The influence of chemical and biochemical oxygen demands on the kinetics of crude oil degradation in salt water pond

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The kinetic of crude oil degradation in salt water pond system was examined upon the influence of chemical and biochemical oxygen demand (COD and BOD) concentration. The coefficient of COD and BOD functional parameters was developed from the mathematical model formulated in this paper. The result obtained revealed that chemical and biochemical oxygen demand (COD and BOD) concentration influence the rate of degradation of crude oil in salt water pond system. The mathematical model developed was simulated with time to ascertain the effect of COD and BOD on biomass formation as well as substrate concentration. Increase and decrease in COD and BOD concentration inhibits the crude oil degradation in salt water pond as well as microbial population. The result obtained from the experimental work was used in evaluating the functional parameters as presented in this paper. The specific rate, maximum specific rate and equilibrium constant for the both COD and BOD were evaluated using the various concepts such as Michael's Menten model. The result obtained demonstrated the usefulness of COD and BOD in monitoring and predicting the rate of degradation of crude oil in salt water pond system upon the influence time and other environmental factors.

Key words: Chemical, biochemical, oxygen, demand, kinetic, model.

INTRODUCTION

The pond system is characterized by minimum energy requirements, functions well against changes in waste water volumes and load and produce less sludge. The pond system is the most appropriate alternative treatment plant for countries with warm sunny weather and land availability. The system has been applied for the treatment of different kinds of waste waters in developing as well as developed countries (Racault et al., 1995, Pearson et al., 1995; Ukpaka, 2010; Ferreia et al., 2003; McGrath and Mason 2004; Nelson et al., 2004; Travieso et al., 2006). Waste stabilization ponds are also useful for the treatment of wastewater in rural and semiarid areas in Egypt (El-Gohary et al., 1992). The waste stabilization pond receives mixed domestic and industrial wastewater with daily flow rate of 33000 m³ and the treated effluent is used to irrigate green belt around the city.

Uncontrolled domestic waste water discharge into pond has resulted in eutrophication of ponds as evidence by substantial algal bloom, dissolve oxygen depletion in the subsurface water leads to large fish kill and other oxygen requiring organism (Pandey, 2003). Effluent is discharge into environment with enhanced concentration of nutrient, sediment and toxic substances may have a serious negative impact on the quality and life forms of the receiving water body when discharge untreated or partially treated (Forenshell, 2001; Miller and Siemmens 2003; Schulz and Howe, 2003). Effluents are composed mainly of either organic, inorganic matter or both and toxic substance depending on it source. The treatment in ponds is a natural process resulting from complex
symbiosis of bacteria and algae (Munoz and Guieysse, 2006). The pond systems provide a natural sustainable process for cotton (Davies-colley et al., 2000; Craggs et al., 2004) without risk of by products. This is because a water system is apriori, capable of self-purification through biological processes (Lakatos et al., 1997), which depends largely on the physiographic features of the stream and climatic conditions as wastes received and charged are within the carrying capacity of the system (Soler et al., 1991). Constructed wetlands and roughing filters have also been used/applied for removal of suspended algae from the pond effluent (Belmont et al., 2004; Kimwaga et al., 2004; Senzia et al., 2003).

Pollution is caused when a change in the physical, chemical or biological condition in the environment harmfully affect quality of human life including other animals' life and plant (Lowel and Thompson, 1992; Okye et al., 2002). Water contaminated by effluent from various sources is associated with heavy disease burden (Okoh, 2007) and this could influence the current shorter life expectancy in the developing countries compared with developed nation (WHO, 2002). However, the water of the ponds is polluted mainly due to discharged waste water from residential areas, sewage outlets, solid wastes, detergents, automobile oil wastes, fishing facilities and agricultural pesticides from farmlands and oil spillage (Ukpaka and David, 2010). As these wastes are been continuously added to water bodies, these affect the physiochemical quality of water making them unfit for use of livestock and other organisms (Dwivedi and Pandey, 2002).

