Modeling and Numerical Solution
of the Fate of Multi-component Substrate in Porous Media

Olanipekun, Ogirima Olawole; Atoke, Olaide Ogunbayo; Bello, Rahmon Adisa*+
Department of Chemical & Petroleum Engineering, University of Lagos, NIGERIA

ABSTRACT: *A mathematical model was proposed to appropriately describe the fate of multicomponent substrates in porous media, especially soil. The model utilized appropriate biodegradation kinetic expressions that better describe the consumption or degradation rate of the substrate. The Equation, with the second and third type boundary conditions in non-dimensionalized form, was solved using the Finite Volume method and simulated in the Matlab environment. An experiment, using a 5 cm (inside diameter) x 60 cm (height) glass column packed with severally autoclaved soil spiked with 2 % substrate (a mixture of hexadecane, heneicosane, 1-methylnaphthalene, 2- methylnaphthalene, and 1, 3-dimethylnapthalene) and a consortium of organisms (Providential rettgeri, Streptococcus salivarius, Trichoderma harzianum, Aspergillus flavipes, and Candida famata) was set up to validate the model. The result showed that the model describes the fate of each component within the multicomponent substrate. It also indicates that both Peclet and Thiele numbers affect the biodegradation of the substrate. It was observed that a small Peclet number should be allowed for effective biodegradation of the substrate. The model was validated with data obtained for an experiment where a mixture of hydrocarbons was degraded with a mixed culture of microorganisms. The results of the experiment were well described by the model indicating that the model can be used to predict the compositions of components of a mixture during biodegradation.*

KEYWORDS: *Model; Multi-component; Kinetic; Peclet number; Consumption rate; Soil.*

INTRODUCTION

The full characterization of the bioremediation process in the porous medium requires an understanding of the mass transport phenomenon in the remediating environment. This is needed to be able to adequately determine what happens to the contaminants in the system, especially when the contaminant is a mixture of compounds, such as in crude oil and some of its fractions, where each component or compound within the mixture, is degraded differently or where the degradation of one can be affected by another in the mixture or requires different conditions to be degraded.

Since individual microorganisms can only metabolize a limited range of hydrocarbons [1,2], the degradation of the multicomponent substrate like crude oil and the likes require a consortium of microorganisms with different degrading abilities. This has really posed some level of difficulty in the prediction of the rate of degradation of the individual component of the substrate.

Therefore, the development of treatment strategies for the crude oil-contaminated porous environment (soil in particular) requires consideration of the individuality of the component hydrocarbons. Many, if not most of the existing numerical models have not adequately described the fate of the substrates, especially, crude oil and its derivatives, which are mixtures of hydrocarbons. Their pollution in the environment gives rise to multi-component substrates, even when the models consider multicomponent substrates, the focus has not been on mixtures of hydrocarbons [3-6]. While *Dhawn et al*. [2] considered the combination of oxygen and crude oil, *Nasrabadi et al.* [4] focused on two-phase systems and not looking at the microbial degradation of the hydrocarbons, and *Owabor* and *Ekwoun* [5] considered hydrocarbons but did not give an adequate account of the multicomponent scenario in the model.

Therefore, existing literature has not adequately addressed the situation of the multicomponent substrate being degraded by a consortium of microorganisms. This has led to set-back in the success of the system, particularly. in predicting the rate of degradation in porous media.

Generally, the ultimate fate and mass transport of chemicals in the porous media are controlled by three important processes: sorption, convective-dispersive flow, and chemical-biological transformation [5, 10]. The model quantitatively describing the fate of the contaminants in porous media is generally referred to as Advective-dispersive Equation, ADE [11, 12]. Along with this, the biochemical reaction and sorption kinetics are processes that do also control the fate of the substrate through soils [13].

Previous models used first-order kinetics to describe the degradation of the substrate in soils [11-13], and this has been reported to be in contrast to findings in laboratory mineralization experiments where there is a lag phase [10, 14-16]. This demands that further study that will attempt to use an appropriate kinetic model that will lead to the prediction of the rate of microbial degradation of the multicomponent substrate within a porous media.

Therefore, this study aims at modeling the fate of each of the components of multicomponent substrates using ADE combined with appropriate biochemical reaction kinetics to account for the fate of the multicomponent substrates. The model will also be simulated numerically by the Finite Volume Method, FVM.

THEORETICAL SECTION
Model formulation

Considering the fate of chemical species within a porous medium, an arbitrarily fixed volume (also referred to as a represented elementary volume, REV) embedded within the porous media through which the chemical species flow in one dimension is assumed. Assuming the flow is saturated, that is all the available pore space is always filled with the fluid and in one direction x. In accordance with the basic physical law, the fate of the organic substance in this section of the medium can be derived from the mass balance of the substance.

The model can be derived based on the procedure adopted by *Lojan* [17] that gives the normal advective-dispersion equation as follows [18]:

$$\varepsilon R_i \frac{\partial C_i}{\partial t} = \varepsilon D_i \frac{\partial^2 C_i}{\partial x^2} - V \frac{\partial C_i}{\partial x} + F_i \tag{1}$$

Where R is the retardation factor (L/L), ε is the porosity (L^3/L^3), D is the effectivity diffusion (L^2/T), C is the concentration (M/L^3), V is the velocity (L/T), x is the direction(L) and F is the source term (M/L^3T). The subscript i indicates individual components. The D_i is the effectivity diffusion of each component that made up the mixture which is determined using the Wilke Equation (Eq. (2)).

