Nigerian Journal of Technology (NIJOTECH)
Vol. 31, No. 2, July, 2012, pp. 161–166.
Copyright ©2012 Faculty of Engineering,
University of Nigeria. ISSN 1115-8443

SIMULATION OF THE BIOREMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN STIRRED REACTORS

C.N. Owabor[a], **J.I. Achebo**[b]

[a]Department of Chemical Engineering, University of Benin, Benin City, Nigeria.
Email: *owabor4you@yahoo.com*
[b]Department of Production Engineering, University of Benin, Benin City, Nigeria.
Email: *josephachebo@yahoo.co.uk*

Abstract

The mathematical solution to a one-dimensional advective-dispersive solute transport model with linear equilibrium sorption and first-order degradation was carried out in this study. Simulation was carried out using MathCad software. The model solution predicted time approximated concentration distribution at varying depths of the selected PAHs (naphthalene, anthracene and pyrene) used in this study at distances. Simulation results showed that the concentrations of naphthalene, anthracene and pyrene within a contact period of 40, 55, and 50 days respectively, decreased in the direction of flow from 200 mg/l at the surface to zero at 9cm subsurface depth within the porous media. The residual concentrations of naphthalene, anthracene and pyrene were found to be 14% (35th day), 44% (50th day) and 29% (45th day) respectively. The simulation results closely fit the data from experiments an indication that the technique significantly provides solution to non-steady state model concerned with contaminant solute transport and degradation.

Keywords: contaminant solutes, finite element method, degradation, mobility, availability

1. Introduction

The frequency of the occurrence of oil spills in transmission pipelines is continuously eliciting attention in the Niger-Delta region of Nigeria. This may not be unrelated to the incidences/widespread releases of toxic chemicals such as polycyclic aromatic hydrocarbons, and volatile organic compounds associated with these spills [1-4]. Generally, the Niger Delta region environment has been subjected to a constant and consistent pollution of its air, land and sea. Some of the spills have been known to seep into the ground and contaminate ground water. Many in the region have complained that water from freshly sunk boreholes showed evidence of oil contamination which renders the water undrinkable even after some treatment. Aside contamination of the water environment, areas that have been known to be fertile for farming in the past have suddenly become barren or are getting close to being so. The mangrove forest is slowly withering away and the agricultural industry is suffering. This is particularly sad because the natives, who used to make their living through subsistent farming, have to look elsewhere [5-7]. The potential negative effects posed by these chemicals has therefore made the quick and safe decontamination of locations that have had shock loading of petroleum or petroleum products very imperative and very desirable. An effective method for detoxifying the contaminants and hence cleaning up the soil is via bioremediation [4,8-12]. However, the process is complex and involves the diffusion of contaminants in the porous soil matrix, adsorption to the soil surface, biodegradation in the biofilm existing on the soil particle surface and in the large pores as well as in the bound and free water phase after desorption from the soil surface [13,14]. The type of reactor forms the basis of many new bioremediation techniques and for the process to be commercially viable, it is important to obtain the best performance from the reactor. This is feasible when there is available information on accurate design parameters and methods. The development of remedial techniques to remove these contaminant solutes and assess their behaviour over relatively long spatial and temporal scales therefore seem to be the only viable solution or management strategy to maintaining the integrity of the environment.

Following the challenges of cost implications and the cumbersome nature of experimental studies over long distances and/or time periods, engineers and researchers are making concerted efforts on the use of theoretical models to describe the process of bioremediation.