Considering a crude oil spill contaminated pond. Other sources of petroleum hydrocarbons to the pond include leaky storage tanks, automotive emissions, elicit dumping and tire particles (Davis and Mc Cuen, 2005). Urban runoff then transports these hydrocarbons to ponds and other aquatic environments (Menzie et al., 2002). Although oil spills aren't permanent, its effect on the environment can be devastating. Water pollution by oil spill has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity to human health and to biological ecosystem (Katsuro et al., 2004). The effluent can alter the physical, chemical, and biological nature of the pond (Sandojin, 1991). The occurrence of heavy hydrocarbons and other metals from the spill constitute a major source of pollutants entering the pond and excessive mineralization of pond water degrades water quality producing an objectionable taste, odor and excessive hardness. Hence there should be regular measures taken to reduce pollution level to the minimum.

Water is an indispensable natural resource on earth. All life including human being depends on water. We have enormous resource on the earth amounting to about 13, 481, 96000 km$^3$ of water. Due to its unique properties water is of multiple uses for living organisms. Human being depends on water for almost every developmental activity. Although water is very abundant on this earth, yet it is very precious. The world’s water resources are under pressure due to increasing industrial and technological advancement, over population, oil spills and other eruptions and must be managed for human survival. It is, therefore, necessary to have most relevant information before arriving at rational decisions that will result in the maximum benefit to people. Accurate and reliable information on the water resource system can, therefore, be a vital aid to strategic management of the water resources. The various water resources include ponds, lakes, lagoons, rivers, seas, oceans and rain falls. Our focus on this study is on the physiochemical properties of a crude oil contaminated ponds and its influence on biodegradation. Kinetic models were developed to monitor and predict the effect COD and BOD on crude oil degradation in salt water environment. The Figure 1a.
illustrates the experimental set up to investigate the effect of BOD and COD on the degradation of crude oil on salt water medium upon the influence of disturbance (stirred) and unstirred as per presented in this article.

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 (0.1 ml) 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 24 h. 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) of water.

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 h. 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 100 ml$^{-1}$ (coliforms 100ml$^{-1}$)

THE FORMULATION OF THE MODEL

The substrate kinetics

The reaction in the reactor can be described as follows:

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

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

$$- \gamma = \frac{dC}{dT} = -KC$$  (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

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

Integrating equation (2) we have

$$\int^{C \to C_0} \frac{dC}{C} = - K \int^{t \to 0} dt$$  (3)

Simplifying equation (3)

$$[ln]^C_{C_0} = - KT$$  (4)

$$\ln C - \ln C_0 = -K(t - 0)$$  (5)

$$\ln \left( \frac{C}{C_0} \right) = -Kt$$  (6)

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

$$K = \frac{1}{T} \ln \left( \frac{C}{C_0} \right)$$  (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

$$\frac{dC}{dt} = -KC$$

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

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

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

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

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

Considering the following necessary boundary conditions such as

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

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

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

Rearranging equation (11), we have

$$SC_{(s)} + KC_{(s)} = C(0)$$  (12)

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

Dividing through equation (13) by (S + K) yields,
\[ C(s) = \frac{C_0}{S + K} \]  
(14)

Considering the time domain of equation (1), we can say that
\[ C_t = C_0 e^{-K_t} \]  
(15)

Relating the material model to the Michael-Menten equation which states that the specific rate of reaction, mathematically can be expressed as
\[ V = \frac{V_{\text{max}} [S]}{K_S + [S]} = \frac{V_{\text{max}} [H]}{K_H + [H]} \]  
(16)

Defining equation (15) in terms of Michael’s Menten expression we have
\[ C_t = \frac{[C_t]_{\text{max}} [S]}{K_S + [S]} = \frac{[C_t]_{\text{max}} [H]}{K_H + [H]} \]  
(17)

Equation (3.17) can further be written as
\[ C_0 e^{-K_t} = \frac{[C_0 e^{-K_t}]_{\text{max}} [H]}{K_H + [H]} \]  
(18)

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

Relating equation (18) into lineWave Burk Plot, we have
\[ [C_0 e^{-K_t}]_{K_H + [H]} = [C_0 e^{-K_t}]_{\text{max}} [H] \]  
(19)

Multiplying equation (19) by \((1/C_0 e^{-K_t})\), yields
\[ \frac{[C_0 e^{-K_t}]_{K_H + [H]}}{[C_0 e^{-K_t}]_{\text{max}} [H]} = \frac{1}{C_0 e^{-K_t}} \]  
(20)

