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Full Length Research Paper

The concept of chemical and biochemical oxygen demand in inhibiting crude oil degradation in fresh water pond system

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Abstract

Experimental analysis was conducted to examine the effect of chemical and biochemical oxygen demand (COD) and BOD) on crude oil degradation in fresh water pond in Niger Delta area of Nigeria. In the research work mathematical model was developed as well to determine the influence of the COD and BOD on the degradation of crude oil in fresh water pond. The specific rate, maximum specific rate and equilibrium constant for COD and BOD as presented in the paper. The characteristics of the COD and BOD moved in the same trend either increasing or decreasing, which in turned influenced the biodegradation of the crude oil by inhibiting the active site of the microorganism. The model developed in this research work was based on increase and decrease in the COD and BOD concentration. The result obtained shows a good match indicating the usefulness of the developed model in monitoring and predicting the inhibiting effect of COD and BOD in crude oil degradation in fresh water pond.

Keywords: Chemical oxygen demand, Biochemical oxygen demand, inhibitor, concept, crude oil, degradation

INTRODUCTION

Water quality can be defined in terms of physical, chemical and biological characterization of water. The major determinant of good growth in ponds includes temperature, dissolved oxygen, pH, conductivity, COD and BOD, nutrients etc. Conversely, other parameters like biological oxygen demand and chemical oxygen demand indicate pollution level of a given pond. In most water bodies, various chemical parameters occur in low concentrations. This concentration level increases due to human activities, and lack of environmental regulation (Collins and Lyne, 1980: Ade and Vankhede, 2001: Davis-colley and Donnison, 2000: Ukpaka and Farrow, 2009: Gupta and Shukle, 2006: Ukpaka and Amadi, 2009).

The study on the physiochemical analysis of water is of great significance in removing the constraints in the pond. Effluent quality evaluation is also based on physicochemical parameters. The physiochemical parameters of the pond have been shown to influence the rate of biodegradation in the pond. Temperature therefore has a direct effect on important factors such as growth, oxygen demand, food requirements and food conversion efficiency.

This refers to the amount of suspended matter dirt, organic particulates, plankton, etc. in the water. Turbidity determines visibility in the pond (how far down into the pond you can see through). Whether turbidity indicates a real problem depends on the type of particulate matter suspended in the water. Water turbidity in fresh-water ponds is caused by phytoplankton and zooplankton

(microscopic plants and animals) and suspended solids such as clay and silt particles in the water column. Water turbidity is important as it determines the amount of light penetration that occurs in the water column of a pond. Green water is due to planktonic algae. Tea-colored water is the result of leaching from decomposing leaves in the pond. Unless leaves are removed promptly this coloring is unavoidable. Brown-colored water has several possible causes- dead and dying planktonic algae produces a brown coloration that disappears once the material settles out, and suspended clay or peat silts can also produce brown colors (El-Gohary, et. Al., 1992; Bhuiyan. Et. Al., 2007; Davis, et. Al., 2005; Adigun, 2005; Ukpaka, 2011; Abd-Ellah, 2003 and Dwivedi, et. Al., 2002).

Odor: A clean pond is odorless. Odor is caused by the biological contamination of the water mass of the pond by organic decays, faeces, urine, etc. Chemical characteristics refer to the water quality parameters that are measured within an aquaculture pond (Ukpaka, 2011a).

It tells the quantity of oxygen present in the water mass. DO is important because it is used by the living animal organisms living in the pond for survival. It can also be produced by the respiratory process of plants in the

Water quality within a pond can affect these functions and therefore will determine the health of the pond and consequently the success or failure of biodegradation operation (Katsuro, et. Al., 2004; Ferreira, et. Al., 2003; Kimwaga, et. Al., 2004; Gupta and Deshpande, 2004; Belmont, et. Al., 2004; Bigss et. Al., 2005). Water quality within a pond is based on the balance of these physiochemical parameters. Water quality in intensive pond systems is to a large extent controlled by the microbial biodegradation of organic residues. Any quantitative treatment or design of intensive pond systems depends upon the availability of rate parameters describing the microbial degradation of organic residues in the pond (Craggs et. Al., 2004; Ash and Jenkins, 2006; Forenshell, 2001).

