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Diffusivity and Kinetics Model for Biodegradation of PAHs in a Saturated Porous Matrix

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Abstract
The commercial implementation of biodegradation of polycyclic aromatic hydrocarbons (PAHs) as a bioremediation technique against physical process was due to lack of its effective and efficient diffusivity model with reaction parameters in a saturated porous matrix. The development and simulation of diffusivity model which involve reaction kinetics was aimed to provide quantitative insight on biodegradation of PAHs. The developed model obtained from the principle of conservation of matter, concepts of Fick's law of diffusion, Malthus equation and Monod kinetics expression under isothermal condition was simulated with experimental data. The result showed that *Corynebacterium sp* and *Pseudomonas putida* were effective and PAHs exhibits pseudo first order reaction. Though, the effective diffusivity of PAHs decreases as degradation of PAHs proceeds with increased microbial mass concentration at increased penetration depth. The developed diffusivity model has been shown to be effective and not only providing quantitative insight into biodegradation of the PAHs but serves as an alternative option in the selection of microbes capable of facilitating the restoration of PAHs contaminated sites.

Keywords: kinetics, conservation laws, microbial degradation, effective diffusivity

INTRODUCTION

The human survival and quality of life have led to enormous anthropogenic activities on the environment (soil and groundwater) due to the proliferation of contaminants through industrial chemical effluent, emissions from combustion processes, spillage of petroleum products and agrochemical discharged to the environment (Mihoko et al, 2003; Kanaly & Harayama, 2000). These environmental concerns become a menace to posterity if left unchecked. The industrial effluent discharged into the environment increased the level of contaminants in soil, sediments and aquatic systems causing environmental degradation and health problems through diffusion (Azeez et al, 2012). The extent of contamination depends on the nature of the contaminant and hydrogeology of the area.

Polycyclic aromatic hydrocarbons (PAHs) are among the most concerned organic contaminants which persistent and toxic in the environment (Azeez et al, 2012; Azeez, 2012). The sources of PAHs include emissions from combustion processes, spillage of petroleum products, vehicle emissions, industrial processes, refuse and open burning, and forest-fire ((Mihoko et al, 2003; Kanaly & Harayama, 2000; Azeez et al, 2012; Azeez, 2012; Kumar et al, 2006; Hsiao-Hsuan et al, 2001). Anthracene and pyrene are examples of PAHs that harmful at high concentration in the contaminated sediments, surface soils and waste slurries due to its hydrophobic nature (Corgie et al, 2004; Masih & Taneja , 2006; Li et al, 2008). PAHs have been recently included in the Substances of Very High Concern list (SVHC) by the European Chemicals Agency (ECHA) due to persistent, bioaccumulative and toxic nature on discharged to environment (Iglesias-Groth et al, 2010; Mrozik et al, 2003; Shor et al, 2004). However, there is a need for the provision and protection of the environment, soil and groundwater from the adverse effects of PAHs (Masih & Taneja , 2006; Samanta et al, 2002). This is one of the reasons for remediation of PAHs in the environments. Clean-up techniques involving physical and chemical intervention are quite widespread which include disposal in a landfill, incineration of the wastes and direct injection of chemical oxidants into contaminated soil, sediment and groundwater, thereby altering nature of environments (Cameotra, & Makkar, 2010; Jacques

et al, 2005). More so, clean-up technique for PAH contaminated environments involve expensive chemical and physical treatments and due to excavation of these methods, they increase potential transfer of contaminants to atmosphere. Thus, among the clean-up techniques, biodegradation has been a promising monitored natural attenuation for depletion of PAHs in the environment but has not been commercially viable due to inability to have quantitative insight on the effects of mass transfer and reaction parameters of degradation of PAHs and heterogeneous nature of most contaminated matrices (Azeez, 2012; Masih & Taneja, 2006; Samanta et al, 2002). Therefore, biodegradation as a biological treatment for the degradation of contaminants will be a better alternative to conventional methods of remediation of the contaminants due to its eco-friendly and effective techniques for PAHs contaminated environment, if the diffusivity model with reaction control of the PAHs is established (Masih & Taneja, 2006; Azeez, 2011; Robles-González et al, 2008). Biodegradation of PAHs depends on the inherent biodegradability, accessibility to degrading microorganisms and optimization of biological activity (Azeez et al, 2012; Yousefi et al, 2009).

Many researchers have work on the biodegradation of PAHs were strictly on the experimental which involve the use of specific microorganisms, specific reducing culture, metabolic path ways, bioavailability and disappearance, growth of the microbes under aerated and unaerated conditions, pH variation, and kinetics of biodegradation (Masih & Taneja, 2006; . Shor et al, 2004;Oleszczuk & Baran, 2003; Pignatello & Li, 2006). Research has not shown the effect of diffusivity of PAHs as penetration depth increases during biodegradation in a saturated porous matrix.
Therefore, objective of this research work was to obtain quantitative insight on diffusion behaviour during biodegradation reaction with effect of kinetics reaction order and rate constant of PAHs using anthracene and pyrene as contaminant solutes in a saturated porous matrix with activity of *Corynebacterium sp* and *Pseudomonas putida*. Moreover, microbe's fitness in restore and degradation of a contaminated environment with anthracene and pyrene as by-products from the oil and gas industry was examined.