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

Making \((1/C_0 e^{-K_t})\) the subject of the equation (21), we have,
\[ \frac{[K_H + [H]]}{[C_0 e^{-K_t}]_{\text{max}} [H]} = \frac{1}{C_0 e^{-K_t}} \]  
(22)

Therefore, equation (22) can be written as
\[ \frac{1}{C_0 e^{-K_t}} = \frac{[K_H]}{[C_0 e^{-K_t}]_{\text{max}} [H]} + \frac{[H]}{[C_0 e^{-K_t}]_{\text{max}} [H]} \]  
(23)

Equation (22) can be further expressed to give the final solution as shown below
\[ \frac{1}{C_0 e^{-K_t}} = \frac{[K_H]}{[C_0 e^{-K_t}]_{\text{max}} [H]} + \frac{1}{C_0 e^{-K_t}} \]  
(24)

Equation (24) is the same as the lineWave Burh Plot method for determining the fundamental parameters of \(K_H\) and \((C_0 e^{-K_t})\). Equation (24) is the same as
\[ \frac{1}{V} = V_{\text{max}} \frac{[H]}{K_H + [H]} + \frac{1}{V_{\text{max}}} \]  
(25)

The inhibition model

Recalling the mathematical expression of Michael-Menten in terms of inhibition, we have
\[ V = \frac{V_{\text{max}} [H]}{K_H + [H]} I \]  
(26)

Model of BOD as an inhibitor

The mathematical model in terms of change in BOD concentration can be defined as
\[ \frac{dBOD}{dt} = \lambda \cdot BOD \]  
(27)

\[ \frac{dBOD}{dt} = -\lambda \cdot BOD \]  
(28)

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
\[ (BOD)_t = (BOD)_{o} e^{-\lambda T} \]  
(29)

For increase in BOD concentration
\[ (BOD)_t = (BOD)_{o} e^{\lambda T} \]  
(30)

Where:
\[ \lambda = \frac{1}{T} \ln \left( \frac{BOD}{BOD_{o}} \right) \]  
(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

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

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

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

In terms of current developed model for increase in BOD concentration

\[ C_o e^{-K_I} = \frac{[C_o e^{-K_I}]_{max}[H]}{K_H + [H]}(BOD)_o e^{-\lambda T} \]  
(34)

In terms of current developed for decrease in BOD concentration

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

Substitute the value of \( \lambda \) from equation (30) into (32) and (33), we have

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

\[ C_o e^{-K_I} = \frac{[C_o e^{-K_I}]_{max}[H]}{K_H + [H]}(BOD)_o e^{\left(-\frac{1}{T} \ln \left[\frac{BOD}{(BOD)_o}\right]\right)T} \]  
(37)

Equation (37) is the inhibition model for increase in BOD. Substitute the value \( \lambda \) of from equation (31) into (33) and (35), we have

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

\[ C_o e^{-K_I} = \frac{[C_o e^{-K_I}]_{max}[H]}{K_H + [H]}(BOD)_o e^{\left(-\frac{1}{T} \ln \left[\frac{BOD}{(BOD)_o}\right]\right)T} \]  
(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

\[ \frac{dCOD}{dt} = \alpha.COD \]  
(40)

\[ \frac{dCOD}{dt} = -\alpha.COD \]  
(41)

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

For decrease in COD

\[ (COD)_t = (COD)_o e^{-\alpha T} \]  
(41)

For increase in COD

\[ (COD)_t = (COD)_o e^{\alpha T} \]  
(42)

Where

\[ \alpha = \frac{1}{T} \ln \left(\frac{COD}{(COD)_o}\right) \] for increase in COD  
(43)

\[ \alpha = -\frac{1}{T} \ln \left(\frac{COD}{(COD)_o}\right) \] for decrease in COD  
(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

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

In terms of Michael Menten model for decrease in COD concentration

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

In terms of current developed model for increase in COD concentration


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

Figure 1b illustrates the laboratory analysis of BOD and COD upon hydrocarbon degradation in salt water medium whereas Figure 2 defines the hydrocarbon content analysis using separating furnace. These component were necessary to enable us achieve the aim of the search.