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 parameters.

The present study is aimed at determining through principal component analysis, the most important variables affecting 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 stop due to changes in the COD and BOD concentration of the pond because of the presence of crude oil pollutants and other contaminants. 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.

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 salinity, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and other physicochemical parameters as presented in the study, caused by the crude oil pollutants.

MATERIALS AND METHODS

The methods employed involve the use of experimental measurements and techniques to generate result from field samples and analytical approach for result analysis

Sample collection

Freshwater pond and salt water pond located within Port Harcourt city of Rivers State in Niger Delta area of Nigeria,

The sample of the freshwater pond was collected respectively with a new, clean container to prevent contamination of samples and taken from the sit to the chemical/petrochemical engineering laboratory of Rivers State University of Science and Technology. The actual samplings were done midstream by dipping each of the 10liters sample container at approximately 20-30cm below the water surface, projecting the mouth of the container against the flow direction. The samples were then transported in cooler boxes to the lab in other to avoid change in concentration. Before sampling, the bottles were rinsed three times clean water before being filled with the sample. This is to avoid contamination of samples. The set-up reactors where allowed to stand for

Figure 1. Experimental setup of biochemical reactors for samples A and B

Figure 2. Experimental setup for BOD and COD analysis

five days which the harvest is carried out and another set of analysis is carried out again. Samples from Oyigbo freshwater pond represented as A and B.

COD and BOD Analysis

The method of APHA 5210D and APHA 5220D was used in analyzing the BOD and COD respectively.
The experimental set-up to determine the COD and BOD are presented in Figure 1 and 2

Water analysis procedure

Enumeration of total heterotrophic bacteria

Aerobic plate count was done by employing serial dilution procedure by Obire and Wmedo (1996); 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℃ 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℃ (total coliform bacteria) and at 44.5℃

(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})

The formulation of the model

The substrate kinetics

The reaction in the reactor can be described as follows: [Crude oil + water]$_{mixed}$ + microorganism ⩾ (gas + heat) + new microbes

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

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

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)

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

$$\ln C - \ln C_o = -K(t - 0) \quad (5)$$

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

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,

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

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

$$C_t = C0\ e^{-Kt} \quad (15)$$

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

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

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

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

Equation (3.17) can further be written as

$$C_0 e^{-K_t} = \frac{[C0e^{-k_t}]_{\max}[H]}{K_H + [H]} \quad (18)$$

18 is the developed model to predict rate of change of physiochemical parameters.
Relating equation (18) into linewave Burkplot, we have

$$[C_0 e^{-kt}][K_H + [H] = [C_0 e^{-kt}]_{\max}[H] \quad (19)$$

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

$$[C_0 e^{-kt}][K_H] + [H]\frac{1}{C_0 e^{-Kt}} = [C_0 e^{-Kt}]_{\max}[H]\frac{1}{C_0 e^{-Kt}} \quad (20)$$

$$[K_H] + [H] = [C_0 e^{-Kt}]_{\max}[H]\frac{1}{C_0 e^{-Kt}} \quad (21)$$

Making (1/$C_0 e^{-Kt}$) the subject of the equation (21), we have,

$$\frac{[K_H + [H]]}{[C_0 e^{-Kt}]_{\max}[H]} = \frac{1}{C_0 e^{-Kt}} \quad (22)$$

Therefore, equation (22) can be written as

$$= \frac{1}{C_0 e^{-Kt}} = \frac{[K_H]}{[C_0 e^{-Kt}]_{\max}} + \frac{[H]}{[C_0 e^{-Kt}]_{\max}[H]} \quad (23)$$

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

$$\frac{1}{C_0 e^{-Kt}} = \frac{[KH]}{[C_0 e^{-Kt}]_{\max}[H]} + \frac{1}{[C_0 e^{-kt}]_{\max}} \quad (24)$$

