International Journal of Engineering and Modern Technology ISSN 2504-8856 Vol. 4 No. 2 2018
www.iiardpub.org

Development of Predictive Model for Diffusion of Oxygen through Petroleum Contaminated Soils at 100cm Depth

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Abstract

A study was carried out on Mathematical Modeling of oxygen diffusion on bioremediation of petroleum contaminated soils at 100cm depth in Niger Delta region of Southern Nigeria. This study is important for the model prediction of oxygen concentration and carbon dioxide production variation with times for petroleum contaminated soils. The Mathematical model was derived from basic principles. Oxygen consumption by Microorganism and Carbon dioxide production as a byproduct of bioremediation during the experiments were used as indicators for monitoring degradation of hydrocarbons in the impacted soils. The model developed was based on oxygen concentration utilized by the microorganism and carbon dioxide produced as a byproduct during the process of bioremediation. Oxygen diffusion rates were obtained as $7.5x10^{-04}$ $mgl^{-1}h^{-1}$, $8.3x10^{-04}$ $mgl^{-1}h^{-1}$ *and* $2x10^{-03}$ $mgl^{-1}h^{-1}$ *for Sandy, Sandy loam and Clay soil respectively. The predictive model results obtained were compared with experimental results and both showed a good fit between the experimental and predicted data. Therefore, the developed model can be used for the prediction of Oxygen concentration utilized and Carbon dioxide production for bioremediation of petroleum contaminated soils at 100cm depth or below*

Keywords: *Carbon dioxide production; Oxygen concentration; Predictive Model*

Introduction

Oil pollution is a worldwide threat to the environment and remediation of oil contaminated soils, sediment and water is a major issue to researchers (Chorom et al., 2010). Bioremediation is a useful method for soil remediation, if pollutant concentrations are moderate and non-biological techniques are not economical (Chorom et al., 2010). Bioremediation is a process that offers the possibilities to destroy or render various contaminants harmless, using natural biological activities (Vidali, 2001). Bioremediation involves three principal approaches namely, natural attenuation, bio-stimulation and bio-argumentation (Chikere et al., 2009a). For effective bioremediation to take place in the soil there must be sufficient soil nutrient and oxygen concentration, to enhance the activities of microorganism (Umeda et al., 2017). Furthermore, in the last few years a great deal of work has been done on several aspects of bioremediation because of its environmental friendliness, cost effectiveness and simplicity in technology (Baptista *et al.*, 2005). However, most of the works carried out were basic proof of concepts, practical oriented and not geared towards modeling and simulation or process development (Abdulsalam, 2012). In addition, a realistic model will enable us to predict the variation of oxygen concentration with time to detoxify a contaminated site at 100cm depth. Also it will enable us to predict the carbon dioxide concentration produced at each time as a byproduct of bioremediation. Gas transport in the soil is a phenomenon in which gases move mainly by diffusion. Diffusion is defined as the random movement of particles due to kinetic energy. It may occur in gaseous or liquid medium, with a net movement of the diffusing substance from a region of higher concentration to a lower concentration (Jose et al., 2015). Gases, including oxygen move in the soil according to diffusion laws. The main parameter related to gas diffusion in the soil is the gas diffusion coefficient of the soil (D), which is a property of the medium and the gas under study and depends upon the texture, structure, distribution, size and connectivity of the pores as well as their tortuosity (Schjonning *et al*., 1999). The aim of this study is to develop a predictive model that can predict oxygen concentration by diffusion through the impacted soils and carbon dioxide production in bioremediation of petroleum contaminated soils at 100cm depth.

Mathematical Model for Prediction of Oxygen Concentration and Carbon dioxide Production in Bioremediation of Petroleum Contaminated Soil At 100cm Depth

