} \quad (32)$$

In terms of Michael-Menten model for decrease in CON concentration

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(CON)_o.e^{\gamma T} \quad (33)$$

In terms of current developed model for increase in CON concentration

$$C_o e^{-KT} = \frac{\left[Coe^{-KT}\right]_{\max}[H]}{K_H + [H]}.(CON)_o.e^{-\lambda T} \quad (34)$$

In terms of current developed model for decrease in CON concentration

$$C_o e^{-KT} = \frac{\left[Coe^{-KT}\right]_{\max}[H]}{K_H + [H]}.(CON)_o.e^{\lambda T} \quad (35)$$

Substitute the value of γ from equation (30) into (31) and (32) we have

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(CON)_o.e^{(\frac{1}{T}In\left[\frac{CON}{(CON)_o}\right])T} \quad (36)$$

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(CON)_o.e^{(\frac{1}{T}In\left[\frac{CON}{(CON)_0}\right])T} \quad (37)$$

Equation(37)is the inhibition model for increase in CON

Substitute the value of γ from equation (32) into (34) and (36) we have

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(CON)_o.e^{-(\frac{1}{T}In\left[\frac{CON}{(CON)_o}\right])T} \quad (38)$$

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(CON)_o.e^{-(\frac{1}{T}In\left[\frac{CON}{(CON)_0}\right])T} \quad (39)$$

Equation (39) is the inhibition model for decrease in CON

3. Results and Discussion

Results obtained from the investigation are presented in tables and the excel spread sheet program was used to plot the possible existing relationships between relevant parameters shown in the various figures below. A total of 1 water sample (Salt water pond) was collected and analyzed for a period of 4weeks only. 2 samples from each sampling point formed the 4 pond Bioreactors. One of each set was kept agitated (stirred C) and the others of each were kept at steady state, not agitated (unstirred D). The samples were identified as follows; Saltwater Pond Agitated (Stirred) be represented as SAMPLE C, Saltwater Pond Not Agitated (Unstirred) be represented as SAMPLE D

Table 1: Values of pH value of sample C and D

Time (WK)	Temperature (^oC) (C)	Conductivity (µs)	Temperature (^oC) (D)	Conductivity (µs)	Hydrocarbon substrate (ml) (C)	Hydrocarbon substrate (ml) (D)
0	26.5	78.8	26.5	78.8	200	200
1	27.2	1000	28.5	1000	192	197.5
2	29	1000	29	1000	184.3	194.5
3	29.5	1000	30	1000	179.5	189.6
4	29.5	1000	29.5	1000	175.6	183.5

Table 1 illustrates the pH values per unit time for stirred (C) and unstirred (D) and the pH value of stirred bioreactor decreases with increase in time via versa for pH value of D as the temperature for both systems remain constant.

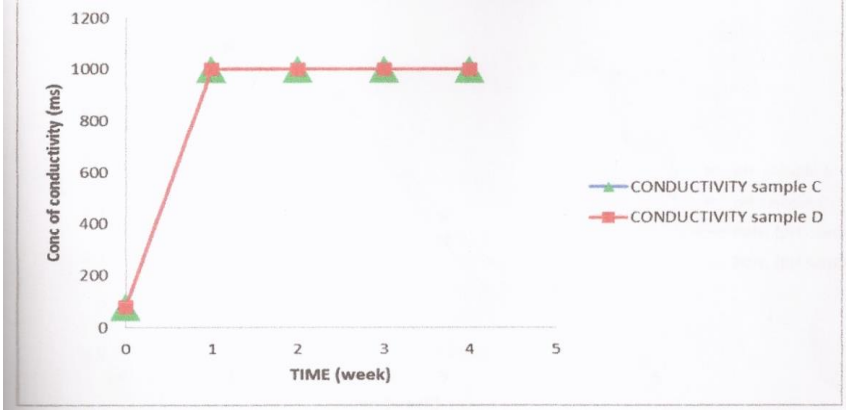

Figure 1: Graph of conductivity versus time for sample C and D

Table 2: Densities of bacteria in water sample C

Time (week)	Total Heterotrophic Bacteria (cfu ml^{-1})	Total coliform Bacteria (MPN index 100 ml^{-1})	Faecal coliform Bacteria (MPN index 100 ml^{-1})
0	11.3*10^3	0	60
1	21.0*10^3	0	50
2	3.6*10^3	20	0
3	9.9*10^2	0	20
4	4.4*10^2	70	0

Table 3: Densities of bacteria in water sample D

Time (week)	Total Heterotrophic Bacteria (cfu ml^{-1})	Total coliform Bacteria (MPN index 100 ml^{-1})	Faecal coliform Bacteria (MPN index 100 ml^{-1})
0	11.3*10^3	0	60
1	21.0*10^3	0	50
2	3.9*10^3	70	20
3	3.8*10^3	0	0
4	8.3*10^2	0	0

From Table 2 and Table 3 the heterotrophic bacteria were high before contamination in sample A and reduced at the 3rd week. No significant difference was noticed in pond C and D.