A number of mathematical and computer models have been developed for simulating contaminant solute transport and degradation through soil columns and fixed bed reactors in porous media [15-23]. Lobo-Ferreira et al [15] developed a model to determine and quantify the important processes that control the chemical behavior of heavy metals and nitrate. The model by [17] based on the mass balance equation including convective transport, dispersive transport, surface adsorption, oxidation and reduction, volatilization, chemical and biological transformation indicated that as the time of simulation increases, the concentration of different selenium species approaches the measured values. Elsewhere, literature report [18] showed the development of mathematical model based on equilibrium sorption approaches to simulate transport and retardation of organic contaminants such as polycyclic aromatic hydrocarbons in a multi-phase groundwater system. The solute transport model of [16, 19] was aimed at analyzing the interplay of degradation and sorption. The modeling results from [20-22] showed that the occlusion of these compounds within the fissures and cavities of the soil particles, renders them not readily bioavailable and thus inaccessible to microbial degradation. Predictions from the feed forward neural network model [23] closely fitted the measured values. Solving these problems presented as computational schemes using the parameters implicated during transport provides a comprehensive information and database on the rate and extent of biodegradation with a view to averting considerably, the prolonged effects of polycyclic aromatic hydrocarbon contamination on the environment.

This study is aimed at predicting contaminant solute concentration over time given varying distances by employing the numerical method of the finite element technique for the solution of a second-order partial differential equation which was used to model the ex-situ bioremediation of contaminated soil.

2. Materials and Methods

2.1. Materials

The data used in this study were obtained from the previous investigation of Owabor et al [24]. The theoretical framework applied here is as described by Owabor and Ekwonu [25].

2.2. Methods

The experimental procedure for determining the concentration of contaminant solutes with time is as correlated by Reardon et al [26] and described by Owabor et al [24]. 1.6 kg of soil sample and 0.4 kg of poultry dung were mixed and put in a clean sterile bowl. 4 litres of distilled water was added to the mixture and stirred to form soil slurry. The slurry was spiked with a mixture of 200mg each of the contaminant solutes. The contaminant-soil slurry was charged into the bioreactor which was continuously agitated and supplied with oxygen at a rate of 2 cc/min. The temperature and pressure of the bioreactor was monitored throughout the period of experiment using digital multimeter and pressure gauge. Sampling was done at an interval of 5 days.

2.2.1. Development of the finite element method

The governing transport equation for the advective-dispersion model for one-dimensional flow of solutes through a homogenous soil matrix to which the finite element technique has been applied in this study was described by Najafi and Hajinezhad [20].

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \lambda C \tag{1}$$

The same initial and boundary conditions as well as the method of solution described by Owabor and Ekwonu [25] is applied here in resolving the second-order differential equation. The initial condition is:

$$\begin{aligned} &c(0,0) = c; \\ &c(0,t) = c; \quad 7 \le t \le 63 \\ &c(x,0) = 0; \quad 0.01 \le x \le 0.09 \end{aligned}$$

and the boundary condition:

$$D\frac{dc}{dx}|_{x=L} = 0$$

Therefore rearranging equation (1), we have

$$0 = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - R\frac{\partial C}{\partial t} - \lambda C \tag{2}$$

In developing the weak form of equation (2), it was multiplied with the weight function w;

$$0 = w\left[D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - R\frac{\partial C}{\partial t} - \lambda C\right] \tag{3}$$

Equation (3) is integrated over an element, Ω^e to obtain the weighted residual equivalent of the equation:

$$0 = \int_{x_e}^{x_{e+1}} w\left[D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - R\frac{\partial C}{\partial t} - \lambda C\right] \tag{4}$$

Further integration using the method of integration by parts yields:

$$\begin{aligned} 0 =& w\left[D\frac{\partial C}{\partial x}\right]_{x_e}^{x_{e+1}} - \int_{x_e}^{x_{e+1}}\left[D\frac{dw}{dx}\frac{dC}{dx} + Vw\frac{\partial C}{\partial x}\right. \\ &\left. -Rw\frac{\partial C}{\partial t} - \lambda wC\right] \end{aligned} \tag{5}$$

Table 1: Model simulation parameters.