Model Formulation

The Mathematical Model was developed from basic principle

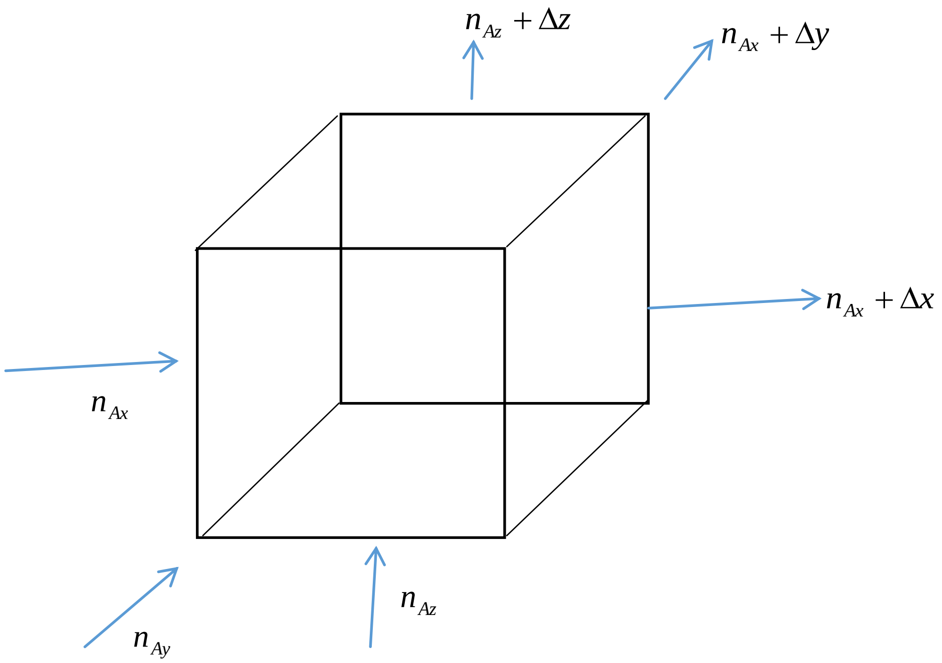


Figure 1: Schematic diagram for the hypothetical control volume representation of soil samples

Consider a homogeneous contaminated soil (Mixture) that is stationary, of which mass transfer occurs only by diffusion. Allowing for a concentration gradient in each of the x y and z coordinate directions. With the concentration gradients, diffusion must result in the transport of oxygen through the control surface. The general relation for mass Balance of oxygen (A) flowing in and out of this control volume may be stated as:

> [Net rate of mass efflux of A from control volume]+[Net rate of accumulation of A within the control volume] ± [Rate of chemical production/depletion of A within the control volume] = 0 (1)

Defining parameters in equation (1)

Rate of mass A entering the control volume in the x-direction relative to fixed coordinates

$= \rho_A V_{AX} \Delta_y \Delta_z /_x \quad = \quad n_{Ax} \Delta_y \Delta_z /_x$ (a)

Rate of mass A entering the control volume in the y direction relative to fixed coordinates

= $n_{Ay}\Delta_x\Delta_z/_y$ (b)

Rate of mass A entering the control volume in the z direction relative to stationary coordinates

= $n_{A,Z}\Delta_X\Delta_Y/_Z$ (c)

Similarly,

Rate of mass A leaving the control volume in the x direction relative to stationary coordinate

= $n_{Ax}\Delta_y\Delta_z/_{x+\Delta x}$ (d)

Rate of mass A leaving the control volume in the y direction relative to fixed coordinates

= $n_{A,y}\Delta_x\Delta_z/_{y+\Delta y}$ (e)

Rate of mass A leaving the control volume in the z direction relative to stationary coordinates

= $n_{A,Z}\Delta_X\Delta_y/_{z+\Delta z}$ (f)

Rate of production or depletion of A due to chemical reaction within the control volume

= $\pm R_A\Delta x\Delta y\Delta z$ (g)

The rate of accumulation of A within the control volume $=\frac{\partial \rho A}{\partial t}\Delta x\Delta y\Delta z$ (h)

Substituting equation (a-h) into equation (1), gives

$$[n_{A,X}\Delta y\Delta z/_{x+\Delta x} - n_{A,X}\Delta_y\Delta z/_x] + [n_{A,y}\Delta_x\Delta_z/_{y+\Delta z} - n_{A,y}\Delta_x\Delta_z/_y] + [n_{A,Z}\Delta x\Delta y/_{z+\Delta z} - n_{Az}\Delta x\Delta y/_z] + \frac{\partial \rho A}{\partial t}\Delta x\Delta y\Delta z \pm R_A\Delta x\Delta y\Delta z = 0 \quad (2)$$

Dividing through resulting equation by incremental volume ΔxΔyΔz and evaluating terms as Δx Δy Δz tends to zero, yields;

$$\frac{\partial}{\partial x}n_{A,x} + \frac{\partial}{\partial y}n_{Ay} + \frac{\partial}{\partial z}n_{A,z} + \frac{\partial \rho_A}{\partial t} \pm R_A = 0 \quad (3)$$

For a stationary medium, the mass average velocity is zero hence mass transfer occur only by diffusion which could involve Fick's law to determine the diffusion rate at any point in the medium. Hence substituting the x, y, z component of Fick's law of diffusion, gives.

$$\frac{\partial}{\partial x}\left[\rho D_{AB}\frac{d\rho_A}{\partial x}\right] + \frac{\partial}{\partial y}\left[\rho D_{AB}\frac{\partial \rho_A}{\partial y}\right] + \frac{\partial}{\partial z}\left[\rho D_{AB}\frac{\partial \rho_A}{\partial z}\right] + \frac{\partial \rho_A}{\partial t} + R_A = 0 \quad (4)$$

In term of molar concentration, dividing density by molar mass we have as follows:

$$\frac{\partial}{\partial x}\left[CD_{AB}\frac{dy_A}{\partial x}\right] + \frac{\partial}{\partial y}\left[CD_{AB}\frac{\partial y_A}{\partial y}\right] + \frac{\partial}{\partial z}\left[CD_{AB}\frac{\partial y_A}{\partial z}\right] + R_A + \frac{\partial C_A}{\partial t} = 0 \quad (5)$$