THEORETICAL FRAMEWORK

This research paper focuses on the development of suitable model for predicting effective diffusivity during biodegradation PAHs as contaminants in soil sediment as a saturated porous matrix with effect of kinetics based on the following theoretical concepts:

i. The transport of PAHs in soil sediment is governed by Fick's law of diffusion under isothermal condition.
ii. Biochemical reaction influenced the flux of the solute PAHs.
iii. The diffusive and convective transfer of the PAHs is in the direction of flow.
iv. The flow is unidirectional with constant porosity in heterogeneous nature of the soil sediment.
v. Effective diffusivity coefficient is a function of mass concentration of the PAHs, microbial cells, kinetics, reaction rate, order of the reaction, distance or depth of soil sample zone and time of biodegradation.
vi. Biodegradation of PAHs based on the growth of the microbes using Malthus correlation of first order reaction rate, size and shape of a contaminated area.
vii. The sorption rate of the PAHs in the soil assumed to be insignificant.
viii. Anthracene represents three benzene rings and pyrene represents four benzene rings.

MATERIALS AND METHOD

Biodegradation of PAHs

0.15 g of each PAH was dissolved in 10% dichloromethane solution and make up to 2 liters of water. The applied PAH concentration was 75 mg/l of water. The solvent was volatized from PAH solution under fume-hood. 250 ml of each of the PAH solution measured into 500 ml cotton-plugged Erlenmeyer flasks wrapped with aluminium foil to prevent contamination and light effect. 5 ml of inoculums was transferred from each agar plate of *Corynebacterium sp* and *Pseudomonas putida* into PAH contaminated water in each 500 ml cotton-plugged Erlenmeyer flasks wrapped with aluminium foil and incubated at 28^0C on a rotary incubator shaker at 150 revolutions per minute for 96 h except only when a flask was withdrawn for the aliquots to be taken for analysis. Non-inoculated sample was considered as the control of the experiment.

Biodegradation Analysis

10 ml of aliquots were taken from each experiment set up at every 12 hours for the analysis of microbial mass concentration of *Corynebacterium sp* and *Pseudomonas putida* respectively, and utilized PAH concentration. The biomass concentration was determined using the procedure described by Azeez et al (2012). The supernatant was centrifuged, decanted and microbial cells that settled down at the bottom of the centrifuge tube were scooped and dried in an oven at a temperature of 60^0C for 8 hours to a constant weight and recorded. The weight obtained was taken as the dry weight of *Corynebacterium sp* and *Pseudomonas putida* in the sample analyzed. UV visible spectrophotometer was used to measure absorbance of the anthracene and pyrene in aliquot (Azeez et al, 2012; Azeez, 2012). The absorbance of the anthracene and pyrene was recorded at a wavelength of 267 nm and 286 nm in the UV region

after isolation of the microbes by centrifuge 10 ml aliquots of rotating at 10,000 revolutions per minute for 20 minutes and allowed to settle for 30minutes to get a clear supernatant. 5 ml of the clear supernatant was extracted with 5ml of hexane for 10 minutes in a separating funnel. The top solution in a separating funnel at the end of the extraction was a solution of the PAH in hexane and poured into the corvettes of the spectrophotometer and absorbance readings at wavelengths of 267 nm for anthracene and 286 nm for pyrene was recorded respectively. The procedure was repeated in twelve hourly intervals immediately after inoculation with *Corynebacteria sp and Pseudomonas putida* for 96 hours of incubation and the kinetics parameters were determined from the data obtained.

Preparation of the Standard Plot

Solutions of anthracene in the hexane were prepared to give a concentration of 0.3mg/ml. The absorbance of the solutions was read at the appropriate wavelengths 267nm and 286nm for the anthracene and pyrene solution respectively. Calculated quantities of the solution of anthracene and pyrene were taken and calculated quantities of hexane were added to give lower concentration of the anthracene and pyrene in hexane 0.27, 0.24, 0.21, 0.18mg/ml etc. The models of the standard plots obtained for the anthracene and pyrene concentration from absorbance to mg/L was used as given by Azeez et al (2012) and Azeez (2012).

Development of Diffusivity Model during Biodegradation of PAHs

The elementary reaction that governed the biodegradation of contaminants or substrates in a medium is given as:

$$C \xrightarrow{X} X + P$$

Where, C is the concentration of the contaminants (PAH), X is the microbial mass concentration and P is the product formation.