Mostinsky [19] explained that this Wilke Equation has shown good agreement in comparison to other equations using about 96 experiments with a wide spread of about 15 %.

$$D_i^t = \frac{1 - X_i}{\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{X_j}{D_{ij}}} \tag{2}$$

Divide through by ε

$$R_i \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - V \frac{\partial C_i}{\partial x} + \frac{1}{\varepsilon} F_i \tag{3}$$

Where $v = V/\varepsilon$ is the average velocity.

For the source term, *Lawrence* and *Marcarty* [20] model as shown in Eq. 4 will be adopted for the degradation of the chemical specie by microbial activity, as this will account for the limitation of the Monod Kinetic model.

$$\frac{dC_i}{dt} = \frac{q_i^m C_i X}{k_{si} + C_i} \tag{4}$$

Substituting Eq. (4) as source term, F in Eq. (3) to give the required equation for individual chemical species (Eq. (5))

$$R \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - v_i \frac{\partial C_i}{\partial x} - \frac{1}{\varepsilon} \frac{q_i^m C_i X}{K_{si} + C_i} \tag{5}$$

Where q_i^m is the maximum consumption rate, X is the biomass concentration and K_{si} is the Monod saturation constant.

The concentration of substances in a model with multi-components would be better expressed as mass fractions. Therefore, Eq. (5) can be re-parameterized to suit the degradation of multiple components by substituting $C_i = w_i C$ into the equation and it becomes

$$R \frac{\partial w_i}{\partial t} = D_i \frac{\partial^2 w_i}{\partial y^2} - v_i \frac{\partial w_i}{\partial y} - Y \frac{q_i^m w_i}{K_a + w_i} \tag{6}$$

That is wi the mass fraction of the individual component and C without subscript i is the sum concentration of all the components together. Y is $(q^m X / \varepsilon)$ and H_a is a dimensionless quantity that can be termed as an Associated Saturation constant' that is assumed to have lumped in the various interactions such as competitions, inhibitions, and sequential utilization. Therefore, Eq. (6) will account for an individual component of the substrate.

Since it is second order ordinary differential equation, two boundary conditions with the initial condition of $w_i = w_o$ at $t = 0$, are required to solve it. The possible boundary conditions used are:

$$\text{At} \, x = 0 \quad , \quad vw_0 = vw\big|_{x=0} - D \frac{\partial w}{\partial x}\bigg|_{x=0} \tag{7}$$

$$\text{At} \, x = L \quad , \quad \frac{\partial w}{\partial x}\bigg|_{x=L} = 0 \tag{8}$$

Eqs. (7) and (8) are the secondary and third-types boundary conditions.

Numerical Solution: Finite Volume Difference

The governing Eq. (6) over a finite domain of length L is developed to describe the mass fraction of the solute in the domain and it is solvable using Computation Fluid Dynamic, CFD approach, especially the Finite Volume Difference, FVM, method. The solution procedures are eased by transforming the equations and the conditions to standard forms and, also bringing out the dimensionless

parameters that control the processes of the developed equation in non-dimensionless forms. This will aid in further analysis (such as sensitivity and scale analysis) of the processes and the system.

The following dimensionless parameters (Eq. (9)) are developed:

$$X = \frac{y}{H} \, , \, T = \frac{t}{t_{max}} \, , \, W = \frac{w}{w_0} \tag{9}$$

The dimensionless Eq. (10) is obtained by substituting Eq. (9) into Eq. (6) as follows:

$$\frac{w_0 R}{t_{max}} \frac{\partial W}{\partial T} = D w_0 \frac{\partial^2 W}{H^2 \partial X^2} - v w_0 \frac{\partial W}{H \partial X}$$
$$+ Y q_i^m w_o \frac{W}{H_a^i + w_o W} \tag{10}$$

Dividing Eq. (10) by w_0 and multiplying through by (H^2/D) gives Eq. 12

$$\frac{RH^2}{t_{max}D} \frac{\partial W}{\partial T} = \frac{\partial^2 W}{\partial X^2} - \frac{VH}{D} \frac{\partial W}{\partial X} - \frac{Y q_i^m H^2}{D} \frac{W}{H_a^i + w_o W} \tag{11}$$

Where VH/D, is the Peclet Number (Pe) (the ratio of advection strength to diffusion strength). This plays a critical role in convection-diffusion problems. If the advection in a limiting case becomes negligible as compared to diffusion strength, it becomes as good as a diffusion type. But there may be a situation where the flow speed is such that advection far overweighs the diffusion strength. This is another limiting condition. The real situation may be somewhere between these two cases.

It could be inferred from the above that

$$t_{max} = \frac{RH^2}{D} \tag{12}$$

Therefore,

$$T = \frac{t}{t_{max}} = \frac{tD}{RH^2} \tag{13}$$

The non-dimensional equation [11] can be written as

$$\frac{\partial W}{\partial T} = \frac{\partial^2 W}{\partial X^2} - Pe \frac{\partial W}{\partial X} - \beta^2 \frac{W}{H^i + W} \tag{14}$$

Where

$$\sqrt{Y \frac{q_i^m H^2}{w_o D}} = \beta \quad \text{and} \quad H^i = \frac{H}{w_o}$$

β is the Thiele modulus,

The calculation domain, including the bed and the boundary layer, is decomposed into a number of non-overlapping subdomains, control volumes, (CVs) such that each control volume (CV) gives one equation for computing nodal values as shown in the Supporting Information.