Assuming $D_{AB,}$ and C to be constant

$$\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \pm \frac{R_A}{D_{AB}} + \frac{1}{D_{AB}}\frac{\partial C_A}{\partial t} = 0 \quad (6)$$

Assuming that diffusion occurs only at the Z direction:

$$\frac{\partial^2 C_A}{\partial z^2} \pm \frac{R_A}{D_{AB}} = \frac{1}{D_{AB}}\frac{\partial C_A}{\partial t} \quad (7)$$

But the oxygen is utilized by the Microorganism to oxidize the contaminated soil: Hence assume 2nd order:

$$R_A = \mu = \frac{\mu_m S}{K_S + S}$$

$$= \frac{\mu_m SX}{K_S + S} - K_d X \qquad (8)$$

For the substrate (contaminant and O_2)

$$-R_A = \frac{1}{Y}\frac{dx}{dt}$$

$$= \frac{1}{Y}\frac{\mu_m SX}{K_s + S} \qquad (9)$$

For Biomass

$$\frac{\partial^2 C_A}{\partial z^2} + \frac{1}{D_{AB}}\left[\frac{\mu_m SX}{K_S + S} - K_d X\right] = \frac{1}{D_{AB}}\frac{\partial C_A}{\partial t} \qquad (10)$$

For O_2 or substrate

$$\frac{\partial^2 C_A}{\partial z^2} - \frac{1}{D_{AB}}\left[\frac{1}{Y}\frac{\mu_{\max} SX}{K_S + S}\right] = \frac{1}{D_{AB}}\frac{\partial C_A}{\partial t} \qquad (11)$$

Defining boundary conditions

1. Let the species concentration at the surface be maintained at a constant value ρ_{AS}, $C_{A,S}$ Expressing the condition on a molar basis for the surface at Z = 0, we have

$\rho_A(0,t) = \rho_{A,S,}$

2. Constant flux at the surface, and using Fick's law

$$-\ CD_{AB}\frac{\partial y_A}{\partial z}\Big/_{z=0} = J_{AS}$$

Further simplification and integration of equation (11) gives

$$C_A = e^{\alpha t} \pm \sqrt{{}^{\alpha}\!/_{DAB}}\,Z\left[C_{AO} - \frac{1}{D_{AB}Y}\left(\frac{U\max + Sx}{Ks + S}\right)Z\right] + \frac{1}{D_{AB}Y}\left(\frac{U\max + Sx}{Ks + S}\right)Z \quad (12)$$

Where, C_{AO} - Initial Oxygen Concentration, D_{AB} - Diffusion coefficient of oxygen in the soil, Y- Yield conversion constant, U_{max} - Maximum specific growth rate, S – Limiting substrate concentration. X- Biomass, K_S – Substrate Saturation constant, Z- Distance, α –Constant of integration, t - Time

Equation (12) is the model for prediction of oxygen concentration with time along the reactor. Also, it can be used to determine carbon dioxide produced or generated with time as a byproduct during the process of bioremediation. The positive sign is used when carbon dioxide is produced or generated in the system, while the negative sign is applied when oxygen concentration is utilized or consumed during the process by the microorganisms. Table 1, 2 and 3 showed the summary of model parameter used in Equation (12) for Sandy, Sandy loam and Clay soils respectively.

Table 1: Summary of Model Parameters for Sandy Soil

Parameters	Reactor A	Reactor B	Reactor C
C_{AO}	2.50	2.50	2,50
D_{AB}	25.2	25.2	25.2
Y	0.3787	0.3787	0.3787
U_{max}	5.42	7.50	23.7
S	1056.34	536.34	325
X	85	103	568
K_S	0.1	0.1	0.1
Z	1	1	1
A	0.000018	0.000018	0.000018
T	1008	1008	1008

Table 2: Summary of Model Parameters for Sandy loam Soil

Parameters	Reactor A	Reactor B	Reactor C
C_{AO}	2.50	2.50	2.50
D_{AB}	14.4	14.4	14.4
Y	0.3787	0.3787	0.3787
U_{max}	7.71	8.8	17.9
S	1134.74	619.73	348.58
X	53	90	430
K_S	0.1	0.1	0.1
Z	1	1	1
A	0.0000129	0.0000129	0.0000129
T	1008	1008	1008

Table 3: Summary of Model Parameters for Clay Soil

Parameters	Reactor A	Reactor B	Reactor C
C_{AO}	2.50	2.50	2,50
D_{AB}	82.8	82.8	82.8
Y	0.3787	0.3787	0.3787
U_{max}	6.83	7.62	28.3
S	1415.96	488.20	219.2
X	62	152	679
K_S	0.1	0.1	0.1
Z	1	1	1
A	0.00007	0.00007	0.00007
T	1008	1008	1008

Results of Predictive Model for Oxygen Concentration at 100cm Depth

Figures 2, 3 and 4 show a plot of oxygen concentration against time. The graphs showed that the concentration of oxygen in the three soil sample, namely Sandy, Sandy loam and Clay soils decreased with time. Comparison of results obtained from soils in reactor A, B, and C, indicated that, the decrease in oxygen concentration in soils in reactor C, was appreciable, compared to Oxygen concentration in soils in reactor A and B. This is as a result of oxygen injection into soils in reactor C. This implied that, the result followed the same trend with the experimental results.

