

Modeling the Reaction and Transport Mechanism for Total Petroleum Hydrocarbon Using Selected Linear and Nonlinear Error Functions

Ehizonomhen Solomon Okonofua^{1*}, Kayode Hassan Lasisi², Sunday Egbiki³

¹Department of Geomatics, University of Benin, PMB 1154, Benin City, Edo State, Nigeria

²Department of Civil Engineering, Federal University of Technology, Akure, PMB 704, Ondo State, Nigeria

³Department of civil Engineering, Nigerian Maritime University, Okereko, Delta State.

*Corresponding author: ehizonomhen.okonofua@uniben.edu

Received 25 June 2019, Received in revised form 25 January 2020

Accepted 02 March 2020, Available online 30 August 2020

ABSTRACT

In this article, field pilot study was undertaken to examine the transport mechanism for total petroleum hydrocarbon remediation in varying concentration using pseudo first order, pseudo second order and intra particle diffusion kinetic models in land farming treatment. Soil samples were artificially contaminated in varying concentration of 1,000 mg/kg (low), 3,000 mg/kg (medium) and 5,000 mg/kg (high) and treated using organic and inorganic fertilizers for a period of 150 days which is the duration for effective remediation treatment. The results from the treated samples were subjected to kinetics studies while coefficient of determination (R^2) was applied on the residual total petroleum hydrocarbon (TPH) after 150 days of treatment, pseudo first order had R^2 values of 0.7898 (low), 0.6776 (medium) and 0.6131 (high). Pseudo second order had R^2 values of 0.9737 (low), 0.9467 (medium), 0.7863 (high) while intra particle diffusion had R^2 values of 0.9940 (low), 0.9821 (medium) and 0.9489 (high) respectively. The results indicate that intra particle diffusion model best described the kinetics mechanism of TPH remediation using land farming treatment; but when the alteration in the error structure associated with transforming a nonlinear kinetic equation into linear equation is minimized using nonlinear regression optimization procedure, pseudo first order emerged as the best kinetic model having the least sum of errors as 0.000270 (low), 0.000185 (medium) and 0.000278 (high).

Keywords: Hydrocarbon; remediation; treatment; land farming; transport; kinetics.

INTRODUCTION

Wastes from crude oil and its refined products are usually from spills or washing of petroleum products processing/transporting vessels or facilities. These wastes are mainly alkanes (paraffin) having 1-40 carbon atoms in a molecule. Most of these wastes emanates from petroleum industries, oil storage yards, tank farms, Oil-water separators, leakage from vessels, faulty plant parts, motor mechanic/generator workshops and petrol dispensing locations (Cutright 1995; Ivančev-Tumbas et. al. 2004, Pala et. al. 2006). A significant fraction from these discharges from these sources enter into the streams and soil as pollutants which must be removed or mineralized completely due to the adverse effect on man, animals and entire ecosystem. Pollution resulting from crude oil spill is visible at the top/sub surface soil of the polluted site and then travels down the soil to greater depth depending on the consistency of the soil formation. This phenomenon makes it essential to thoroughly understand the dispersion and transportation mechanism of crude oil pollutants before and after treatment in the soil or water medium. Understanding the complete kinetics of the pollutant transport in the contaminating medium is quite a difficult task, same herculean task is encountered in the modeling of the biodegradation kinetics during treatment of polluted media (soil/water).

Crude oil contaminated site/field examination is most often expensive, imprecise procedures and arduous. Apart from considering environmental concerns during such investigations, proper field characterization is necessary in order to have reasonable estimation of soil's formation which aids crude oil pollutants migration. In most instances, as in the oil rich Niger Delta, the history of several spills in the existing contaminated oil fields are unknown. Numerical models are useful in these cases in estimating the extent and severity of these contaminations. However, such models require intense and concise data sets and must be verified (Rončević et al. 2005; Bazin et al. 1976).

The need to remediate crude oil polluted soils have long been a global challenge and resulted from researches have led to the utilization of different methods such as bioremediation, bioaugmentation, phytoremediation, enhanced land farming, chemico- biological stabilization and phytoextraction. Fertilizers (inorganic and organic) have also been of great use in minimizing the effects of spill although it also has adverse effect on soil if not properly applied. The need for more current approach to remediation techniques is on the increase and so is the need for thorough understanding of transporting mechanism involved in crude oil pollution migration (flow) and remediation. Before implementing any new remediation technology in the field, it is necessary to first evaluate its potential of

success in laboratory scale. Conventionally, the first stage of screening a new remedial technology is by "1-D column studies". However, several researches have been carried out with respect to contaminant flow, and transportation during treatment (Morrow et al. 1988; Priddle and MacQuarrie 1994; Renshaw et al. 1997; Abdul and Gibson 1991), they reported that column studies limitation due to flow boundaries condition makes it less desirable for studying flow processes and kinetics of contaminants movement in sub soils. With a view to gaining more understanding into crude oil pollution remediation degradation kinetics, most researches turned to linear and nonlinear error functions which are mathematical models (Pennell et al. 1996; Kumar, 2006; Wong et al. 2004; Porter et al. 1999; Ng et al. 2002; Allen et al. 2003; Ho et al. 2002; Kumar and Porkodi, 2007). Some of these error functions include coefficient of determination (R^2), hybrid functional error function (HYBRID), sum of errors squared and Marquardt percentage standard deviation. Coefficient of determination is mostly used error functions in minimizing error distributions between experiment data set and remediation (degradation of contaminants).