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

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

The inhibition model

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

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

Model of BOD as an inhibitor

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

$$\frac{dBOD}{dt} = \lambda.BOD \quad (27)$$

$$\frac{dBOD}{dt} = -\lambda.BOD$$

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

For decrease in BOD concentration

$$(BOD)_t = (BOD)_o e^{\lambda T} \quad (28)$$

For increase in BOD concentration

$$(BOD)_t = (BOD)_o e^{-\lambda T} \quad (29)$$

Where:

$$\lambda = \frac{1}{T} In\left(\frac{BOD}{BOD_o}\right)$$ for increase in BOD concentration (30)

$$\lambda = -\frac{1}{T} In\left(\frac{BOD}{BOD_o}\right)$$ for decrease in BOD concentration (31)

Relating the general equation in equation (28), (29), (30) and (31) into equation (26) and (33) we have

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

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

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

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

In terms of current developed model for increase in BOD concentration

$$C_o e^{-Kt} = \frac{[C_o e^{-Kt}]_{\max}[H]}{K_H + [H]}.(BOD)_o.e^{-\lambda t} \quad (34)$$

In terms of current developed for decrease in BOD concentration

$$C_o e^{-Kt} = \frac{[C_o e^{-Kt}]_{\max}[H]}{K_H + [H]}.(BOD)_o.e^{-\lambda T} \quad (35)$$

Substitute the value of λ from equation (30) into (32) and (35), we have

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

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

37 is the inhibition model for increase in BOD.

Substitute the value λ of from equation (31) into (33) and (35), we have

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

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

39 is the inhibition model for decrease in BOD

Model of COD as an inhibitor

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

$$\frac{dCOD}{dt} = \alpha.COD \quad (40)$$

$$\frac{dCOD}{dt} = -\alpha.COD$$

Using the same boundary conditions as stated above for pH. The general solution for equation (40) can be written as

For decrease in COD

$$(COD)_t = (COD)oe^{\alpha T} \quad (41)$$

For increase in COD

$$(COD)_t = (COD)oe^{-\alpha T} \quad (42)$$

Where

$$\alpha = \frac{1}{T} In\left(\frac{COD}{(COD)_o}\right)$$ for increase in COD (43)

Table 1. Values of COD, BOD and hydrocarbon concentration of sample A and B

Time (WK)	COD Conc (mg/l (A)	BOD Conc. (m/l) (A)	Hydrocarbon Conc. (ml)(A)	COD Conc (mg/l (B)	BOD Conc(m/l) (B)	Hydrocarbon Conc.(ml)(B)
0	2.4	2	200	2.4	2	200
1	4.693333	3.911111	194	3.68	3.066667	195.5
2	6.666667	5.555556	186	8.053333	6.711111	192.2
3	6.346667	5.299999	175.5	6.56	5.466667	189.9
4	5.013333	4.177778	162.2	6.506667	5.422222	186.2

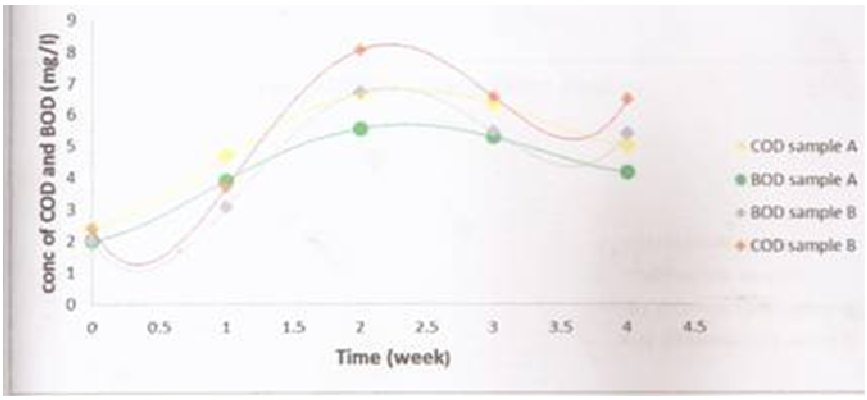

Figure 3. Graph of COD and BOD Concentration versus Time for sample A and B

$$\alpha = -\frac{1}{T}\, In\left(\frac{COD}{(COD)_o}\right) \text{ for decrease in COD} \quad (44)$$