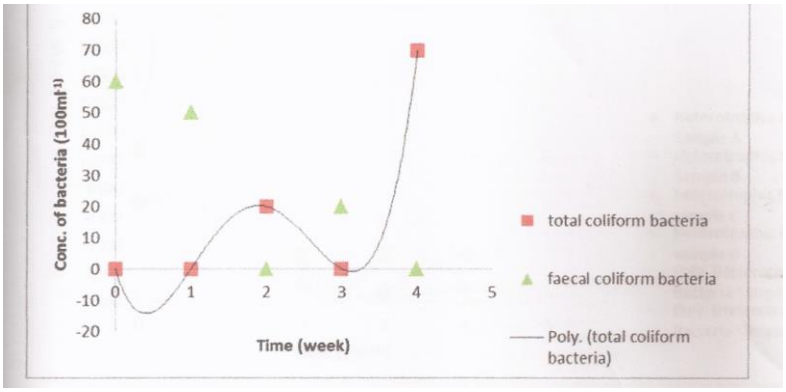

Figure 2: Graph of Bacteria Conc. Versus Time for sample C

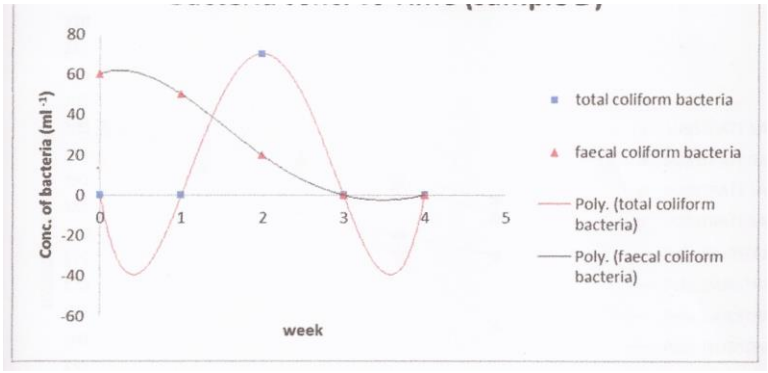

Figure 3: Graph of Bacteria Conc. versus Time for Sample D

The result presented in Figure 1 revealed the initial increase in conductivity with increase in as well on microbial population for both samples. After contamination of the pond with crude oil, the total coliform bacterial found at the second week was 60(mpn index 100ml). From Figure 2 and 3, it was found in sample C that the organisms died at the 3rd and 4th week of the experiment. The total faecal coliform bacterial were also seen at the 1st week of the experiment which also went into extinction throughout the end of the experiment. This could be due to the inhibiting factors which affected the lives of the microorganisms. The trend is similar for pond sample B. However the total coliform bacterial found in the pond D is 70mpn index at the 3 week.

Evaluation of rate of change of physiochemical parameters, we have to recall our developed model equation (18)

$$C_o e^{-KT} = \frac{\left[C_o e^{-KT}\right]\max\left[H\right]}{K_H + \left[H\right]}$$

The coefficients $\left[C_o e^{-kt}\right]_{\max}$ and K_H will be determined from the line waver bulk plot.

Table 4: Table of values for the line waver bulk plot of sample C

Time T(weeks)	Substrate H(ml)	1/H	C_oe^{-kt}	$1/C_oe^{-kt}$
0	200	0.005	-	-
1	192	0.005208	8	0.125
2	184.3	0.005426	7.7	0.12987
3	179.5	0.005571	4.8	0.208333
4	175.6	0.005695	3.9	0.25641

Table 5: Table of values for the line waver bulk plot of sample D

Time T(weeks)	Substrate H(ml)	1/H	C_oe^{-kt}	$1/C_oe^{-kt}$
0	200	0.005	-	-
1	197.5	0.005063	2.5	0.4
2	194.5	0.005141	3	0.333333
3	189.6	0.005274	4.9	0.204082
4	183.5	o.oo545	6.1	o.163934

Table 4 and 5 illustrate the mathematical computation of the reciprocal of specific rate and reciprocal of the substrate. An increase in reciprocal of substrate was observed with increase in time, whereas a decrease upto day 3rd was observed before sudden increase in day 4. In terms of reciprocal of the specific rate increase in coefficient values was observed from day 1 to day 3 with sudden decrease in day 4. The variations in these values can be attributed to the variation in time, material activity and substrate degradation.