All the coefficients generated from the discretized equations for the first node, second node, the remaining nodes, and last node after applying the boundary conditions as shown in Eq. [A16], [A21] and [A24] generated 10 by 10 matrix which was solved in a Matlab environment with a flowchart shown in Fig. B1.

EXPERIMENTAL SECTION

Soil Column Experiment

The column experiment was designed according to the *Amos et al*. [22] and *Chen et al.* [23] methods. A 5 cm (inside diameter) x 60 cm (height) glass column was constructed with eleven glass sampling points located on alternate sides of the column at 5 cm intervals within the span of 50 cm of the column. The sampling points are to allow for monitoring of the aqueous phase of the model substrate in space and time (Fig. 1) and Fig. 2 gives a picture of the experimental setup.

The column was packed with soil which has been autoclaved severally and mixed basal media containing 2% (v/v) of the substrate (a mixture of hexadecane, heneicosane, 1-methylnaphthalene, 2- methylnaphthalene and 1, 3-dimethylnapthalene) and 10 % (v/v) of a consortium of organisms (*Providential rettgeri*, *Streptococcus salivarius*, *Trichoderma harzianum*, *Aspergillus flavipes,* and *Candida famata*). Each of the experimental setups was allowed to stand for 21 days, and samples were withdrawn from the sample points at the end and analyzed.

Analytical methods

Chemical analysis was used for the estimation of the concentration of the components of the mixed substrate. The hydrocarbons mixture concentration in hexane extract was analyzed on Agilent 7890 gas chromatography coupled with an Agilent 7000B triple quadrupole (QqQ) mass spectrometer, MS, fitted with an electron ionization, EI, source, and a collision cell.
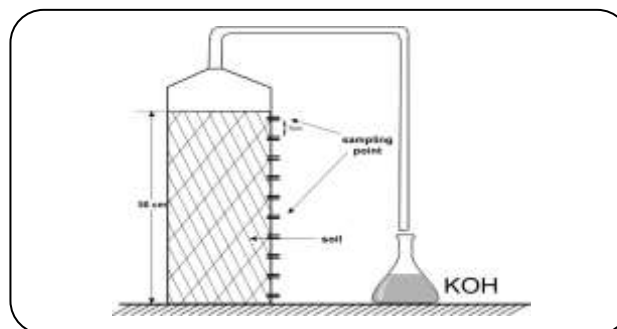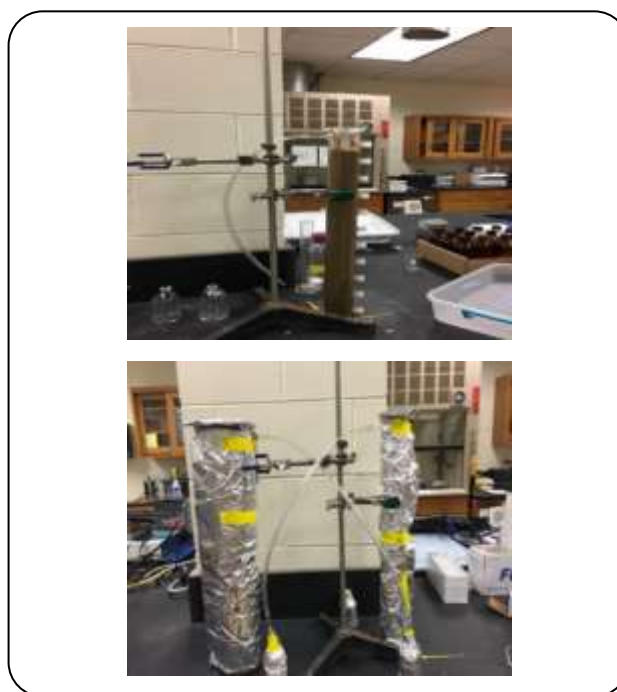

Fig. 1: Column experiment.

Fig. 2: Pictures of the column experiment

The MS was operated in the scan mode to obtain spectral data for the identification of individual components and selected ions monitoring, SIM mode for quantification of the target compounds. An Agilent Technologies DB-5ms column with a dimension of 20mm by 180 m by 0.14 m was used. The chromatography conditions were as follows, carrier gas helium (0.8 mL/min). The injection mode was pulse splitless injection and detector temperatures were 290 and 320 ℃ respectively and the oven temperature program was 50 ℃ (0.8 min hold), 40 ℃/min to 250 ℃ (2 min hold); 30 ℃/min to 325 ℃ (1 min hold), and a total run time of 11 min were used.

The quantification was carried out on the GC-MS in SIM mode rapid response factors, RRFs for each compound were determined during the instrument calibration.

The ions monitored were 141 for 1-methylnaphthalene, 2-methylnaphthalene and 1, 3-dimethylnaphthalene, 57 for hexadecane, and heneicosane. The RRF for each target compound was calculated from the authentic standards. The hydrocarbons were quantified by employing Agilent Technologies Masshunter Ms quantification software. The results of the residual hydrocarbon at the end of the experimental runs, which are shown in Fig. 9, are average values from the analysis of duplicate results, and the reproducibility was within ± 6%.

RESULT AND DISCUSSION
Simulation

The solution of the non-dimensionalized equation model allows for the study of the effect of the Peclet number and Thiele's number on the degradation of the contaminant. The simulation results, presented in Fig. 3 through 7show the effects of both the Peclet number and Thiele modulus on the profile of the contaminant over the dimensionless height at some dimensionless time.