Solutes [PAHS]	**Retardation factor (R)**	**Dispersion coefficient/ Diffusivity (D)**	**Pore – water velocity (V)**
Naphthalene	25.77	8.61 E-6m^2/day	0.36m/day
Anthracene	41.62	8.59 E-6m^2/day	0.36m/day
Pyrene	35.66	8.597 E-6m^2/day	0.36m/day

Table 2: Concentration distribution of naphthalene in a stirred reactor.

x(m)	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.070	0.080	0.090	Experimental Result
t(days)	Concentration (mg/l)										
0	200.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	200
5	92.000	42.372	26.609	20.183	17.513	15.902	14.841	14.139	13.545	13.140	92
10	54.000	240869	15.618	11.846	10.276	9.334	8.771	8.299	7.950	7.713	54
15	92.000	13.359	13.359	6.362	5.520	5.013	4.678	4.457	4.270	4.142	29
20	24.000	11.059	11.059	5.265	4.568	4.148	3.872	3.688	3.534	3.428	24
25	16.640	7.667	7.667	3.650	3.168	2.876	2.687	2.557	2.450	2.377	16.64
30	9.920	4.563	4.563	2.177	1.889	1.714	1.601	1.525	1.461	1.417	9.92
35	4.300	1.976	1.976	0.943	0.818	0.818	0.694	0.694	0.633	0.614	4.3
40	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
45	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
50	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
55	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
60	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0

Let $x_e = x_A$ and $x_{e+1} = x_B$

$$-Q_A = \left[D\frac{dC}{dx}\right]_{X_A} \quad \text{and} \quad Q_B = \left[D\frac{dC}{dx}\right]_{X_B}$$

Representing the values of the secondary variable at the boundary x_A and x_B respectively, we have

$$\begin{aligned}0 =& w(x_A)\left[D\frac{dC}{dx}\right]_{x_A} - w(x_B)\left[D\frac{dC}{dx}\right]_{x_B} \\ &+ \int_{x_B}^{x_A}\left[-Vw\frac{dC}{dx} - D\frac{dw}{dx}\frac{dC}{dx} - \lambda wC\right]dx\end{aligned} \tag{6}$$

$$\begin{aligned}0 =& \int_{x_B}^{x_A}\left[-Vw\frac{dC}{dx} - D\frac{dw}{dx}\frac{dC}{dx} - \lambda wC\right]dx \\ &- w(x_A)Q(x_A) - w(x_B)Q(x_B)\end{aligned} \tag{7}$$

Where $w(x)$ is the weight function and $\Omega^e = (x_A, x_B)$ is the domain of a typical element Substituting the finite element approximation function $C \approx \sum^n C_i^\theta(t)\psi_i^\theta(x)$ into equation (7);

$$\begin{aligned}0 =& \int_{x_B}^{x_A}\left[-V\psi_j^e\left(\sum_{j=1}^n C_j^e(t)\frac{d\psi_j^e}{dx}\right) - D\frac{d\psi_j^e}{dx}\left(\sum_{j=1}^n C_j^e(t)\frac{d\psi_j^e}{dx}\right)\right. \\ &\left. -R\psi_j^e\left(\sum_{j=1}^n C_j^e(t)\frac{d\psi_j^e}{dx}\right) - \lambda\psi_j^e\left(\sum_{j=1}^n C_j^e(t)\frac{d\psi_j^e}{dx}\right)\right]dx \\ &- \sum_{j=1}^n \psi_j^e(x_j^e)Q_j^e\end{aligned} \tag{8}$$

where $w = \psi_j^e$

Rearranging equation (8), we have

$$\begin{aligned}0 =& \sum_{j=1}^n \int_{x_B}^{x_A}\left\{-V\psi_j^e\frac{d\psi_j^e}{dx} - D\frac{d\psi_j^e}{dx}\frac{d\psi_j^e}{dx} - \lambda\psi_j^e\psi_j^e\right\}C_j^e(t)dx \\ &- \sum_{j=1}^n \int_{x_B}^{x_A} R\psi_j^e\psi_j^e\frac{dC_j^e}{dt}dx - \sum_{j=1}^n \psi_j^e(x_j^e)Q_j^e\end{aligned} \tag{9}$$