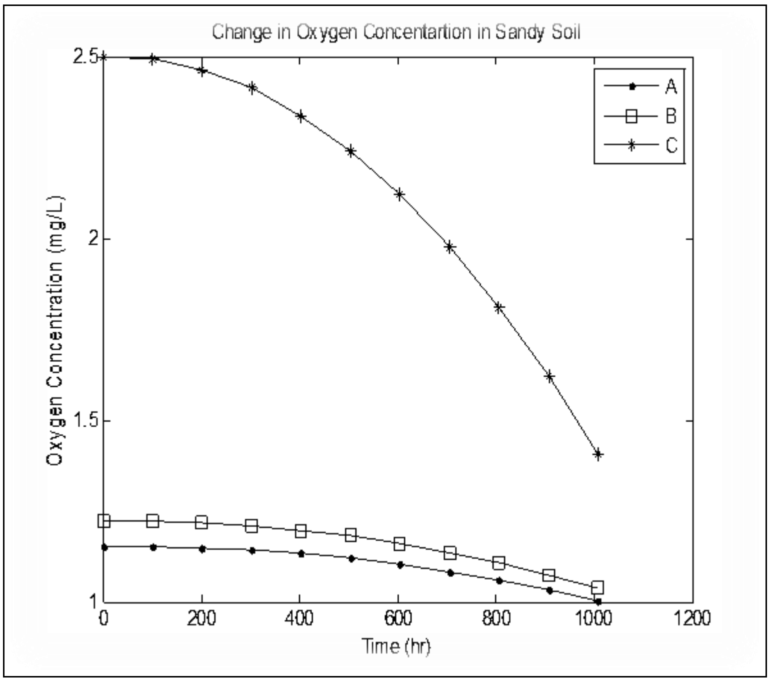


Figure 2: Graph of Oxygen concentration against Time for sandy soil

Also, it showed that the developed model predicted the experimental result reasonably well. Oxygen diffusion rate of the soils were obtained from the graphs of the developed model as 7.5x10^{-04} mgl^{-1}h^{-1}, 8.3x10^{-04}mgl^{-1}h^{-1} and 2x10^{-03}mgl^{-1}h^{-1}for Sandy, Sandy loam and Clay soil respectively. These values were obtained by calculating the area under the representative curve.