The general trend of observation is that as the Peclet number increases, the effect of the Thiele modulus, specifically the biological reaction reduces as the Thiele modulus is a function of the biological reaction.[24] The explanation for this is that at a high Peclet number the convection term is dominating resulting in the rapid flow of the contaminant from the domain and hence preventing the access of microbial action on the contaminant. This is depicted in Fig. 3 - 5. This is also in accordance with the explanation of Godongwana [25] that as the Peclet number increases, the contact time between substrate and microbes is reduced and thus leads to a reduction of the substrate degradation rate.

Figs. 3-5 show the effect of the Thiele number for certain Peclet numbers on the fate of the contaminant. They illustrate that change in the Peclet number affects the Thiele number, this also influences the contaminant profile. Figs 3a, 4a, and 5a show that the weight of the contaminant remains the same at all the points despite the flow and diffusion because there is no reaction.

If the process is diffusion dominated, that is Peclet number is zero, and Thiele modulus is small there was little reduction in the profile of the contaminant (Fig. 3b). As the Peclet number increases in the domain, this means the contaminant is quickly removed from the domain, and the breakthrough occurs earlier. Therefore, this reduces
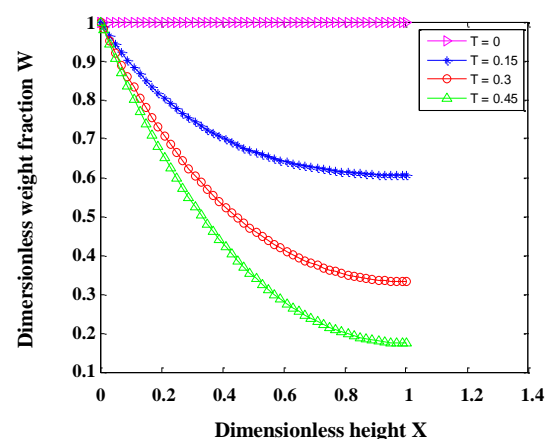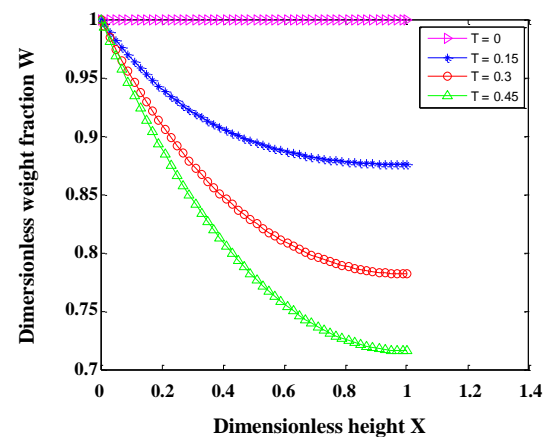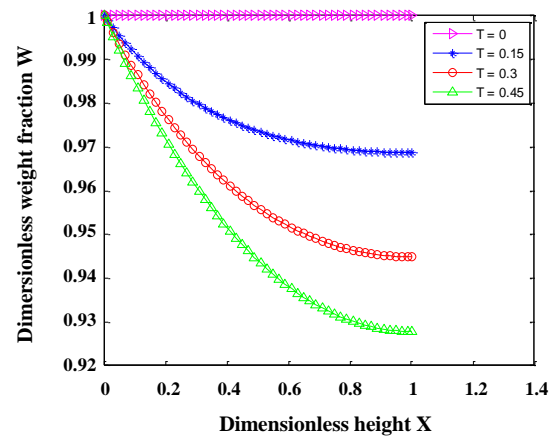