The rate of consumption of PAHs by microbial mass is governed by Malthus correlation as given by equation (1):

$$\frac{\partial X}{\partial t} = \mu X \qquad (1)$$

Where, t is the degradation of PAH or production of microbial enmasse and μ is the specific growth rate. Integration of equation (1) at the boundary conditions: $X = X_0$ at $t = 0$ and $X = X$ at $t = t$ gives:

$$\frac{Ln\left(X/X_0\right)}{t} = \mu \qquad (2)$$

But Monod's model expressed the growth rate of the microbial cells as a function of concentration of the substrate (PAHs) (Azeez, 2011) and it is given as:

$$\mu = \frac{\mu_m C}{k_s + C} \qquad (3)$$

Where, μ_m is the maximum specific growth rate and $k_s$is the Monod's kinetics coefficient. Linearization of equation (3) gives:

$$\frac{1}{\mu} = \frac{k_s}{\mu_m}\frac{1}{C} + \frac{1}{\mu_m} \qquad (4)$$

The combination of equations (2) and (4) yields:

$$\frac{t}{Ln\left(X/X_0\right)} = \frac{k_s}{\mu_m}\frac{1}{C} + \frac{1}{\mu_m} \qquad (5)$$

Equation (5) is a biodegradation kinetics linear model in which $\frac{k_s}{\mu_m}$ is the gradient of the plot of $t/lnX\ against\ 1/C$ and $\frac{1}{\mu_m}$ is an intercept of the plot. The reaction rate of PAHs for the nth order reaction under isothermal condition is given by Owabor et al (2010) as equation (6):

$$-\frac{\partial C}{\partial t} = k_n C^n \qquad (6)$$

Where, n is the order of reaction of PAH. The negative sign indicates disappearance of PAH. Integration of equation (6) within the boundary limit of $C = C_0$ at $t = 0$ and $C = C$at $t = t$:

$$-\int_{C_0}^{C}\frac{\partial C}{C^n} = k_n\int_0^t \partial t$$

$$\frac{C^{-(n-1)} - C_0^{-(n-1)}}{n-1} = k_n t$$

$$C^{-(n-1)} - C_0^{-(n-1)} = (n-1)k_n t \qquad (7)$$

Natural logarithm of both sides of equation (7) gives:

$$lnC = lnC_0 + \frac{1}{(1-n)}ln(n-1)k_n + \frac{1}{(1-n)}lnt$$

$$lnC = \emptyset + \propto lnt \qquad (8)$$

Equation (8) is a linear equation with the gradient $\propto$ and intercept $\emptyset$

$$where \quad \emptyset = lnC_0 + \frac{1}{(1-n)}ln(n-1)\mathrm{k_n} \text{ and } \propto = \frac{1}{(1-n)}$$

The mass transfer rate of PAH in the subsurface soil from the bulk liquid to the active region of the microbial mass in the soil sediment governed by Fick's model (Tosun, 2002).

$$J_{C,z} = -D\frac{\partial C}{\partial z} \qquad (9)$$

$J_{C,z}$ is the rate of mass transfer of PAH over a distance Z, *D* is the diffusivity of the PAHs in the subsurface soil and $\frac{\partial C}{\partial z}$ is the concentration gradient of PAHs.

The mass flow rate of PAHs at steady state was taken within the active of the microbial mass where biodegradation occurred in an idealized geometric

shape of a contaminated sample zone was considered as shown in the Figure 1.

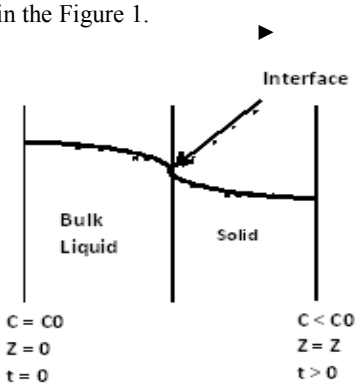

Figure 1: Idealized sample geometry

Rate of mass transfer of PAHs + *Rate of mass transfer of PAHs at a distance of PAHs over the distance at the surface z* + *Rate of production* = 0 (10)
$Z+\Delta Z$
ΔZ *by mass transfer*

$J_{c,z} - J_{c,z+\Delta z} - R\Delta Z = 0$

Since $-R = -\frac{\partial C}{\partial t} = k_n C^n$

$$\frac{dJ_c}{dZ} = k_n C^n \quad (11)$$

Integrate equation (11) within the boundary limit

Inlet: $C = C_0, J = 0$ at $Z = 0$ and

Outlet: $C < C, J = J_c$ at $Z = Z$.

$$J_{c,z} = k_n C^n Z \quad (12)$$

Since mass flow rate of PAHs depends on the concentration of PAHs, the combination of equation (9) and (12) yields:

$$\frac{dC}{dz} = -\frac{k_n}{D} C^n Z \quad (13)$$

Set equation (13) to unsteady state condition. i.e. multiply both sides by $\frac{dZ}{dt}$ gives:

$$-\frac{dC}{dt} = \frac{k_n}{D} C^n Z \frac{dZ}{dt} \quad (14)$$

The production rate of microbial mass is a function of rate of consumption of PAHs (Owabor et al, 2012; Levenspiel, 2002).