Relating the general equation in equation (40) (41) (43) and (44) into equation (26) (33) we have

In terms of Michael-Menten Model for increase in COD concentration

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(COD)_o.e^{-\lambda T} \quad (45)$$

In terms of Michael Menten model for decrease in COD concentration

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(COD)_o.e^{\lambda T} \quad (46)$$

In terms of current developed model for increase in COD concentration

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(COD)_o.e^{-\alpha T} \quad (47)$$

In terms of current developed model for decrease in COD concentration

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(COD)_o.e^{\alpha T} \quad (48)$$

Substitute the value of α from equation (44) into (46) and (48), we have

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(COD)_o.e^{(\frac{1}{T} In\left[\frac{COD}{(COD)_o}\right])T} \quad (49)$$

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(COD)_o.e^{(\frac{1}{t} In\left[\frac{COD}{(COD)o}\right])T} \quad (50)$$

50 is the inhibition model for increase in COD

Substitute the value of α from equation (45) into (47) and (49), we have

$$V = \frac{V_{\max}[H]}{K_H + [H]}.(COD)_o.e^{-(\frac{1}{T} In\left[\frac{COD}{(COD)_o}\right])T} \quad (51)$$

$$C_o e^{-Kt} = \frac{\left[C_o e^{-Kt}\right]_{\max}[H]}{K_H + [H]}.(COD)_o.e^{-(\frac{1}{t} In\left[\frac{COD}{(COD)o}\right])T} \quad (52)$$

Equation (52) is the inhibition model for decrease in COD

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 (Freshwater pond) was collected and analyzed for a period of 4weeks only. 2 samples from each sampling point formed the 4 pond Bioreactors. One

Table 2. Densities of bacteria in water sample A

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	7.5*10^3	0	0
1	6.2*10^3	0	60
2	13.6*10^2	60	0
3	12.6*10^2	0	0
4	3.8*10^3	0	0

Table 3. Densities of bacteria in water sample B

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	7.5*10^3	0	0
1	6.2*10^3	0	60
2	24.0*10^2	70	10
3	8.2*10^2	0	0
4	15.7*10^2	0	0