The finite element model is represented as:

$$0 = \left[K_{ij}^e\right]\left\{C_j^e(t)\right\} - \left[M_{ij}^e\right]\left\{\frac{dC_j^e(t)}{dt}\right\} - \left\{Q_j^e\right\}$$

$$\left[K_{ij}^e\right]\left\{C_j^e(t)\right\} - \left[M_{ij}^e\right]\left\{\frac{dC_j^e(t)}{dt}\right\} = \left\{Q_j^e\right\}$$

where,

$$\left[K_{ij}^e\right] = \int_0^{h_e}\left(-V\psi_j^e\frac{d\psi_j^e}{dx} - D\frac{d\psi_j^e}{dx}\frac{d\psi_j^e}{dx} - \lambda\psi_j^e\psi_j^e\right)\overline{dx}$$

$$\left[M_{ij}^e\right] = \int_0^{h_e} R\psi_j^e\psi_j^e\overline{dx}$$

$$Q_i^e = \sum_{j=1}^n \psi_j^e(x_j^e)Q_i^e$$

Over the domain $\Omega^e = (0, h_e), h_e$ is the height of the element and $\overline{x}$ is the local coordinate.

For a quadratic element mesh, ψ_j^e is defined as the quadratic Lagrange interpolation functions given as:

$$\psi_i^e(\overline{x}) = \left(1 - \frac{\overline{x}}{h}\right)\left(1 - \frac{2\overline{x}}{h}\right)$$

Table 3: Concentration distribution of anthracene in a stirred reactor.

x(m)	0.000	0.010	0.020	0.030	0.040	0050	0.060	0.070	0.080	0.090	Experimental Result
t(days)	Concentration(mg/1)										
0	200.00	0.000	0.000	0.000	0.000	0.000	0.000		0.000	0.000	200
5	124.000	192.712	64.937	100.381	82.992	72.556	64.601	61.210	57.896	55.115	124
10	107.730	77.039	56.520	87.206	72.102	63.037	56.993	53.178	50.297	47.883	107.73
15	94.980	67.918	49.743	76.893	63.570	55.574	50.247	46.885	44.344	42.216	94.98
20	75.000	53.630	39.276	60.714	50.194	43.855	39.678	37.022	35.016	33.336	75.00
25	50.950	36.426	26.677	41.246	34.102	29.811	26.953	25.151	23.788	22.646	50.95
30	37.530	26.840	19.655	30.383	25.120	21.960	19.854	18.527	17.521	16.681	37.53
35	28.940	20.707	15.154	23.430	19.370	16.936	15.310	14.286	13.511	12.863	28.94
40	17.510	12.525	9.174	14.180	11.718	10.245	9.264	8.644	8.174	7.789	17.51
45	11.690	8.357	6.126	9.468	7.822	6.839	6.185	5.771	5.457	5.196	11.67
55	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
60	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0

$$\psi_2^e(\overline{x}) = 4 - \frac{\overline{x}}{h}\left(1 - \frac{\overline{x}}{h}\right)$$

$$\psi_3^e(\overline{x}) = \frac{\overline{x}}{h}\left(1 - \frac{2\overline{x}}{h}\right)$$

The coefficients of K_{ij}^e and M_{ij}^e were evaluated using MathCad software and for one element, the following matrices in the form shown below were generated.