$$\frac{dX}{dt} = -Y_{x/s} \frac{dC}{dt} \quad (15)$$

Integration of equation (15) with the boundary conditions

Inlet: $C = C_0, X = X_0$ at $t = 0$ and

Outlet: $C = C, X = X$ at $t > 0$.

$$X - X_0 = Y_{x/s}(C_0 - C) \quad (16)$$

Substitution of equations (15) into equation (16) yields:

$$\frac{1}{Y_{x/s}} \frac{dX}{dt} = \frac{k_n}{D} C^n Z \frac{dZ}{dt} \quad (17)$$

Substitution of equations (1) and (3) into equation (17) gives:

$$ZdZ = \frac{2\mu_m CX}{Y_{x/s} k_n C^n (k_s + C)} dt \quad (18)$$

Integrate equation (18) with the boundary conditions

Inlet: $Z = 0$ at $t = 0$ and

Outlet: $Z = Z$ at $t > t$

Therefore,

$$Z^2 = \frac{2D\mu_m XtC^{-(n-1)}}{Y_{x/s} k_n (k_s + C)} \quad (19)$$

$$Z^2 k_s + Z^2 C = \frac{2D\mu_m}{Y_{x/s} k_n} XtC^{-(n-1)} \quad (20)$$

Natural logarithm of both sides of equation (20) gives:

$$Ln(Z^2 k_s) + Ln(Z^2 C) = Ln\left(\frac{2D\mu_m}{Y_{x/s} k_n} Xt\right) - (n-1)LnC$$

$$4LnZ = Ln\left(\frac{2D\mu_m}{Y_{x/s} k_n} Xt\right) - Lnk_s - LnC - (n-1)LnC$$

$$LnZ^4 = Ln\left\{\left(\frac{2D\mu_m}{Y_{x/s} k_n k_s}\right)\left(\frac{X}{C^n}\right)t\right\} \quad (21)$$

Removal of natural logarithms from both sides yield:

$$Z = \left(\frac{2D\mu_m X}{Y_{x/s} k_n k_s C^n}\right)^{1/4} t^{1/4} \quad (22)$$

$$Z = \beta t^{1/4} \quad (23)$$

Where,

$$\beta = \left(\frac{2D\mu_m X}{Y_{x/s} k_n k_s C^n}\right)^{1/4} \quad (24)$$

$$D = \frac{\beta^4 Y_{x/s} k_n k_s C^n}{2\mu_m X} \quad (25)$$

Where D is effective diffusivity (cm^2/hr) and β is predictive transport parameter.

Equation (25) is an effective diffusivity model of the PAHs as contaminants in the microcosm's environment. The biomass concentration serves as a depleting agent and PAHs concentration as a driving force over distance ΔZ with the effect of order of the degradation reaction and time dependent. The gradient value of β predicts effective diffusivity of the PAHs within the contaminated porous matrix contains degradable microbes for small increment of time.

The standard model for anthracene concentration from absorbance as reported by Azeez et al (2012) was used and it is given as equation (26):

$$C = 63.96C_{abs} - 2.929 \quad (26)$$

The standard model for pyrene concentration from absorbance as reported by Azeez (2012) was used and it is given as equation (27):

$$C = 66.91C_{abs} - 0.301 \quad (27)$$

RESULTS AND DISCUSSION

The simulation results presented in this paper clearly demonstrates the efficacy of using a theoretical model described and predicted effective diffusivity during the biodegradation of anthracene and pyrene as homologous substrates in a microcosm. The biodegradation kinetics parameters were determined from the results of the batch experiments on substrate limiting microbial degradation using Monod kinetics equation.

The magnitude of the yield $Y_{x/s}$ of *Corynebacterium sp* and *Pseudomonas putida* on anthracene and pyrene quantified to be 0.001 with slight difference in the correlation coefficient of the data as shown in Figure 1. This indicates that the yield of microbes may be the same in the degradation of the PAHs contaminated environment using *Corynebacterium sp* and *Pseudomonas putida* but slight difference in correlation coefficient which indicates degree of fitness of the data from the experiments. This could be attributed to the fitness of the microbes in the PAHs contaminated environment as presumed by (Azeez, 2012) but did not indicated that *Pseudomonas putida* utilized anthracene more than *Corynebacterium sp* and vice-versa. Though, there is no significant difference the in their correlation coefficient.