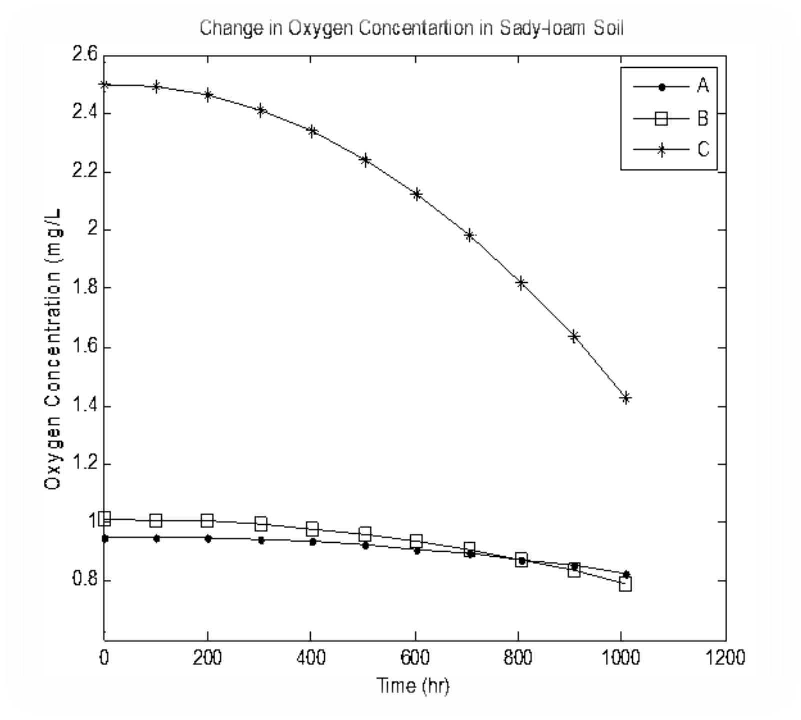


Figure 3: Graph of Oxygen concentration against Time for sandy loam soil

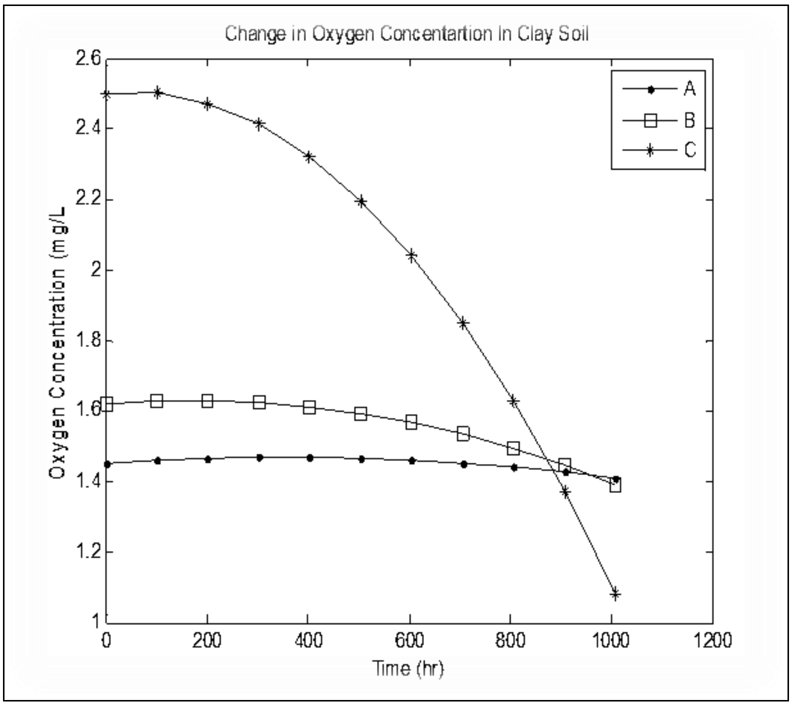


Figure 4: Graph of Oxygen concentration against Time for clay soil

Comparison between Experimental Data and Model predictions for Oxygen Concentration

Figure 5, 6 and 7, show the comparison between experimental data and model predictions for oxygen concentration, which indicated that the predictive model gives very good fit of the experimental data at all data- points with maximum error of 0.78% for sandy, 0.87% for sandy loam and 0.41% for clay soils

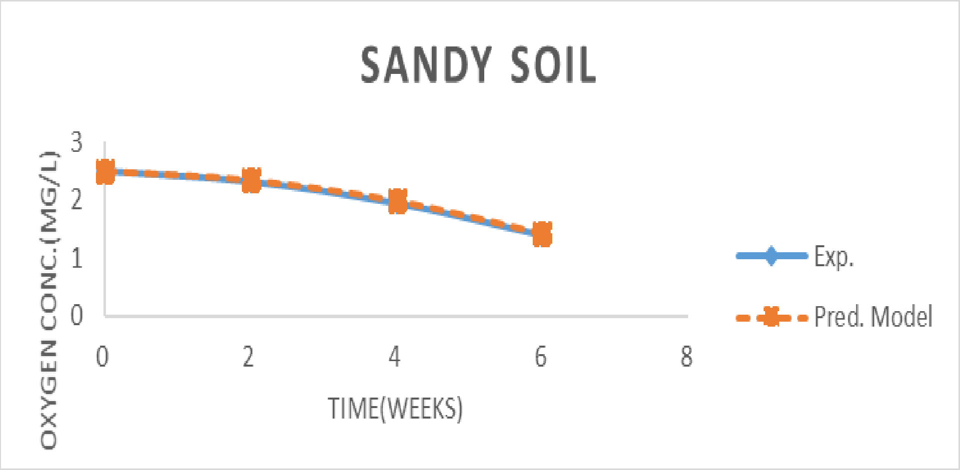


Figure 5: Comparison between experimental data and model predictions for sandy.

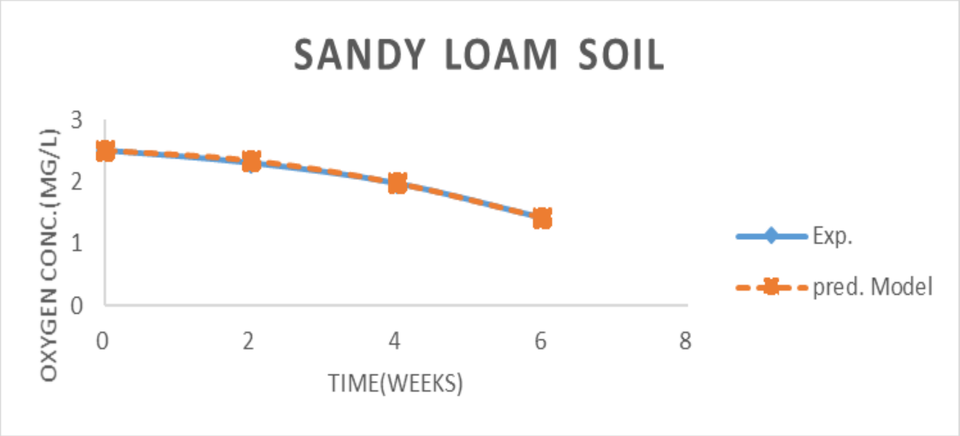


Figure 6: Comparison between experimental data and model predictions for sandy loam