Fig. 3: Effect of Thiele number for Pe = 0 on the dimensionless weight fraction profile of the contaminant. (a) Pe=0, β = 0.5, H^i = 0.1,   (b) Pe = 0, β = 1, H^i =0.1,   (c) Pe = 0, β = 1.8, H^i = 0.1.
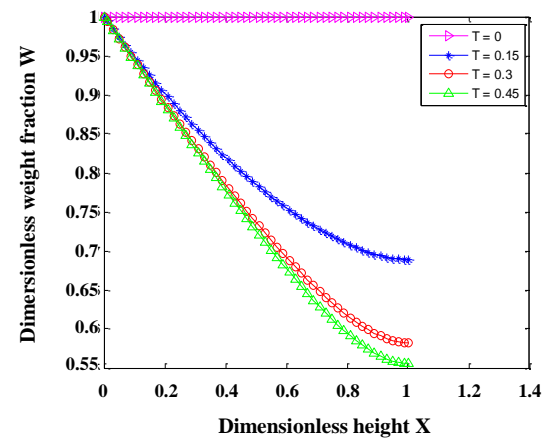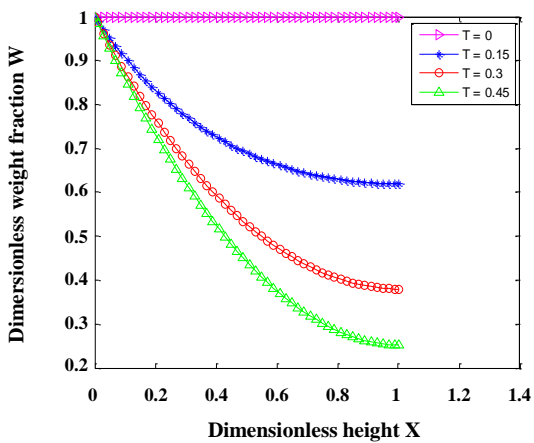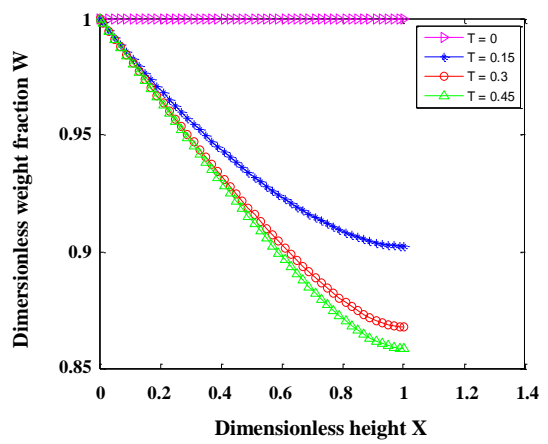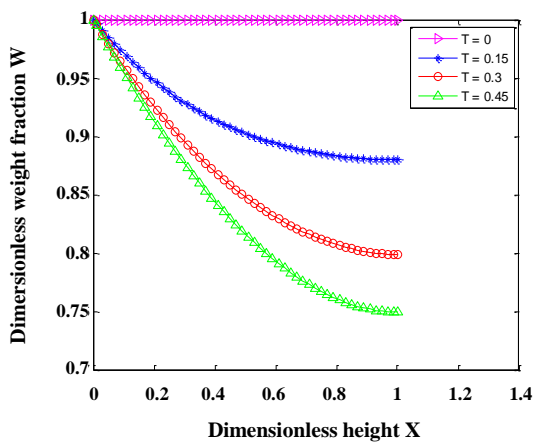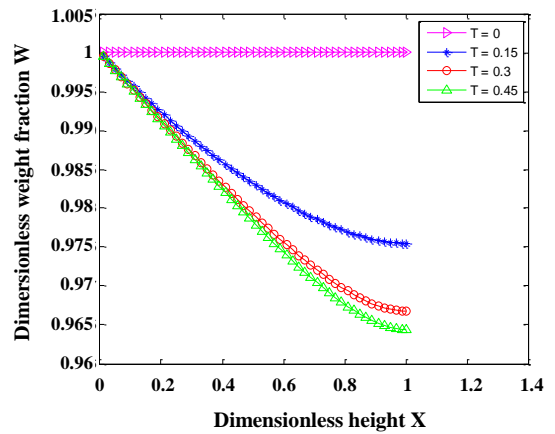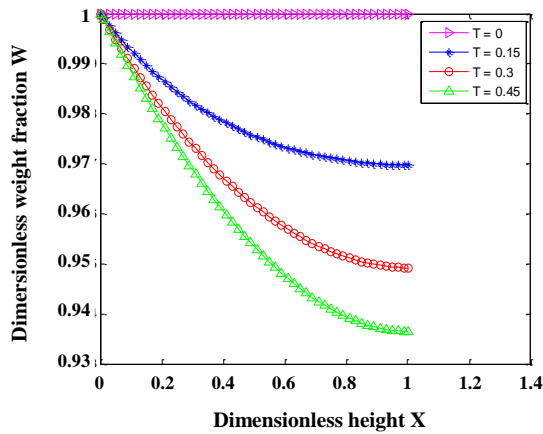
Fig. 4: Effect of Thiele number for Pe = 1 on the dimensionless weight fraction profile of the contaminant. (a) Pe= 1, $H^i = 0.1$, $\beta = 0.5$, (b) Pe = 1, $\beta = 1$, $H^i = 0.1$, (c) Pe = 1, $\beta = 1.8$, $H^i = 0.1$.

Fig. 5: Effect of Thiele number for Pe = 5 on the dimensionless weight fraction profile of the contaminant. (a) Pe= 5, $\beta = 0.5$, $H^i = 0.1$, (b) Pe = 5, $\beta = 1$, $H^i = 0.1$, (c) Pe = 5, $H^i = 0.1$, $\beta = 1.8$.

effect of Thiele modulus, that is, the strength of the microbial reaction on the contaminant. This means that high convection will require high reaction or high microbial activity (high Thiele value).

Fig. 6 shows the weight fraction profile for four different values of Thiele modulus at a specific Peclet number. This is clearly illustrating the effect of the microbial reaction term and the diffusion term on the contaminant profile. Small values of Thiele modulus, especially 0.5 indicate that diffusion is dominating the process. At large values of Thiele modulus, for example, 1.8 indicate that microbial activity is in control of the process.

It is observed also that large values of Peclet number reduce the microbial conversion, resulting in a high weight fraction of the contaminant remaining within the considered domain of the system as shown in Fig. 6. Comparing Fig. 6 (a-c) showing the effect of different Thiele modulus for different values of Peclet number, for instance, at Thiele modulus of 1.8, that is where the biological reaction is dominating in the system it was observed that the last value of the weight fractions is approximately 0.15, 0.26, and 0.54 for *Pe* of 1, 2, and 5 respectively. This explained that for good or better bioremediation (biodegradation) in soil convection the flow-dominated scenario should be avoided.

High intensity of microbial conversion of the contaminant should be enhanced to have at least Thiele modulus greater than or equal to 1 as this will reduce (sharp decline) the profile of the contaminant more. This could be achieved in bioremediation through bioaugmentation or biostimulation. Finally, as shown in the plots, as the Thiele modulus increases, the effect of the Peclet number becomes less profound.