**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 as shown in Figure 3 to 9. Salt water pond was used for the investigation and samples were collected as well analyzed for a period of 4 weeks 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 was kept at steady state, not agitated (unstirred D). The samples were identified as follows; saltwater pond agitated (stirred) be represented as sample C, pond not agitated (unstirred) be represented as sample D

The COD and BOD concentration increases with increase in time for sample C for the period of 0 day to day 2 and suddenly decrease on day 3 whereas for sample D the COD and BOD concentration increase from day 0 to day 3 and suddenly decrease in day 4 as presented on Table 1. Similarly, the concentration of the COD and BOD for C and D concentration can be attributed to the variation in time and microbial
Table 1. Values of COD, BOD and hydrocarbon concentration of sample C and D.

<table>
<thead>
<tr>
<th>Time (WK)</th>
<th>COD (mg/l) (C)</th>
<th>BOD (m/l) (C)</th>
<th>Hydrocarbon Conc. (ml) (C)</th>
<th>COD (mg/l) (D)</th>
<th>BOD (m/l) (D)</th>
<th>Hydrocarbon Conc. (ml) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.76</td>
<td>1.47</td>
<td>200.00</td>
<td>1.76</td>
<td>1.47</td>
<td>200.00</td>
</tr>
<tr>
<td>1</td>
<td>3.47</td>
<td>2.89</td>
<td>192.00</td>
<td>4.59</td>
<td>3.82</td>
<td>197.50</td>
</tr>
<tr>
<td>2</td>
<td>7.73</td>
<td>6.44</td>
<td>184.30</td>
<td>6.24</td>
<td>5.20</td>
<td>194.50</td>
</tr>
<tr>
<td>3</td>
<td>5.76</td>
<td>4.80</td>
<td>179.50</td>
<td>7.63</td>
<td>6.35</td>
<td>189.60</td>
</tr>
<tr>
<td>4</td>
<td>8.00</td>
<td>6.67</td>
<td>175.60</td>
<td>6.67</td>
<td>5.56</td>
<td>183.50</td>
</tr>
</tbody>
</table>

From Tables 2 and 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.

After contamination of the pond with crude oil, the total concentration as presented in Figure 3.

Figure 2. Hydrocarbon content analysis using separating furnace.

Figure 3. Graph of COD and BOD concentration versus time for sample C and D.
Table 2. Densities of bacteria in water sample C.

<table>
<thead>
<tr>
<th>Time (week)</th>
<th>Total Heterotrophic Bacteria (cfu ml(^{-1}))</th>
<th>Total coliform Bacteria (MPN index 100 ml(^{-1}))</th>
<th>Faecal coliform Bacteria (MPN index 100 ml(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.3(\times)10(^3)</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>1</td>
<td>21.0(\times)10(^3)</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>3.6(\times)10(^3)</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>9.9(\times)10(^2)</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>4.4(\times)10(^2)</td>
<td>70</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3. Densities of bacteria in water sample D.

<table>
<thead>
<tr>
<th>Time (week)</th>
<th>Total Heterotrophic Bacteria (cfu ml(^{-1}))</th>
<th>Total coliform Bacteria (MPN index 100 ml(^{-1}))</th>
<th>Faecal coliform Bacteria (MPN index 100 ml(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.3(\times)10(^3)</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>1</td>
<td>21.0(\times)10(^3)</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>3.9(\times)10(^3)</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>3.8(\times)10(^3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>8.3(\times)10(^2)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

![Graph of bacteria conc. versus time for sample C.](image)

The coefficients \(C_o e^{-KT}\) and \(K_H\) will be determined from the line- wave bulk plot.

The coefficients \(\left[C_o e^{-KT}\right]_{\text{max}}\) and \(K_H\) will be determined from the line-wave 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 3\(^{rd}\) was observed before sudden increase in day 4. In
Figure 5. Graph of bacteria conc. versus time for sample D.