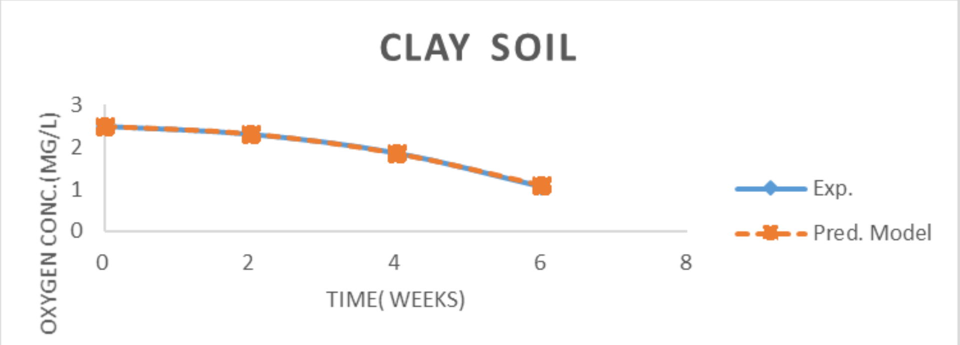


Figure 7: Comparison between experimental data and model predictions for clay.

Results of Predictive Model for Carbon dioxide Production in the Soils

Figure 8, 9 and 10 show a plot of concentration of carbon dioxide production in soils in reactor A, B and C against time