Profiles of all the components in the substrate

This section gives the simulation of the fate of the substrates in the experimental set-up, and it shows that the weight fraction of the various components can be predicted at different heights at a specific velocity and a particular time (Fig. 7), and also the weight fraction of the various components predicted at a different time for a particular height within the medium as depicted in Fig. 8. The model has shown a clear indication that it can predict the extent of degradation of the component of the mixture of hydrocarbons.
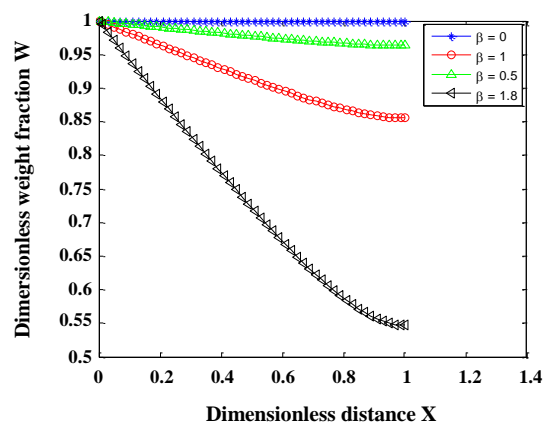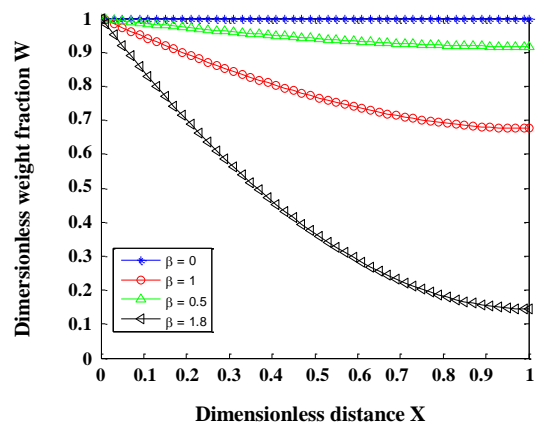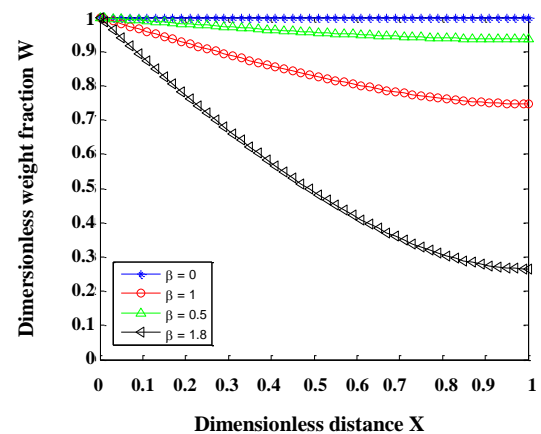

Fig. 6: Effect of Different Thiele modulus at specific Peclet number. (a) Pe= 1, ^{i} = 0.1, (b) Pe = 2, H =0.1, (c) Pe = 5, H = 0.1.

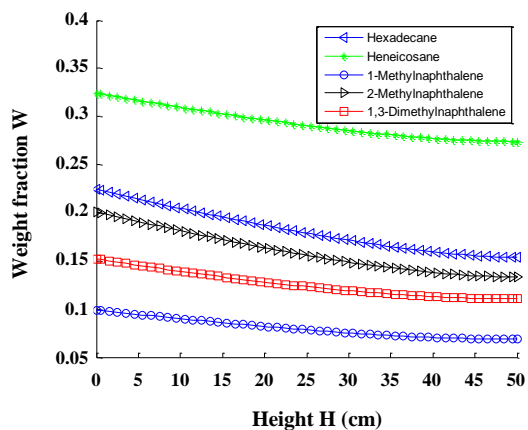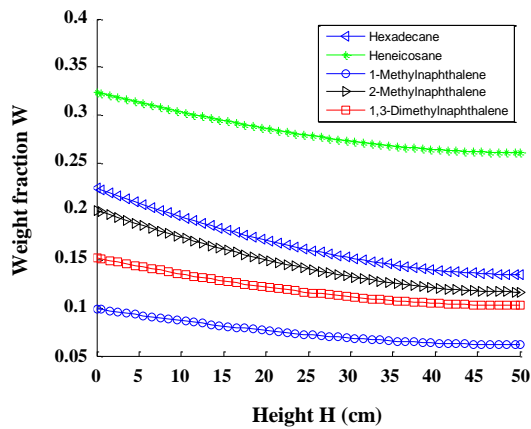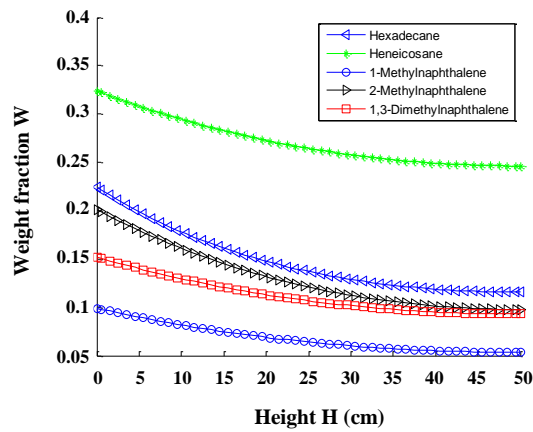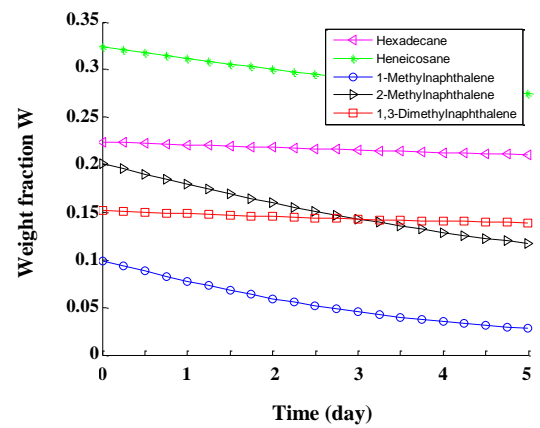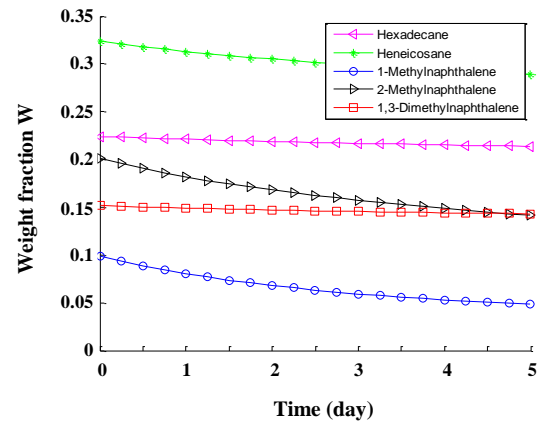*Fig. 8: Weight fraction profile for all the components at a particular height for a specific velocity and reaction. (a) At height of 20 cm, (b) Height of 45 cm.*