$$\left[K_{ij}^e\right] = \begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix}$$

$$\left[M_{ij}^e\right] = \begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix}$$

$$\left[K_{ij}^e\right] = \begin{bmatrix} \frac{V}{2} - \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} & -\frac{2V}{3} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & \frac{V}{6} - \frac{D}{3h_e} - \frac{\lambda h_e}{30} \\ \frac{2V}{2} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{16D}{3h_e} - \frac{8\lambda h_e}{15} & -\frac{2V}{3} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} \\ \frac{V}{6} - \frac{D}{3h_e} - \frac{\lambda h_e}{30} & \frac{2V}{2} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & \frac{V}{2} - \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} \end{bmatrix}$$

$$\left[M_{ij}^e\right] = \begin{bmatrix} \frac{2Rh_e}{15} & \frac{Rh_e}{15} & \frac{-Rh_e}{30} \\ \frac{Rh_e}{15} & \frac{8Rh_e}{15} & \frac{Rh_e}{15} \\ \frac{-Rh_e}{30} & \frac{Rh_e}{15} & \frac{2Rh_e}{15} \end{bmatrix}$$

The Assemblage of two-element mesh was given as:

$$[K] = \begin{bmatrix} \frac{V}{2} - \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} & -\frac{2V}{3} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & \frac{V}{6} - \frac{D}{3h_e} - \frac{\lambda h_e}{30} & 0 & 0 \\ \frac{2V}{2} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{16D}{3h_e} - \frac{8\lambda h_e}{15} & -\frac{2V}{3} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & 0 & 0 \\ \frac{\lambda h_e}{30} - \frac{D}{3h_e} - \frac{V}{6} & \frac{2V}{3} - \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{14D}{3h_e} - \frac{4\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} & \frac{V}{6} - \frac{D}{3h_e} - \frac{\lambda h_e}{30} \\ 0 & 0 & \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & -\frac{16D}{3h_e} - \frac{8\lambda h_e}{15} & \frac{8D}{3h_e} - \frac{2V}{3} - \frac{\lambda h_e}{15} \\ 0 & 0 & \frac{\lambda h_e}{30} - \frac{D}{3h_e} - \frac{V}{6} & \frac{2V}{3} + \frac{8D}{3h_e} - \frac{\lambda h_e}{15} & \frac{V}{2} - \frac{7D}{3h_e} - \frac{2\lambda h_e}{15} \end{bmatrix}$$

$$\left[M_{ij}^e\right] = \begin{bmatrix} \frac{2Rh_e}{15} & \frac{Rh_e}{15} & \frac{-Rh_e}{30} & 0 & 0 \\ \frac{Rh_e}{15} & \frac{8Rh_e}{15} & \frac{Rh_e}{15} & 0 & 0 \\ \frac{-Rh_e}{30} & \frac{Rh_e}{15} & \frac{4Rh_e}{15} & \frac{Rh_e}{15} & \frac{-Rh_e}{30} \\ 0 & 0 & \frac{Rh_e}{15} & \frac{8Rh_e}{15} & \frac{Rh_e}{15} \\ 0 & 0 & \frac{-Rh_e}{30} & \frac{Rh_e}{15} & \frac{2Rh_e}{15} \end{bmatrix}$$

For the final solution of the developed model, the time approximated solution was given as:

$$[M]C_s = [M] - \Delta t_{s+1}[K]C_{s+1} + \Delta t_{s+1}Q_{s+1} \qquad (10)$$

2.2.2. Simulation using MathCad

The simulation technique used to generate the concentration distribution of the test contaminant PAHs (naphthalene, anthracene and pyrene) in soils was the MathCad software. The assumption of linear sorption equilibra as an experimental condition forms the basis of an initial reduction of the set of PDEs to a set of ODEs using the Finite Element Method. A mathematical algorithm was developed to solve these equations and incorporated into MathCad software. The estimated values of the transport parameters necessary for the solution of the governing non-steady state model equation for the biodegradation process in the stirred reactor was adapted from the result Owabor et al [27] and they are given in Table 1.