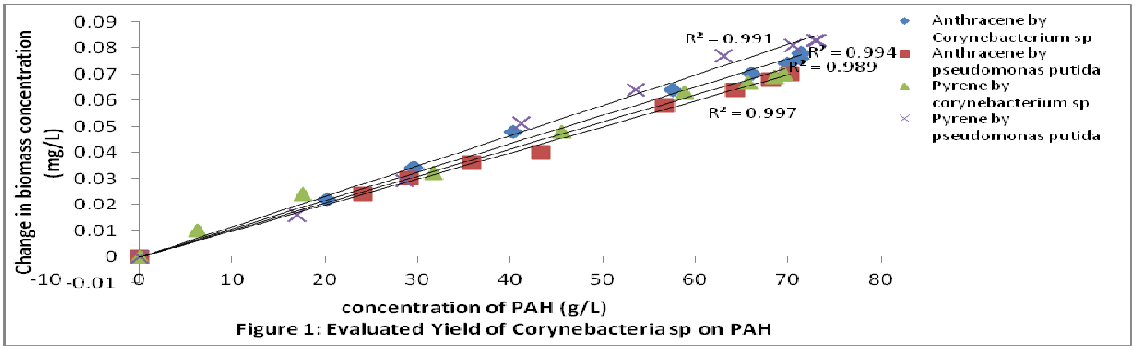

Figure 1: Evaluated Yield of Corynebacteria sp on PAH

Table 1: Biodegradation kinetics, Order of reaction and Reaction Rate of PAHs

Sample	$Y_{x/s}$	k_s (mg/L)	μ_m (hr^{-1})	n	k_n	β
Corynebacterium sp on Anthracene	0.001	4.339	0.0456	1.405	0.112	2.560
Pseudomonas putida on Anthracene	0.001	3.487	0.0343	1.444	0.090	2.489
Corynebacterium sp on Pyrene	0.001	0.080	0.0310	1.442	0.091	1.892
Pseudomonas putida on Pyrene	0.001	1.356	0.0372	1.307	0.120	1.846

The maximum specific growth rate of the microbes and Monod's kinetics coefficient of the PAHs were evaluated from Figure 2 and 3 for degradation of anthracene and pyrene respectively as presented in the Table 1. The maximum specific growth rate of *Corynebacterium sp* was higher compared with that of *Pseudomonas putida* in anthracene contaminated medium but in the case of pyrene, the maximum specific growth rate was higher when *Pseudomonas putida* was used compared with *Corynebacterium sp*.

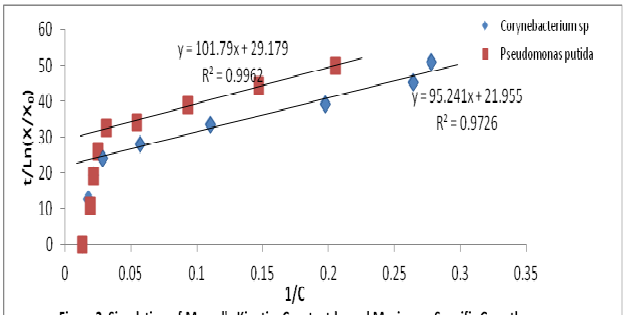

Figure 2: Simulation of Monod's Kinetics Constant ks and Maximum Specific Growth Rate for anthracene

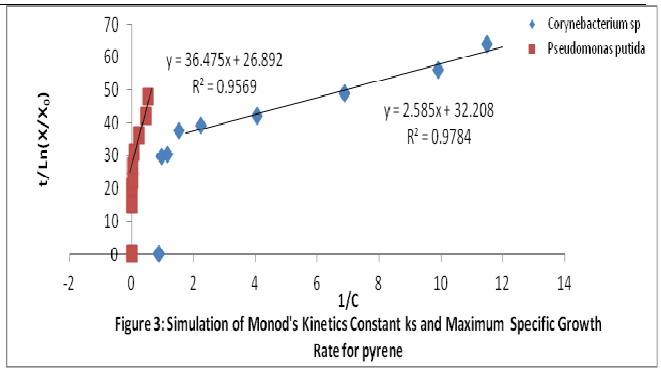

Figure 3: Simulation of Monod's Kinetics Constant ks and Maximum Specific Growth Rate for pyrene

This indicates that the rate of degradation of anthracene with three carbon atoms by *Corynebacterium sp* was higher compared with the *Pseudomonas putida* while the rate of consumption of pyrene with four carbon atoms by *Pseudomonas putida* was higher compared with the activity of *Corynebacterium sp.* This may be associated with molecular weight of the PAHs. Monod's kinetics coefficient measures metabolic activity of the microbes to utilize the contaminant solute as a source of carbon and energy. The promise nature of the

microbe strains used may be attributed to high level of metabolic activity of the microbes in the presence of the PAH. The higher the Monod's kinetics coefficient indicates lower affinity of microbes to the substrate in the contaminated medium and vice versa Azeez (2012). The lower value of Monod's kinetics coefficient of *Pseudomonas putida* on anthracene was obtained compared with when *Corynebacterium sp* was used as presented in Table 1. This indicated that *Pseudomonas putida* have higher affinity to anthracene compared with *Corynebacterium sp*. In contrast, the lower value of Monod's kinetics coefficient of *Corynebacteria sp on* pyrene was obtained compared with *Pseudomonas putida*. The affinity of the microbes may be due to order of the reaction and biodegradation of the PAHs.