The effect of microbial activity, that is, the extent of biodegradation is evident in the profiles observed because as the reaction factor increased the minimum values of the contaminants in the profile at any time decreased. Therefore, microbial activity is key to the fate of the contaminants within the media.

Comparison of the model with experimental results

The applicability of the model to the real situation was validated with the column experiment, simulating a typical bioremediation process. The results, shown in Fig. 9, was found to exhibit the same trend as the model result for all the components of the substrate. In Fig. 9, the experimental data points are plotted while the lines correspond to the model predictions. The experiment
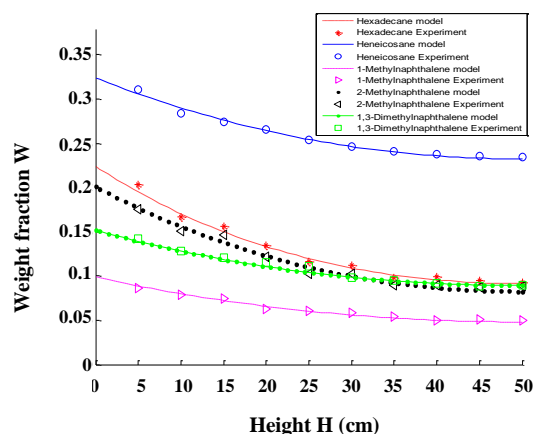
Fig. 7: Weight fraction profile at a different velocity, the same reaction factor, and retardation factor. (a) U = 0 cm/day, t = 10 days, (b) U = 10 cm/day, t = 10 days, (c) U = 20 cm/day, t = 10 days.

Fig. 9: The plots of the experimental and model simulated results.

was carried out at a specific Peclet factor and a particular time, this makes the profile of Fig. 9 similar to that shown in Fig. 7. It is an indication that the model can be adopted to predict the biodegradation rate within porous media.

Statistical analysis of the experimental data points and the model for each of the components give the sum error square, R^2 (x 10^{-6}), values of 0.1608, 7.156, 5.158, 0.2322, and 7.347 for Hexadecane, Heneicosane. 1-Methylnaphthalene, 2-Methylnaphthalene, and 1, 3-Dimethylnaphthalene respectively**.** This agreement confirms the validity of the model as proposed for the multi-component substrate.

CONCLUSIONS

The one-dimension advective-dispersion equation model with an appropriate multi-component substrate degradation kinetics is developed and this offers a better prediction of the fate of individual components in a multi-component substrate in porous media, such as soil. The model was solved numerically by applying the Finite Volume Difference method and the results were validated with an experiment with five components of the substrate and a consortium of microorganisms. The following conclusion was drawn.

Expectedly, an increase in Peclet number, which is an increase in average flow velocity led to a reduction in microbial activities which are not encouraging for effective biodegradation of the contaminants in the soil.

The model is found also to be sensitive to microbial activity and generally the flow of the hydrocarbons and this will enable better design of bioremediation systems.

The model can, therefore, be adapted to developing effective bioremediation techniques since it can be useful in determining the fate of the contaminant in the soil. It can cope with the substrate with more components.

Acknowledgment

REFERENCES

[1] Al-Wasify R.S., Hamed S.R., Bacterial Biodegradation of Crude Oil Using Localisolates, *International Journal of Bacteriology*, 1-8 (2014).

[2] Truskewycz A., Gundry T.D., Khudur L.S., Kolobaric A., Taha M., Aburto-Medina A., Ball A.S., Shahsavari E., Petroleum Hydrocarbon Contamination in Terrestrial Ecosystems—Fate and Microbial Responses, *Molecules*, **24**: 3400 (2019).

[3] Dhawan S., Erickson L.E., Fan L.T., Model Development and Stimulation of Bioremediation in Soil Beds with Aggregates, *Ground Water*, **31**: 271-284 (1993).