3. Results and Discussion

The FEM was applied to the non steady state model defined by equation (1) to simulate the biodegradation of naphthalene, anthracene and pyrene in a stirred reactor over a contact period of 60 days and at a depth ranging from 0-9 cm. The model took into account the effect of mass transfer on bioavailability and degradation by incorporating the transport parameters (diffusion coefficients and pore-water velocities) of the contaminant solutes in reducing the dimensionality of the equation. The results as shown in Tables 2, 3 and 4 indicate that the degree of degradation of the solutes differed significantly. This variation is strongly related to the

Table 4: Concentration distribution of pyrene in a stirred reactor.

x(m)	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.070	0.080	0.090	Experimental Result
t(days)	Concentration(mg/1)										
0	200.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	200
5	95.060	79.387	62.318	47.567	40.111	35.705	32.650	30.551	29.089	27.881	95.06
10	91.210	76.156	59.789	45.274	38.489	34.260	31.328	29.314	27.911	26.752	91.21
15	48.210	40.247	31.603	24.120	20.344	18.109	16.559	15.494	14.752	14.140	48.21
20	34.190	28.549	22.408	17.107	14.427	12.842	11.743	10.988	10.426	10.028	34.19
25	24.830	20.783	16.276	12.425	10.478	9.327	8.529	7.979	7.597	7.282	24.83
30	17.660	14.753	11.577	8.833	7.450	6.633	6.066	5.676	5.404	5.179	17.66
35	8.610	7.185	5.643	4.307	3.634	3.233	2.958	2.767	2.635	2.525	8.61
40	4.590	3.828	3.011	2.295	1.905	1.723	1.576	1..475	1.404	1.347	4.59
45	0.102	0.085	0.065	0.053	0.042	0.038	0.038	0.033	0.032	0.030	0.102
50	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
55	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
60	0.000	0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.000	0.000	0

differences in the physical properties of the solutes such as molecule topology and number of rings as well as their solubility and diffusivity (Table 1) in solution.

Mineralization was found to be faster for low molecular weights PAHs with less degree of fusion. This was evident in the simulations results which followed same trend with experimental laboratory data. The trends observed for anthracene and pyrene within the same contact period were not particularly different from the behavior exhibited by naphthalene. These observations are consistent with previous literature results of Barkay et al [28], Pravecek et al [29], Rodriquez and Bishop [30], Owabor et al [22].

Result from Table 2 shows that with increasing time, the concentration of naphthalene decreases from 200mg/l at the surface to zero by the 40th day of exposure within the soil matrix. The percentage solute concentration left was 14% (35^{th}). The concentration of naphthalene decreased in the direction of flow with the least value at the subsurface distance of 9 cm. The concentrations of naphthalene at the surface and at a subsurface distance of 9cm were 4.30mg/l and 0.614 mg/l respectively.

Similarly, the concentration of anthracene decreased from 200mg/l at the onset of the experiment to zero by the 55^{th} day of exposure within the soil matrix. The percentage of solute concentration left was 44% (50^{th}). The decreasing concentration of anthracene was in the direction of flow. The residual concentrations were 6.792mg/l and 3.019mg/l respectively at the surface and subsurface distance of 9cm.

The pattern of distribution of the pyrene followed closely that observed with naphthalene and anthracene. The concentration of the solute decreased from 200mg/l at the surface to zero by the 50th day of exposure within the soil matrix. The residual concentration was 29% by the 45^{th} day.

The result for anthracene and pyrene present some degree of variation, which explains the observed selective decay of one over the other. Anthracene exhibits a lower solubility in water and hence it was not readily available for microbial uptake. The effects of these limitations are reflected in the simulated residual concentrations

4. Conclusion

The finite element method has been found to be effective in solving non-steady state model equations as it has been shown to be capable of serving as an alternative mathematical tool for predicting the extent of degradation of contaminant solutes during remedial studies involving long distances.

The role of bioavailability of the organic chemicals can certainly not be overemphasized as contributions of some functional transport properties such as dispersion coefficient and retardation factor can be seen to be interfering with degradation.

The residual concentrations confirmed that naphthalene was more selectively mineralized in the stirred reactor and that the microbial utilization of pyrene and anthracene for metabolic activities were greatly limited by their resistance to mass transfer due to their low aqueous solubility.