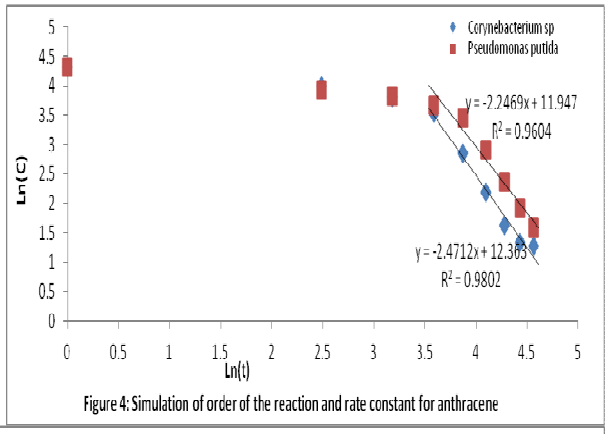

Figure 4: Simulation of order of the reaction and rate constant for anthracene

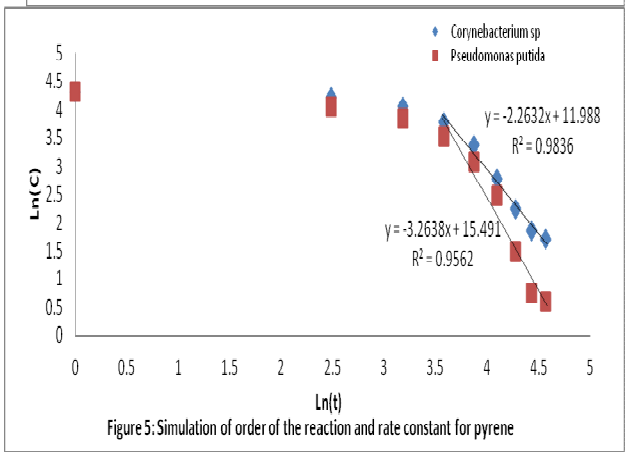

Figure 5: Simulation of order of the reaction and rate constant for pyrene

The order of the reaction and reaction rate constants for anthracene and pyrene by the activity of *Corynebacterium sp* and *Pseudomonas putida* were evaluated from Figure 4 and 5 respectively. The order of reaction of anthracene was approximately 1.405 and 1.444, and for pyrene was 1.442 and 1.307 by the activity of the *Corynebacterium sp* and *Pseudomonas putida* respectively. This indicated that the order of the degradation reaction of PAH in the saturated porous medium is pseudo-first order reaction irrespective of microorganism used, molecular weight and matrix kinetics. The higher reaction rate constant of anthracene was obtained when *Corynebacterium sp* (0.112 hr^{-1}) was used compared with *Pseudomonas putida* (0.090 hr^{-1}) and vice-versa for pyrene with a magnitude of 0.120 hr^{-1} and 0.091 hr^{-1} by the activity of the *Pseudomonas putida* and *Corynebacterium sp* respectively. The susceptible of the microbes may be attributed to molecular weight of the PAHs.

More so, *Corynebacterium sp* degraded 93.91wt% of the anthracene while *Pseudomonas putida* degraded 93.69wt% of the anthracene, and 92.6wt% of pyrene was degraded by *Corynebacterium sp* while 97.6wt% of pyrene was degraded by *Pseudomonas putida* in the contaminated saturated porous medium. The developed diffusivity model in this work was based on the estimation of predictive transport parameter from Figure 6 and 7 as presented in the Table 1 which depends on the penetration depth, reaction kinetics and time.

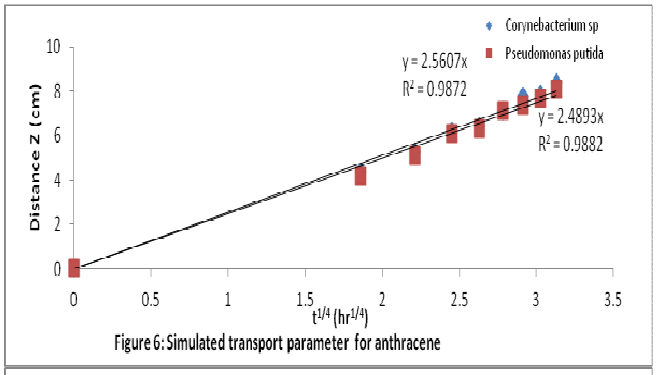

Figure 6: Simulated transport parameter for anthracene

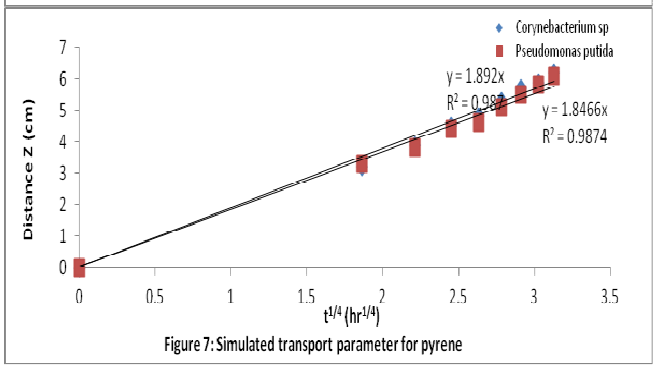

Figure 7: Simulated transport parameter for pyrene

The results shows that the biodegradation of anthracene and pyrene by the effect of *Corynebacterium sp* and *Pseudomonas putida* are to a large extent limited by the flow of these contaminants into the active site of the microbial cells since their membranes adapted to exposure of the hydrophobic solutes (anthracene and pyrene). Interestingly, the effective diffusivity of PAH estimated as presented in Tables 2-5 decreases with decreased PAH concentration at increased penetration depth into subsurface soil and increased concentration of the microbial mass. This may be attributed to the reaction rate controlling degradation

of PAHs since diffusion into pores or biologically active sites reduces contaminant concentration.