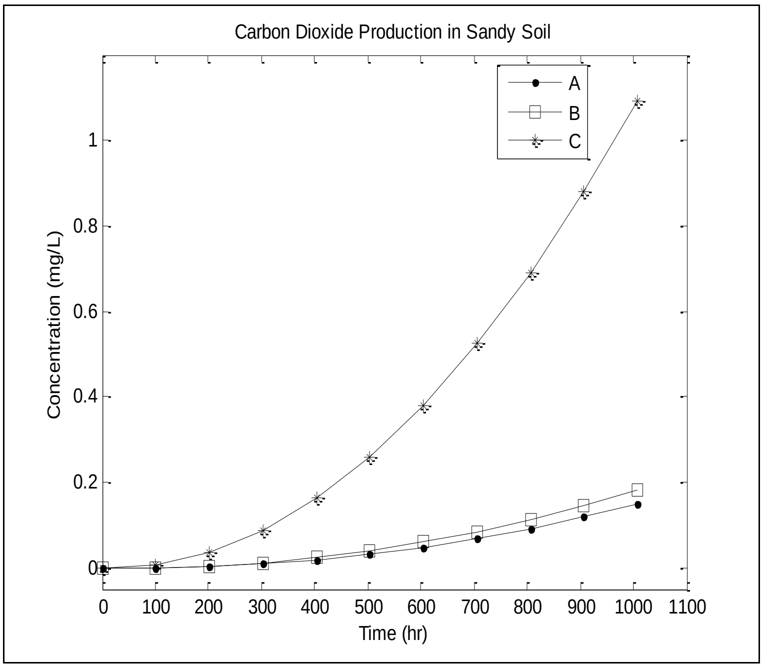


Figure 8: Carbon Dioxide Concentration versus Time in Sandy Soil

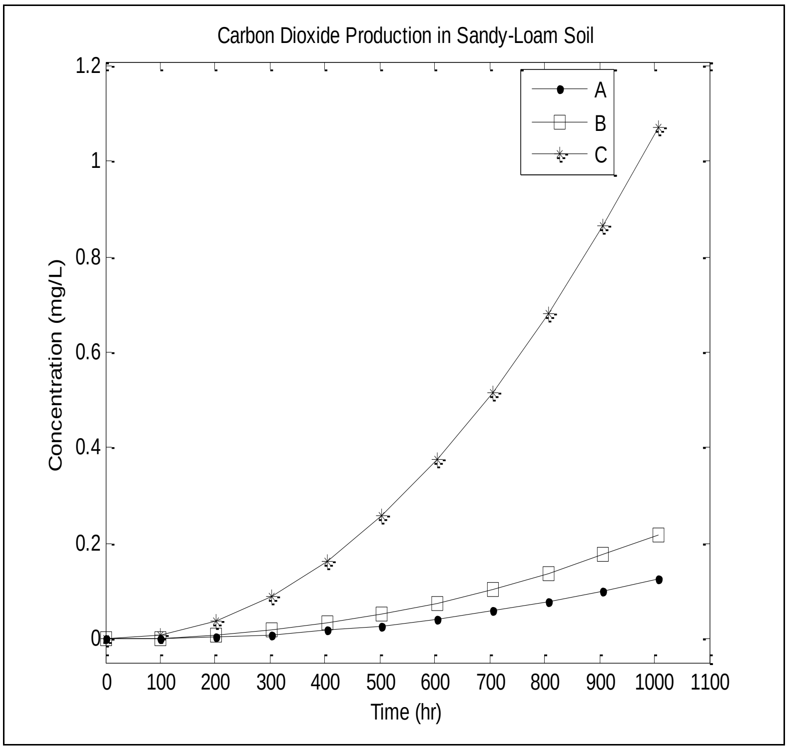


Figure 9: Carbon Dioxide Production versus Time in Sandy-Loam Soil

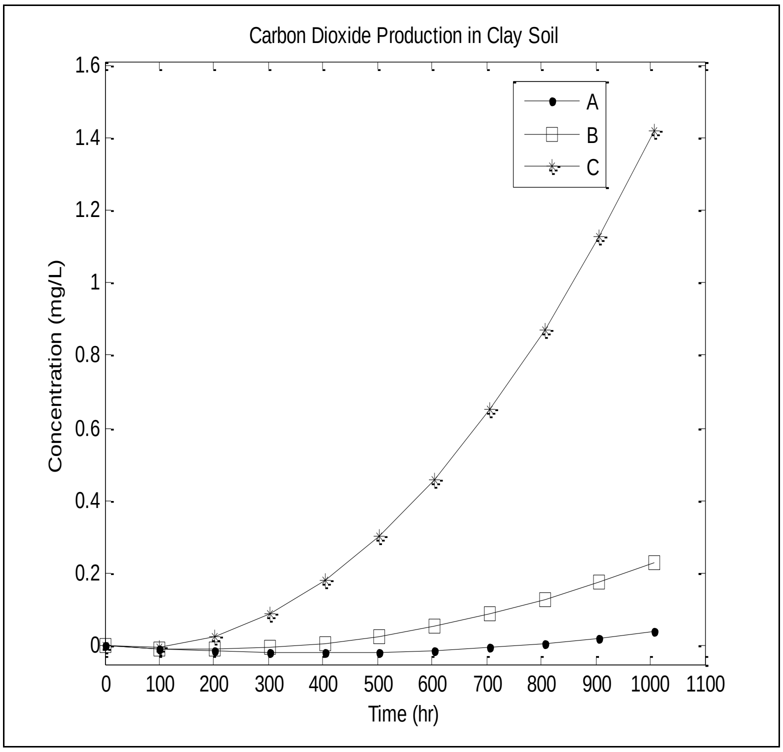
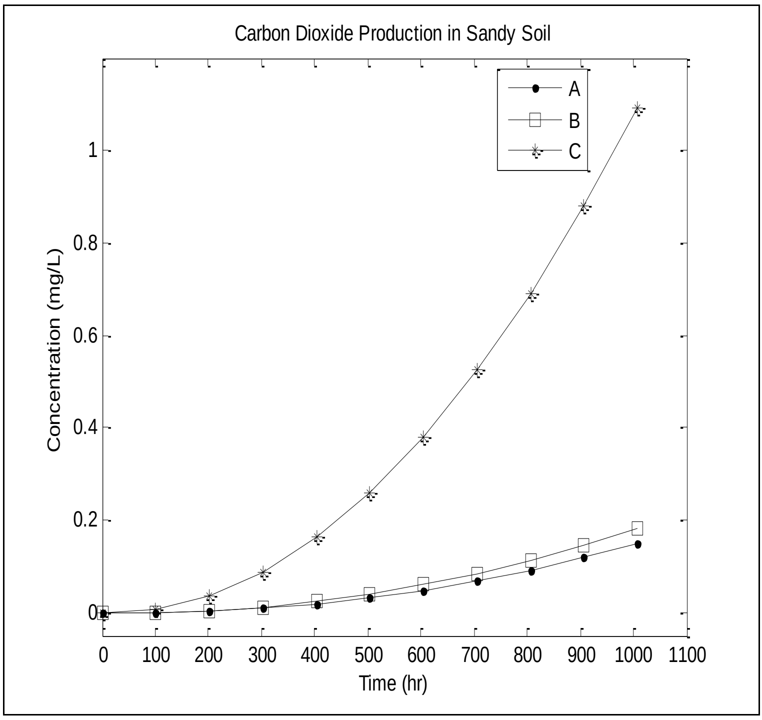


Figure 10: Carbon Dioxide Production versus Time in Clay Soil

The results showed that the concentration of carbon dioxide produced in the three soil, namely Sandy, Sandy loam and Clay increased with time. Comparison of the carbon dioxide concentration produced in the soils in reactor A, B and C showed that the soils in reactor C did reasonably well. This revealed that bioremediation was more effective in soil in reactor C than reactor A and B, due to oxygen diffusion through the petroleum contaminated soils. Also this indicated that, the results followed the same trend with the experimental results. However, it showed that the developed model predicted the experimental result reasonably well.



Comparison between Experimental Data and Model Predictions for Carbon dioxide Production in the Soils

Figures 11, 12 and 13 show the comparison between experimental data and model predictions for Carbon dioxide production as a byproduct of bioremediation in the soil.