References

1. Oleszezuk, P., and Baran, S. Degradation of Individual Polycyclic Aromatic Hydrocarbons (PAHs) in Soil Polluted with Aircraft Fuel. *Polish Journal of Environmental Studies*, Vol. 12, No. 4, 2003, pp. 431-437.
2. Townsend, G.T., Prince, R.C. and Suflita, J.M. Anaerobic biodegradation of alicyclic constituents of gasoline and natural gas condensate by bacteria from an anoxic acquifer. *FEMS Microbiology Ecology*, Vol.49, Issue 1, 2004, pp. 129-135.
3. Onwurah, I.N.E., Ogugua, V.N., Onyike, N.B., Ochonogor, A.E. and Otitoju, O.F. Crude oil spills in the environment, effects and some innovative clean-up Biotechnology.

International Journal of Environmental Research, Vol.1, No.4, 2007, pp.307-320.

4. Nilanjana, D. and Preethy, C. Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnology Research International*, 2010, doi:10.4061/2011/941810.
5. Nwilo, P.C. and Badejo, O.T. *Soil sediment and water: Impacts of oil spills along the Nigerian coast.* The Association for Environmental Health and Sciences (AEHS), 2001.
6. Akpofure, E.A., Efere, M.L. and Ayawei, P. Integrated grass root post-impact assessment of acute damaging effects of continuous oil spills in the Niger Delta January 1998-January 2000, in: *Oil spillage in Nigerias Niger Delta*, Urhobo Historical Society, 2007.
7. Kinigoma, B.S. Effects of drilling fluid additives on the Niger Delta environment: A case study of the Soku oil fields. *J. Appl. Sci. Environ.*, 5, 2001, pp 57-61.
8. Sahle-Demessie, E. and Richardson, T. Cleaning up pesticide contaminated soils: comparing effectiveness of supercritical fluid extraction with solvent extraction and low temperature thermal desorption. *Environmental Technology*, Vol.21, Issue 4, 2000, pp.447-456.
9. Medina-Bellver, J.I., Marin, P., Delgado, A., Rodriquez-Sanchez, A., Reyes, E., Ramos, J.L. and Marques, S. Evidence for in situ crudeoil biodegradation after the prestige oil spill. *Environment Microbiology*, Vol.7, No.6, 2005, pp. 773-779.
10. Johnsen, A.R., Wick, L.Y., and Harms, H. Principles of Microbial Degradation in Soil. *Environmental Pollution*, Vol.133, 2005, pp 71-84.
11. Atlas, R. and Bragg, J. Bioremediation of marine oil spills: when and when not – the Exxon Valdez experience. *Microbial Biotechnology*, Vol.2, No.2, 2009, pp 213-221.
12. Nikolopoulou, M. and Kalogerakis, N. Biostimulation strategies for fresh and chronically polluted marine environment with petroleum hydrocarbons. *Journal of Chemical Technology and Biotechnology*, Vol.84, No.6, 2009, pp 802-807.
13. Tabak, H.H. and Govind, R. Bioavailability and biodegradation kinetics protocol for organic pollutant compounds to achieve environmentally acceptable endpoints during bioremediation in: bioremediation of surface and subsurface contamination. *Annals of the New York Academy of Sciences*, 829, 1997, pp 36-61.
14. Knightes, C.D. *Mechanisms governing sole-substrate and multisubstrate biodegradation kinetics of polycyclic aromatic hydrocarbons.* PhD Dissertation, Princeton University, Princeton, NJ. 2000.
15. Lobo-Ferreira, J.P., Leitoa, T., Quigley, S.P., and Theves, T. On Flow and Transport of Miscible Tracers in the Vadose Zone. *Acta Carsologica*, 29 (1), 2000, pp127-139.
16. Pang, L., Goltz, M., and Close, M. Application of the Method of Temporal Moments to Interpret Solute Transport with Sorption and Degradation. *Journal of Contaminant Hydrology*, Vol. 60, 2003, pp.123-134.