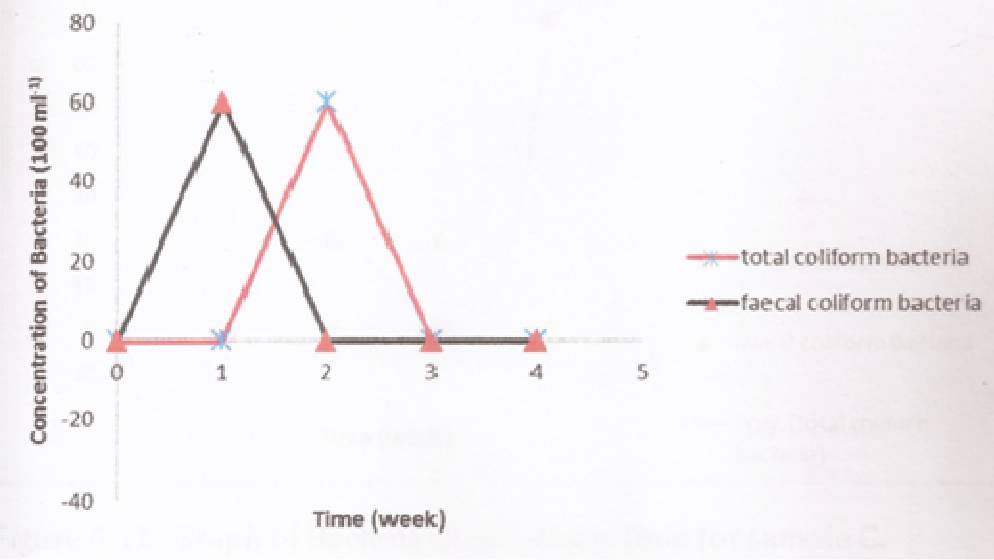

Figure 4. Graph of Bacteria Conc. Versus Time for sample A

of each set was kept agitated (stirred A) and the others of each were kept at steady state, not agitated (unstirred B). The samples were identified as follows; Freshwater Pond Agitated (Stirred) be represented as SAMPLE A, Freshwater Pond Not Agitated (Unstirred) be represented as SAMPLE B

Table 1 illustrates the concentration of COD and BOD, hydrocarbon on stirred and unstirred reactor. In some cases a decrease is experience between 0 to 1 day before sudden increase before day 1 to the day 3, this is seen in COD and BOD concentration for stirred bioreactor whereas for the unstirred bioreactor an increase is observe from 0 day to day 2 before sudden increase from day 3 to day 4. The concentration for the hydrocarbon decreases for both stirred and unstirred bioreactor with increase in time of exposure

Figure 4 illustrate the relationship of COD and BOD concentration for both sample located in A and B reactor. The variation to the concentration of COD and BOD can be attributed to the variation in time as well as microbial population.

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 A and B.

After contamination of the pond with crude oil, the total coliform bacterial found at the second week was 60 (mpn index 100ml). From Figure 4 and 5, it was found in

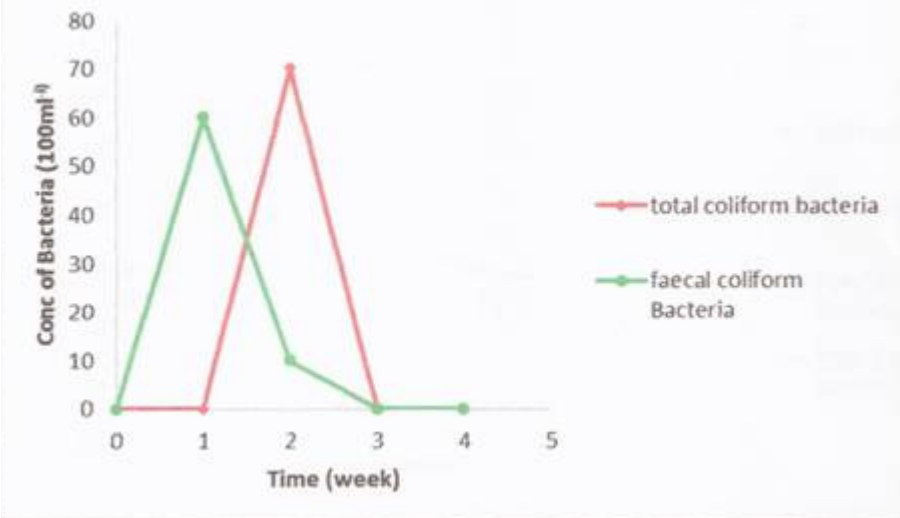

Figure 5. Graph of bacteria conc. versus time for sample B

Table 4. Table of values for the line waver bulk plot of sample A

Time T(weeks)	Substrate H(ml)	1/H	C_oe^{-kt}	$1/C_oe^{-kt}$
0	200	0.005	-	-
1	194	0.005155	6	0.166667
2	186	0.005376	8	0.125
3	175.5	0.005698	10.5	0.095238
4	162.2	0.006165	13.3	0.075188

Table 5. Table of values for the line waver bulk plot of sample B

Time T(weeks)	Substrate H(ml)	1/H	C_oe^{-kt}	$1/C_oe^{-kt}$
0	200	0.005	-	-
1	195.5	0.005115	4.5	0.222222
2	192.2	0.005203	3.3	0.30303
3	189.9	0.005266	2.3	0.434783
4	186.2	0.005371	3.7	0.27027

sample A 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 B is 70mpn index at the 3 week.