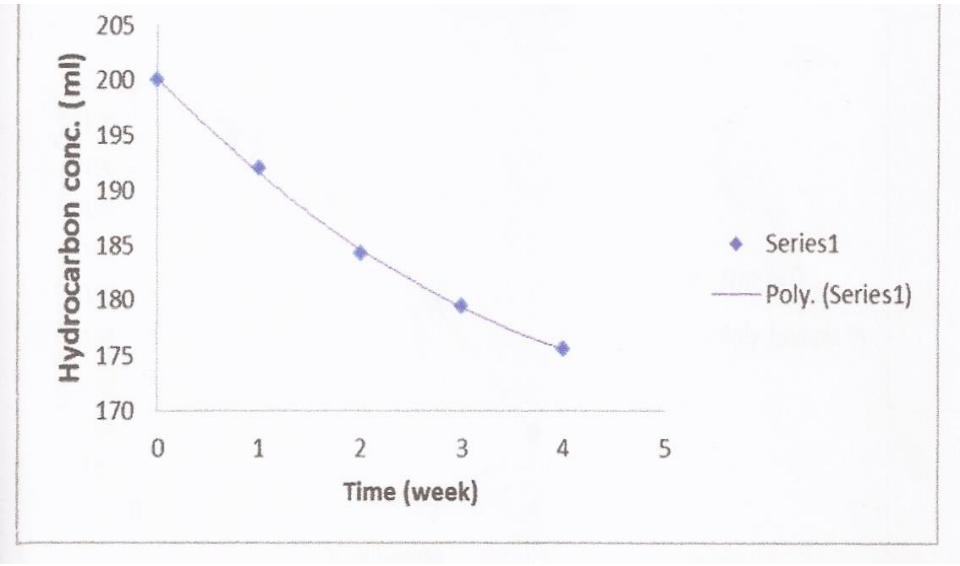

Figure 4: Graph of Hydrocarbon Conc. against Time for Sample C

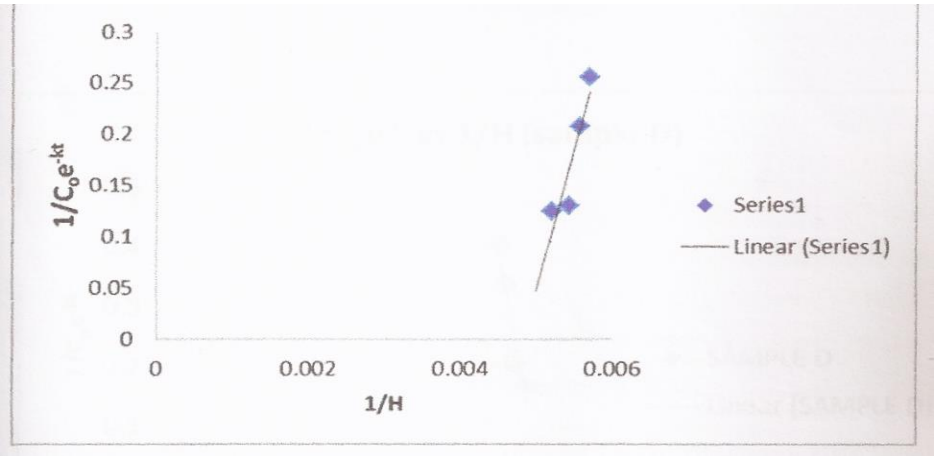

Figure 5: LineWaver Bulk Plot for Sample C

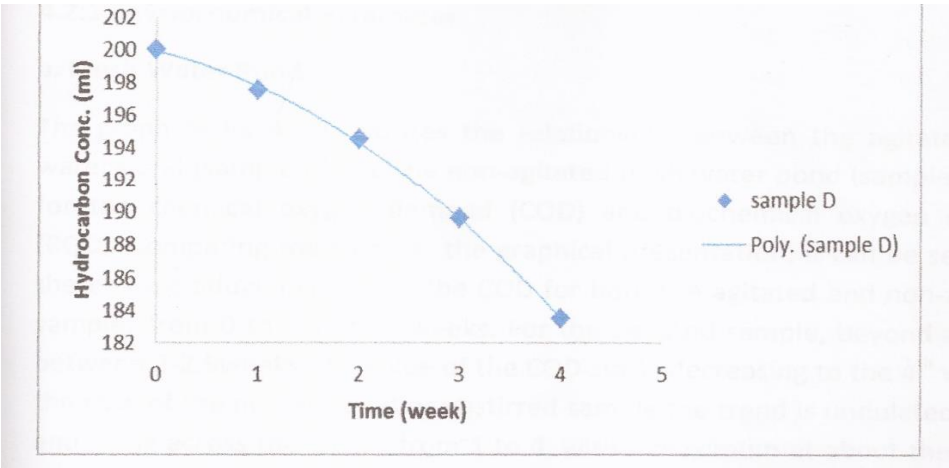

Figure 6: Graph of Hydrocarbon Conc. against Time for sample D

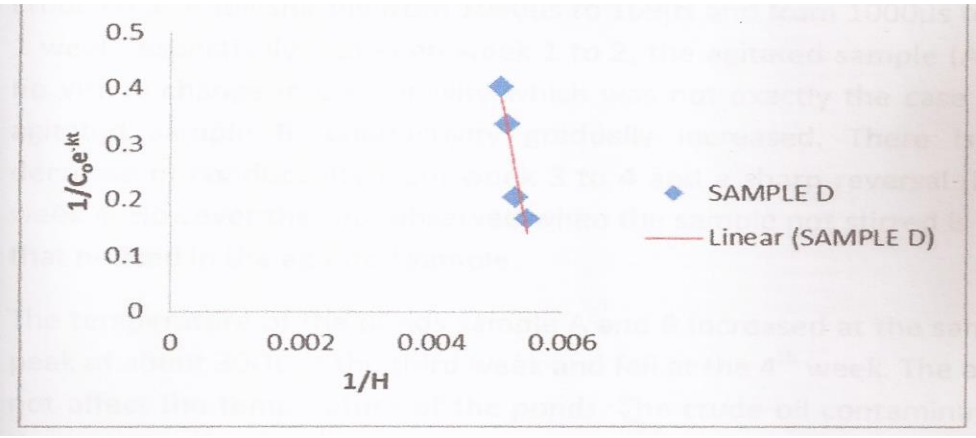

Figure 7: LineWaver Bulk Plot of Sample D

Due to changes in the conductivity concentration caused by the presence of crude oil contamination, the microorganisms that would have acted on the substrates (crude oil) were affected; however whenever there was a slight favorable condition in the pond, the microorganism will feed and live again. The activities of the microorganisms fluctuated as they feed, die and rose up again. The rate of degradation of the hydrocarbon substrate (crude oil) can be seen in Figure 4 and 6 Sample C degraded more than sample D, from 200 to 160m1. In Figure 5, the line waver bulk plot for the evaluation of the maximum specific rate $\left(\left[C_o e^{-Kt}\right]_{\max}\right)$ and the equilibrium rate value could not be obtained due to the insignificants action of the microorganism in the bioreactor which was attributed to the inhibiting components of the system. It is evident from the nature of the line waver bulk plot shown in the graphs of Figure 7. Since the intercept on the y-axis did not cut through the positive side of the axis. This condition makes it impossible for the parameters above to be determined. However the models developed are applicable for ponds in which the line waver bulk plot will cut in such a way that the values can be determined.

4. Conclusion