17. Mirbagheri, S.A. Modelling Contaminant Transport in Soil Column and Groundwater Pollution Control. *International Journal of Environmental Science and Technology*, Vol. 1, No. 2, 2004, pp.141-150.
18. Kim,S.B. Equilibrium Approaches to organic Contaminant Transport Modelling in a Multi-phase Groundwater System. *Environmental Technology*, Vol.25, 2004, pp 873-880.
19. Kurniawan, B, and Jinno, K. Numerical Transport Model of Chlorinated Compounds in Saturated Porous Media. *Memoris of the Faculty of Engineering, Kyushu University*, Vol. 66, No. 2, 2006, pp 83-97.
20. Najafi, S.H. and Hajinezhad, H. Solving One-dimensional Advection-Disperson with Reaction Using Some Finite-Difference Methods. *Applied mathematical Sciences*, Vol. 2, No. 53, 2008, pp.2611-2618.
21. Owabor, C.N., Agarry, S.E and Azeez, T.O . Development of a transport model for the microbial degradation of polycyclic aromatic hydrocarbons in a saturated porous medium. *Journal of the Nigerian Association of Mathematical Physics.* Vol.16, 2009, pp. 317-324.
22. Owabor, C.N., Ogbeide, S.E. and Susu, A.A. Degradation of polycyclic aromatic hydrocarbons: Model simulation for bioavailability and biodegradation. *Canadian Journal of Chemical Engineering*, Vol. 88, Issue 2, 2010a, pp. 268-276.
23. Owabor, C.N. and Ayodele, B.V. Predicting the Biodegradation of Polycyclic Aromatic Hydrocarbons (PAHs) in Continuous Stirred Tank Reactor by Artificial Neural Network. *Journal of the Nigerian Association of Mathematical Physics*, Vol.19, 2011, pp395-398.
24. Owabor, C.N., Ayodele, B.V. and Eze, J.O. Biodegradation of naphthalene, anthracene and pyrene on contaminated aqueous-soil matrix using continuously stirred bioreactor. *Journal of Engineering for Development*, Vol. 7, 2007, pp. 118-129.
25. Owabor, C.N. and Ekwonu, C.M. Use of finite element method as a simulation technique for bioremediation of naphthalene, anthracene and pyrene contaminated soil in a fixed bed reactor. *International Journal of Physical Sciences*, Vol. 4 (5), 2009, pp. 321-326.
26. Reardon, K.F., Mosteller, D.C., Rogers, J.B., DuTeau, N.M. and Kim, K. Biodegradation kinetics of aromatic hydrocarbon mixtures by pure and mixed bacterial cultures. *Environmental Health Perspectives*, 110, 2002, pp.1005-1011.
27. Owabor, C.N., Ogbeide, S.E. and Susu, A.A. Estimation of transport and degradation parameters for naphthalene and anthracene: Influence of mass transfer on kinetics. *Environ Monit Assess.* 169, 2010b, pp.607-617.
28. Barkay, T., Navon-Venezia, S., Ron, E.Z. and Rosenberg, E. Enhancement of solubilizatio n and biodegradation of polyaromatic hydrocarbons by bioemusifier Alasan. *Appl. Environ. Microbiol.* Vol.65, No.6, 1999, pp. 2697-2702.
29. Pravecek, T.L., Christman, R.F. and Pfaender, F.K. Impact of imposed anaerobic conditions and microbial activity on aqueous-phase solubility of polycyclic aromatic hydrocarbons from soil. *Enviromental Toxicology and Chemistry*, Vol.24, Issue 2, 2005, pp. 286-293
30. Rodriquez, S. and Bishop, P.L. Enhancing the biodegradation of polycyclic aromatic hydrocarbons: Effects of nonionic surfactant addition on biofilm function and structure. *Journal of Environmental Engineering*, Vol.134, Issue 7, 2008, pp. 505-512.