Table 2: Effective Diffusivity of Anthracene during Biodegradation by the activity of C*orynebacteria sp*.

t(hr)	Z (cm)	X(mg/l)	C(mg/l)	D (cm^2/hr)
0	0	0.014	74.99986	0.002245
12	4.4	0.036	54.82688	0.003787
24	5.3	0.048	45.42476	0.00392
36	6.2	0.062	34.61552	0.003512
48	6.4	0.078	17.47424	0.001761
60	7.1	0.084	9.03152	0.00078
72	7.8	0.088	5.066	0.000375
84	7.9	0.09	3.7868	0.000259
96	8.4	0.092	3.59492	0.000247

Table 3: Effective Diffusivity of Anthracene during Biodegradation by the activity of *Pseudomonas putida*

t(hr)	Z (cm)	X(mg/l)	C(mg/l)	D (cm2/hr)
0	0	0.012	74.99986	0.001259
12	4.2	0.036	50.92532	0.002158
24	5.1	0.042	45.87248	0.002165
36	6.1	0.048	39.22064	0.001973
48	6.3	0.052	31.73732	0.001574
60	7.1	0.07	18.30572	0.000957
72	7.4	0.076	10.75844	0.000482
84	7.7	0.08	6.79292	0.000261
96	8.1	0.082	4.87412	0.000166

Table 4: Effective diffusivity of pyrene during Biodegradation by the activity of C*orynebacterium sp*

t(hr)	Z (cm)	X(mg/l)	C(mg/l)	D (cm2/hr)
0	0	0.02	74.99951	1.46E-05
12	3.2	0.03	68.75012	1.93E-05
24	3.9	0.044	57.44233	2.19E-05
36	4.5	0.052	43.32432	1.72E-05
48	4.8	0.068	29.47395	1.29E-05
60	5.3	0.083	16.22577	6.67E-06
72	5.7	0.087	9.40095	3.18E-06
84	5.9	0.089	6.45691	1.89E-06
96	6.2	0.09	5.52017	1.53E-06

Table 5: Effective diffusivity of pyrene during biodegradation by the activity of *pseudomonas putida*

t(hr)	Z (cm)	X(mg/l)	C(mg/l)	D (cm2/hr)
0	0	0.013	74.99951	0.000128
12	3.3	0.029	58.04452	0.000205
24	3.8	0.042	46.40218	0.000221
36	4.4	0.064	33.8231	0.000223
48	4.6	0.077	21.51166	0.000149
60	5.1	0.09	11.94353	8.05E-05
72	5.5	0.094	4.51652	2.36E-05
84	5.8	0.096	2.10776	8.89E-06
96	6.1	0.096	1.84012	7.45E-06

This work was not only affirms that the biodegradation of the contaminant PAH as a function of transport parameters but rather shows that effective diffusivity decreases with decreased PAHs concentration at increased penetration depth as microbial concentration increases. Thus, Fick's first law of diffusion depicts the concentration gradient of PAHs as the only driving force and microbial mass concentration as frictional and depleting effects of the flow of PAHs.

CONCLUSIONS

Corynebacterium sp and Pseudomonas putida in a pure culture was significantly effective and suitable for the biodegradation of PAHs so as to relief humans from the danger that might be posed by PAHs especially anthracene and pyrene in a saturated porous matrix. The effective diffusivity model developed based on the concentration of the contaminant, not only serves as an alternative option in the selection of microbes capable of facilitating the restoration of PAHs contaminated sites due to decreased diffusivity which attributed to reaction kinetics and penetration depth but also demonstrated to be adequate in providing insight into an appropriate methodology of classifying microbes in order of their preference for contaminants solute.

NOMENCLATURE

X = Concentration of microbial mass (g/l)
μ = Specific growth rate of microbial mass (hr^{-1})
μ_m = Maximum specific growth rate of microbial mass (hr^{-1})
k_s= Monod kinetic Constant (mg/l)
Y= Yield coefficient of microbial mass on substrate
J = Rate of mass transfer of PAHs over a distance z per unit area (mg/cm^2hr)
D = Effective diffusivity (cm^2/hr)
C = Concentration of PAHs (mg/l) at any time t
C_0 = Concentration of PAHs (mg/l) at time t = 0
Z = Distance covered by PAHs (cm)
M = Microbial mass
P = Product of microbial degradation
k_n = Reaction rate constant for nth order of reaction (hr^{-1})
R = Rate of product formation (mg/l. hr)
β= Predictive Transport Parameter
t = Time (hr).