The results obtained indicate that pH values considered posse a great influence in the biodegrading of the petroleum hydrocarbon in freshwater medium, thereby inhibiting the active site of the microorganism. The maximum specific rate and equilibrium rate values were not obtained due to insignificant action of the microorganism in the bioreactor which was attributed to the inhibiting components in the system. It is thus very likely that within the period of investigation, the time was not long enough for the system and its pH values to act in a way that the line waver bulk plot could have shifted the plot parameters to the region which could have certainly allowed the values to be determined, which is the maximum specific rate of $\left(\left[C_o e^{-Kt}\right]_{\max}\right)$each physiochemical parameter as well as the equilibrium constant rate of the parameters.

Also the counts on the aerobic bacteria were high in the first and second analysis but decreased in subsequent analysis. Numbers of coliform bacteria fluctuated in all the samples. Contamination of the water with crude oil decreased bacterial population.

Nomenclature

$\frac{dc}{dt}$	=	Substrate concentrates per unit time (mgi/day)
K	=	Equilibrium constant dimensionless
C	=	Substrate concentration (mg/l)
E	=	Enzyme concentration (cfu/lm)
H	=	Substrate concentration (mg/l)
K_1	=	Equilibrium constant for forward reaction
K_2	=	Equilibrium constant for backward reaction
EH	=	Enzyme substrate complex

P	=	Product concentration (mg/l)
K_3	=	Equilibrium constant for the product
E_t	=	Total enzyme concentration (cfu/ml)
$K_p = K_H$ =		Equilibrium constant of the product
V = R	=	Specific rate of reaction (substrate) (mg/l/day)
$V_{max} = R_{max}$	=	$\left[C_o e^{-kt}\right]_{max}$ = Maximum specific rate of reaction (mg/l/day)
K, β, λ, α, γ	=	Constants
C_o	=	Initial substrate concentration (mg/l)
T	=	Time (week)
T_0	=	week before contamination
$T_{1,2,3,4}$	=	Weeks after contamination
CON_o	=	Initial conductivity
CON	=	Final conductivity
CFU	=	Colony forming units
MPN	=	Most probable number technique

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