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

$$C_oe^{-KT} = \frac{[C_oe^{-KT}]\max\,[H]}{K_H + [H]}$$

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

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 upon 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.

Due to changes in COD and BOD parameters caused by the presence of crude oil contamination, the micro-

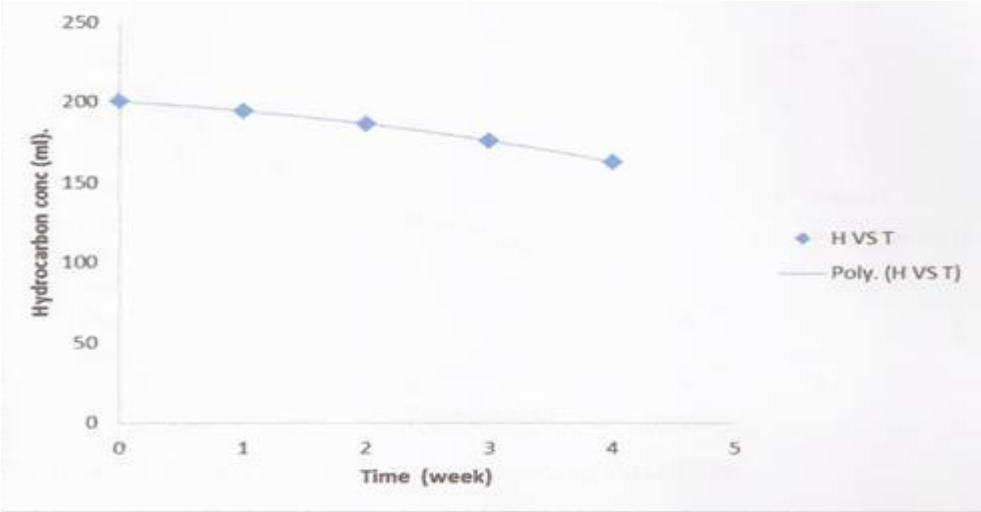

Figure 6. Graph of hydrocarbon conc. against time for sample A

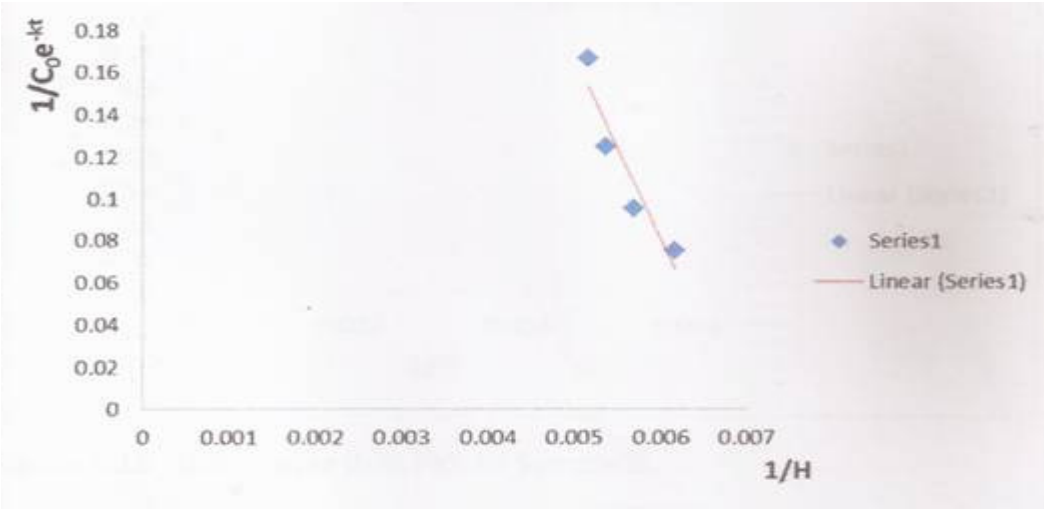

Figure 7. Linewaver bulk plot for sample A

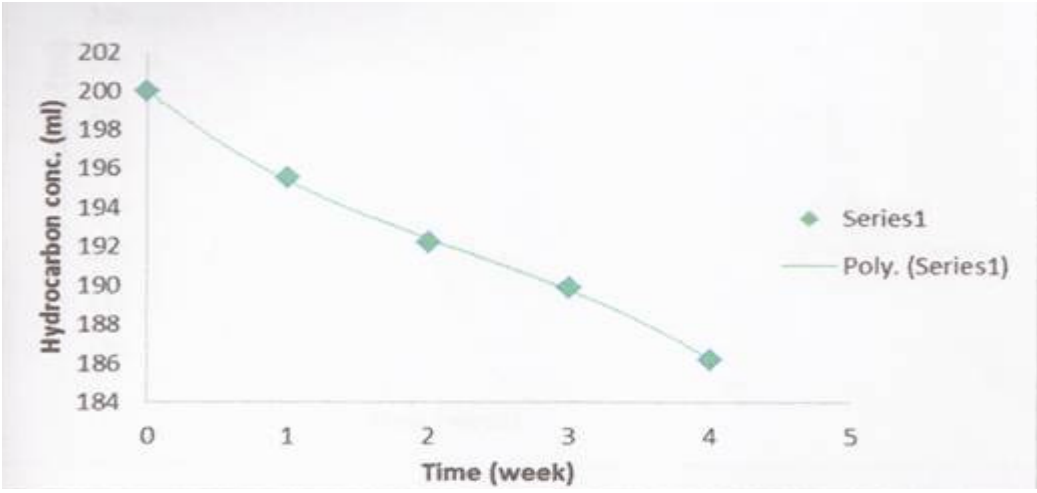

Figure 8. Graph of hydrocarbon conc. against time for sample B

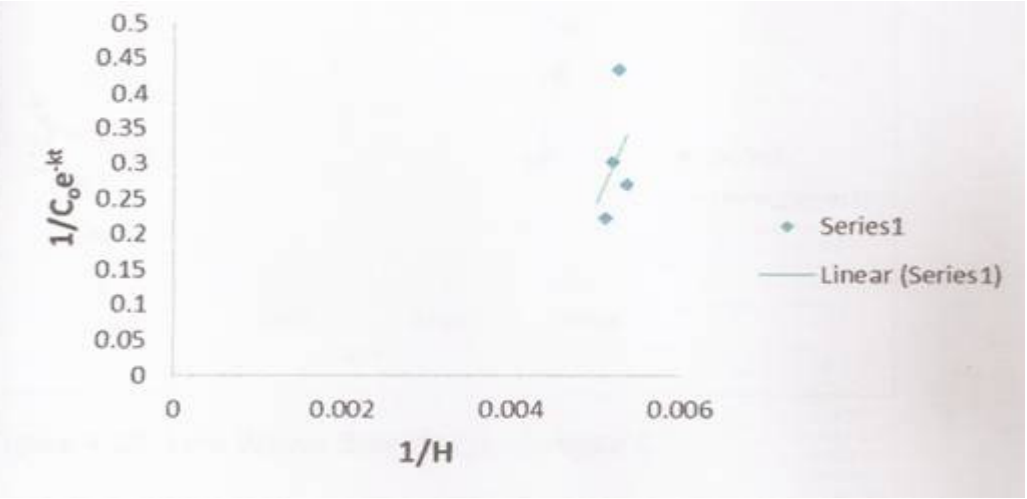

Figure 9. Linewaver bulk plot of sample B

organisms 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 6 and 8 Sample A degraded more than sample B, from 200 to 160m1. In Figure 7, 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 (K_{COD}) and (K_{BOD}) 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 9. 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.

CONCLUSION

The results obtained indicate that COD and BOD 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 dimension-less
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 back-ward 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
BOD_o = Initial concentration of Biochemical oxygen demand (mg/l)
BOD = Final concentration of Biochemical oxygen demand (mg/l)
COD_o = Initial chemical oxygen demand (mg/l)
COD = Final chemical oxygen demand (mg/l)
CFU = Colony forming units
MPN = Most probable number technique

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