[4] Clement T.P., Peyton B.M., Skeen R.S., Jennings D.A., Peterson J.N., Microbial Growth and Transport in Porous Media under Denitrification Conditions: Experiment and Simulations, *Journal of Contaminant Hydrology*, **24**: 269-285 (1997).

[5] Nasrabadi H., Ghorayeb K, Firoozabadi A., Two-Phase Multicomponent Diffusion and Convection for Reservoir Initialization, *SPE Reservoir & Engineering,* 530-542 (2006).

[6] Owabor C.N., Ekwonu C.M., Use of Finite Element Method as a Stimulation Technique for Bioremediation of Naphthalene, Anthracene and Pyrene Contaminated Soil in a Fixed Bed Reactor.*International Journal of Physical Sciences*, **4 (5)**: 321- 326 (2009).

[7] Gogoi B.K., Dutta N.N., Goswami P., Krishna Mohan T.R., A Bioremediation of Petroleum-Hydrocarbon Contaminated Soil at a Crude Oil Spill Site, *Advances in Environmental Research,* **7**: 767-782 (2002).

[8] Najafi S.H., Hajinezhad H., Solving One-dimensional Advection-Dispersion with Reaction Using Some Finite-Difference Methods, *Applied Mathematical Sciences,* **2(53)**: 2611-2618 (2008).

[9] Sanjaya F., Mungkasi S., "A Simple but Accurate Explicit Finite Difference Method for the Advection-Diffusion Equation", International Conference on Science and Applied Science 2017. IOP Publishing IOP Conf. Series: *Journal of Physics: Conf. Series* 909 (2017).

[10] Chenys K., Mertens J., Diels J., Smolders E., Springael.: Monod Kinetics Rather Than a First-Order Degradation Model Explain Atrazine Fate in Soil Mini- Columns: Implications for Pesticide Fate Modelling, *Environmental Pollution*, **158(5)**: 1405-1411 (2010).

[11] Tiktak A., van der Linden A.M.A., Swartjes F., " A One Dimensional Model for Assesssing Leaching and Accumulation of Pesticides in Soil", RIVM report, 715501003, Bilthoven the Netherlands. Pestras (1994).

[12] Dubus I.G., Beulke S., Brown C.D., Gottesburen B., Dieses A., Inverse Modelling for Estimating Sorption and Degradation Parameters for Pesticides, *Pest Management Science*, **60(9)**: 859–874 (2004).

[13] Simunek J., Sejrta M., Saito H., Sakai M., van Genuchten M.T., "The FIYDRUS-1D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in variably-Saturated Media", Department of Environmental Sciences, University of California Riverside, Riverside. (2005).

[14] Alexander, M. "Biodegradation and Bioremediation", 2nd ed., Academic Press, New York. (1999).

[15] De Wilde T., Mertens J., Simunek J., Sniegowksi K., Ryckeboer J., Jaeken P., Springael D., Spanoghe P., Characterizing Pesticide Sorption and Degradation in Microscale Biopurification Systems Using Column Displacement Experiments, *Environmental Pollution*, **157(2)**: 463–473 (2009).

[16] Sniegowski K., Mertens J., Diels J., Smolders E., Springael D., Inverse Modelling of Pesticide Degradation and Pesticide-Degrading Population Size Dynamics in a Bioremediation System: Parameterizing the Monod Model, *Chemosphere*, **75(6)**: 726–731 (2009).

[17] Lojan J.D., Transport Modelling in Hydrogeochemical System, *Interdisciplinary Applied Mathematics*, *XIV*: 29-73 (2001).

[18] Bertelkamp C., Reungoat J., Cornelissen E.R., Singhal N., Reynisson J., Cabo A.J., van der Hoeka J.P., Verliefde, A.R.D., Sorption and Biodegradation of Organic Micropollutants During River Bank Filtration: A Laboratory Column Study, *Water Research,* **52**: 231-241 (2014).

[19] Mostinsky I.L., Diffusion Coefficient, in "International Encyclopedia of Heat and Mass Transfer", Hewitt G.F., Shires G.L., Polezhaev Y.V., (eds.), CRC Press, Florida (1996).

[20] Lawrence, A. W., McCarty, P. L.: Unified Basis for Biological Treatment, Design and Operation, *J. Sanit. Eng. Div. Proc. ASCE*, **96**: 757-778 (1970).

[21] Versteeg H.K., Malalasekera W., "Introduction to Computational Fluid Dynamic. the Finite Volume Method". 2nd ed. Longman Group Ltd, England (2005).

[22] Amos B.K., Suchomel\, E.J., Pennell\ K.D., Löffler F.E., Spatial and Temporal Distributions of Geobacterlovleyi and *Dehalococcoides spp*. During Bioenhanced PCE-NAPL Dissolution. *Environmental Sciences and Technology*, *43*: 1977–1985 (2009)

[23] Chen M., Abriola L.M., Amos B.K., Suchomel E.J., Pennell K.D., Löffler F.E., Microbially Enhanced Dissolution and Reductive Dechlorination of PCE by a Mixed Culture: Model Validation and Sensitivity Analysis, *Journal Contamination and Hydrology,* **151**: 117–130 (2013).

[24] Kapellos G.E., Paraskeva C.A, Kalogerakis N., Doyle P.S., Theoretical Insight into the Biodegradation of Solitary Oil Microdroplets Moving through a Water Column, *Bioengineering*, **5(1)**: 15(2018).

[25] Godongwana B., Effectiveness Factors and Conversion in a Biocatalytic Membrane Reactor. *PLoS ONE,* **11(4)**: - (2016).