REFERENCES

Azeez T. O. (2011). Kinetics of microbial production of 2, 3-Butanediol fromcheese whey using klebsiella pneumonia, International Journal of Bioscience, Biochemistry and Bioinformatics, 1(3): 177-183.

Azeez T. O. (2012). Biodegradation of Pyrene Using Corynebacteria sp and Pseudomonas Putida in Contaminated Water. International Journal of Biotechnology Research. 5(1): 31-38.

Azeez T. O., Owabor C. N. and Nwacha R. (2012). Kinetics of Degradation of Anthracene by the activity of corynebacteria sp and pseudomonas putida in Contaminated Water. International Journal of Chemical Sciences and applications. 3(2): 314-322.

Cameotra S. S, and Makkar R. S (2010). Biosurfactant-Enhanced bioremediation of hydrophobic pollutants, Pure Appl. Chem., 82(1): 97–116.

Corgie S. C, Beguiristain T and Leyval C. (2004). Spatial Distribution of Bacterial Communities and Phenanthrene Degradation in the Rhizosphere of Loliumperenne L. Appl. Environ. Microbiol., 70(6): 3552-3557.

Hsiao-Hsuan H, Lee W, Pering-JY, T. and Chang-Ban C. (2001). A Comparison of the Emission of Polycyclic Aromatic Hydrocarbons. Environ. Health Perspective, 109(12): 1285

Iglesias-Groth S, Manchado A, Rebolo R,.I, Gonzalez-Hernandez R.I, D, Garcia-Hernandez D. A, and Lambert D. L. (2010). A search for interstellar anthracene toward the Perseus anomalous microwave emission region. Monthly Notices of the Royal Astronomical Society. 407(4): 2157-2165.

Jacques R. J. S, Santos E. C, Bento F. M, Peralba M. C. R, Selbach P. A, Sá E. L. S and Camargo F. A. O. (2005). Anthracene biodegradation by pseudomonas sp. isolated from a petrochemical sludge land farming site. International biodeterioration and biodegradation, 56(3): 143-150.

Kanaly R. A, and Harayama S. (2000). Minireview on Biodegradation of HMW PAHS by bacteria,"Journal of Bacteriology, 182(8): 2059-2067.

Kumar G, Singla R, and Kumar R. (2006). Plasmid Associated Anthracene Degradation by Pseudomonas sp. Isolated from Filling Station Site, Nature and Science, 8(4): 89-94.

Levenspiel O. I. (2002). Chemical Reaction Engneering. 3rd ed, New York: John Wiley and Sons Inc., pp.13- 641.

Li X. J, Li P. J, Lin X, Zhang C. G, Li Q, Gong Z. O. (2008). Biodegradation of aged polycyclic aromatic hydrocarbons (PAHs) by microbial consortia in soil and slurry phases. J. Hazard. Mater., 150: 21–26.

Masih A and Taneja A. (2006). Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. Chemosphere, 65: 449–456.

Mihoko Y, Takada H, Toyoda K, Toshida A, Akira S, Hideak N, Wada M, Masahiko N, Ken. O and Ohwada K. (2003). PAHs. Marine Pollution Bulletin, 47:105-113.

Mrozik A, Piotrowska-Seget Z, and Labuzek S. (2003). Review: Bacterial Degradation of Polycyclic aromatic Hydrocarbons. Polish Journal of Environmental Studies, 12(1): 15-25.

Oleszczuk P and Baran S. (2003). Degradation of Individual Polycyclic Aromatic hydrocarbons (PAHs) in Soil Polluted with aircraft fuel. Polish J. Environ. Studies, 12: 431-437.

Owabor C. N, Agarry S. E and Azeez T. O. (2010). 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. 16: 317-324.

Pignatello J. J, and Li F. J. (2006). Bioavailability of pahs to native soil bacteria promoted by nutrient addition american geophysical union, Fall meeting, H331-05.

Robles-González I. V, Fava F and Poggi-Varaldo H. M. (2008). A review on slurry bioreactors for bioremediation of soils and sediments. Microbial Cell Factories, 7(5): 1-16.

Samanta S. K, Singh O. V, Jain P. K. (2002). Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. Trends Biotechnol. 20: 243–248.

Shor L. M, D. Kosson S, Rockne K. J, Young L. Y and Taghon G. L. (2004). Combined Effects of Contaminant Desorption and Toxicity on Risk from PAH Contaminated Sediments. Risk Analysis, 24: 1109-1119.

Tosun I. (2002). Modelling in Transport Phenomena: A Conceptual Approach". Elsevier, Amsterdam, Netherlands, 1st edition, pp. 21, ISBN: 0-444-51052-4.

Yousefi K. A, Khodadadi A, Ganjidoust H, Badkoubi I, and Amoozegar M. A. (2009). Isolation and characterization of a novel native Bacillus strain capable of degrading diesel fuel. Int. J. Environ. Sci. Tech., 6(3): 435-442.