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

<table>
<thead>
<tr>
<th>Time T(weeks)</th>
<th>Substrate H(ml)</th>
<th>1/H</th>
<th>C₀e⁻ᵏᵗ</th>
<th>1/C₀e⁻ᵏᵗ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200.0000</td>
<td>0.0050</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>192.0000</td>
<td>0.0052</td>
<td>8.0000</td>
<td>0.1250</td>
</tr>
<tr>
<td>2</td>
<td>184.3000</td>
<td>0.0054</td>
<td>7.7000</td>
<td>0.1299</td>
</tr>
<tr>
<td>3</td>
<td>179.5000</td>
<td>0.0056</td>
<td>4.8000</td>
<td>0.2083</td>
</tr>
<tr>
<td>4</td>
<td>175.6000</td>
<td>0.0057</td>
<td>3.9000</td>
<td>0.2564</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Time T(weeks)</th>
<th>Substrate H(ml)</th>
<th>1/H</th>
<th>C₀e⁻ᵏᵗ</th>
<th>1/C₀e⁻ᵏᵗ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200.0000</td>
<td>0.0050</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>197.5000</td>
<td>0.0051</td>
<td>2.5000</td>
<td>0.4000</td>
</tr>
<tr>
<td>2</td>
<td>194.5000</td>
<td>0.0051</td>
<td>3.0000</td>
<td>0.3333</td>
</tr>
<tr>
<td>3</td>
<td>189.6000</td>
<td>0.0053</td>
<td>4.9000</td>
<td>0.2041</td>
</tr>
<tr>
<td>4</td>
<td>183.5000</td>
<td>0.0055</td>
<td>6.1000</td>
<td>0.1639</td>
</tr>
</tbody>
</table>
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 the physiochemical parameters 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 on the hydrocarbon for their growth. The activities of the microorganisms fluctuated in the pond system which causes lag, progressive, stationary and decline phase. The rate of degradation of the hydrocarbon substrate (crude oil) can be seen in Figure 6 and 8. Sample C degraded more than sample D, from 200 to 160 ml. In Figure 7, the line-waver bulk plot for the evaluation of the maximum specific rate \( \left[ C_o e^{-Kt} \right]_{\text{max}} \) and the equilibrium rate value (K) could not be obtained due to the insignificant action of the microorganism in the bioreactor which was attributed to the inhibiting components of the COD and BOD in the system. It is difficult to evaluate line-waver bulk plot shown in the graphs of Figure 9 since the curve does not obey the principle. Since the intercept on the y-axis did not cut
through the positive side of the axis. This condition makes it impossible for the evaluation of maximum specific rate for COD and BOD as well as the equilibrium rate for COD and BOD parameter. 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 pose 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 \( \left( \frac{C_o e^{-Kt}}{C_{OE}} \right) \) each
physicochemical 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**

\[
\frac{dc}{dt} = \text{Substrate concentrates per unit time (mgl/day)}
\]

\[K = \text{Equilibrium constant dimensionless} \]

\[C = \text{Substrate concentration (mg/l)} \]

\[E = \text{Enzyme concentration (cfu/ml)} \]

\[H = \text{Substrate concentration (mg/l)} \]

\[K_1 = \text{Equilibrium constant for forward reaction} \]

\[K_2 = \text{Equilibrium constant for backward reaction} \]

\[EH = \text{Enzyme substrate complex} \]

\[P = \text{Product concentration (mg/l)} \]

\[E_1 = \text{Total enzyme concentration (cfu/ml)} \]

\[K_3 = \text{Equilibrium constant for the product} \]

\[V = \text{R = Specific rate of reaction (substrate) (mg/l/day)} \]

\[v_{\text{max}} = \text{R}_{\text{max}} = \left[C_0 e^{-K_1 T} \right]_{\text{max}} = \text{Maximum specific rate of reaction (mg/l/day)} \]

\[K, \beta, \lambda, \alpha, \gamma = \text{Constants} \]

\[C_0 = \text{Initial substrate concentration (mg/l)} \]

\[T = \text{Time (week)} \]

\[T_0 = \text{week before contamination} \]

\[T_{1,2,3,4} = \text{Weeks after contamination} \]

\[\text{BOD}_0 = \text{Initial concentration of biochemical oxygen demand (mg/l)} \]

\[\text{BOD} = \text{Final concentration of biochemical oxygen demand (mg/l)} \]

\[\text{COD}_0 = \text{Initial chemical oxygen demand (mg/l)} \]

\[\text{COD} = \text{Final chemical oxygen demand (mg/l)} \]

\[\text{CFU} = \text{Colony forming units} \]

\[\text{MPN} = \text{Most probable number technique} \]

**REFERENCES**