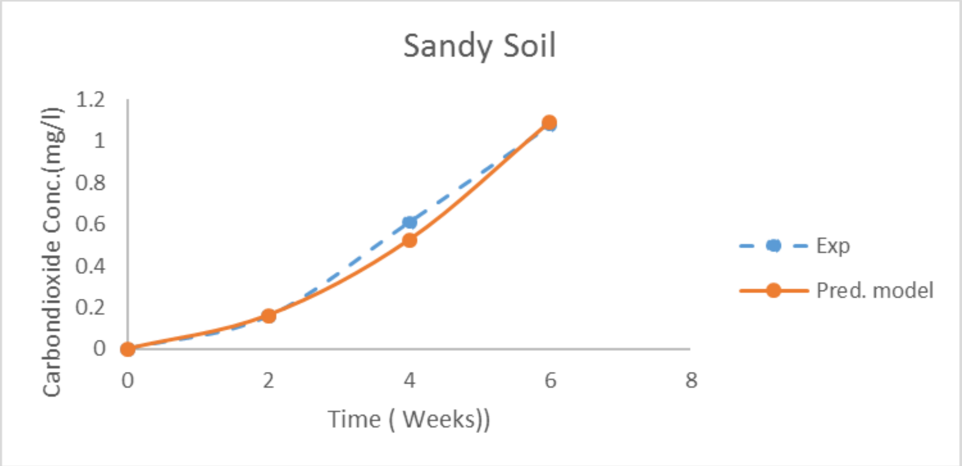


Figure 11: Comparison between experimental data and model predictions for sandy soils.

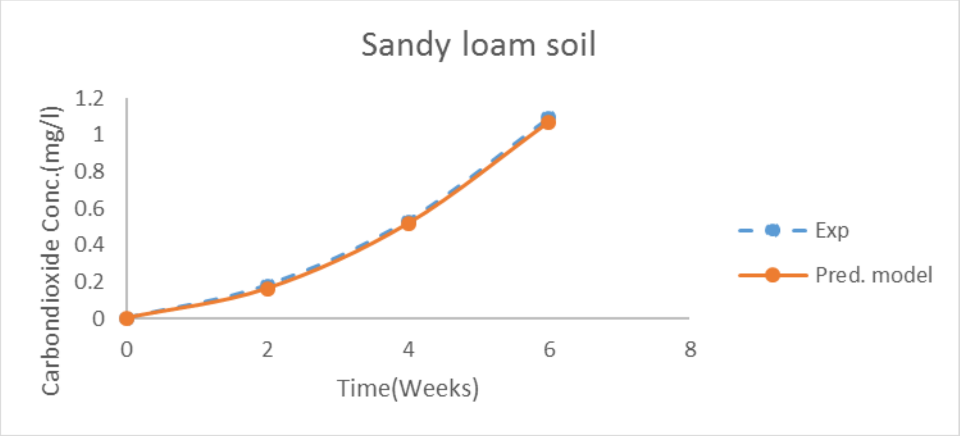


Figure 12: Comparison between experimental data and model predictions for sandy loam soils.

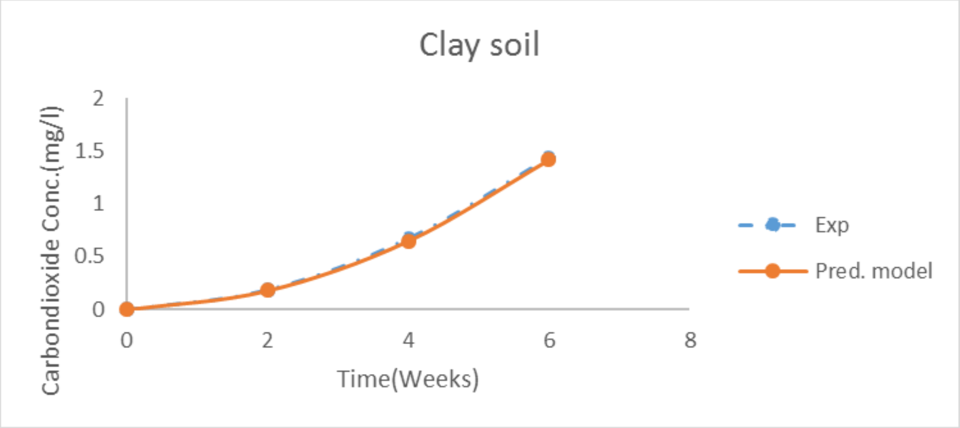


Figure 13: Comparison between experimental data and model predictions for Clay soils.

Figure 11, 12 and13 indicate that the predictive model gives very good fit of the experimental data at all data- points with a maximum error of 2.99% for Sandy loam and 2.219% for clay soil, but slight deviation at one data point for Sandy soil with maximum error of 3.74%, which confirmed that the model predicted the experimental data reasonably well.

Conclusion

The results made available in this study revealed that the model can be used to predict the oxygen concentration at 100cm depth and carbon dioxide produced as a byproduct during bioremediation of petroleum contaminated soils, namely, Sandy soil, Sandy loam soil and Clay soil respectively. This result showed that bioremediation with Oxygen diffusion could be very effective even at a depth below 100cm.

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