In time past, researchers had difficulty in comparison of accuracies of error functions with respect to remediation but the recent application of statistical software as Statistical Package for Social Sciences (SPSS), it is now possible to predict optimum performance in various error functions in kinetic modelling of biodegradation. This study utilizes three control kinetic models: intra particle diffusion model, pseudo first order and pseudo second order models to ascertain the exact nature and rate of chemical reaction that occurs during land farming treatment of crude oil hydrocarbon contaminated soil. This study aims to monitor the change in the concentration of total petroleum hydrocarbon (TPH) with treatment time.

MATERIALS AND METHODS

PROJECT LOCATION

The location for this study is located at the faculty of Agricultural sciences remediation site inside University of Benin, Ugbowo Campus. The site is bounded in the east by faculty of agricultural science vegetable farm and on the west is female hostel. Its latitude ranges from $05^{\circ} 44' - 07^{\circ} 34'N$ and longitude is within $05^{\circ} 04' - 06^{\circ} 45'E$. On the west, it slopes from 3-8% gently towards Ikpoba stream. In the same western sector (at the back of University capitol), the slope terminated. At this spot, the change in gradient causes high acceleration of runoff into Ikpoba stream (Ehiorobo, 2010). This explains the routine protection of the field pilot study site in order to prevent river pollution by runoff from leachate.

SOIL RECOVERY AND PREPARATION

Soil was taken at the project location with depth not greater than 45 cm using calibrated hand auger and the coordinates

of the locations were obtained using handheld GPS. Depth of sampling collection was maintained at 45cm because the pipe conveying the crude was laid on the earth surface and maximum depth of crude percolation from previous study in the area is about 30 – 35 cm. Also, most plants in the study area have roots not exceeding 40cm and hence the need to evaluate the transport mechanism of crude within this dept. Sampling was systemic so as to ensure that only topsoil were taken as it affects plants growth the most. The recovered soil samples were placed in cellophane bags and transported to university of Benin Geotechnical Laboratory where it was dried, pulverized, sieved and preserved before taken to Chemistry Laboratory for the determination of the baseline TPH concentration levels. This was to ensure that the TPH content was below detection level before the artificial contamination using the crude oil from the flow station. The physical and chemical properties of the soil used are shown in Table 1.

Three (3) cells with sub cell attached, each measuring 170 cm * 90 cm was prepared for the remediation research. Cellophane bags were placed at the base of each cell so as to prevent the samples from contaminating the ground. The prepared soil samples were divided into three groups with each group having about 100 kg of soil and delineated as low, medium and high concentrations. The *low* samples were spiked with 6.1 kg of crude oil sample an equivalent of 1000 mgkg^{-1} concentration, the *medium* samples were spiked with 12.2 kg of crude oil an equivalent of 3000 mgkg^{-1} concentration while the *high* samples were contaminated with 18.3kg of crude oil samples an equivalent of 5000 mgkg^{-1} concentration respectively. These three levels of concentration meet United States Environmental Protection Agency standard; pollution within the range of 1 mgkg^{-1} to 999 mgkg^{-1} is regarded as low, from 1000 mgkg^{-1} to 2999 mgkg^{-1} is regarded as mild/medium while 3000 mgkg^{-1} to above 5000 mgkg^{-1} is classified as high/intervention level. Samples from the three concentrations (low, medium and high) were taken to the laboratory for the quantification of TPH content and the values are presented in Table 2. The research was carried out for a period of 150days while samples were taken to the laboratory every 30days for determination of residual TPH.

SOIL TREATMENT

The cow dung, crude oil samples, organic and inorganic fertilizers used for the soil treatment were first taken to Chemistry Laboratory at the University of Benin for characterization, and determination of physical and chemical properties. Values obtained are shown in Tables 3-4 respectively. The summary of the land farming treatments which were carried out under pilot study is as follows:

Land Farming Treatment = 100 kg of soil sample + 25 kg NPK fertilizer + 25 kg organic amendment (cow dung). 10 kg of contaminated samples were also placed in the sub cell but were not treated, this was used as control (natural attenuation). The initial

moisture content of 20% was maintained at the commencement of the study.

SAMPLES ANALYSIS AND INSTRUMENTATION

Samples recovered for monthly analysis were placed in plastic bags and put into a glass jar with seal. Each sample was labelled differently and stored in a refrigerator at 4°C. Sample extraction was carried out using extraction procedure detailed in USEPA method 3540 and ASTM method D5369 with little adjustments on flask size, choice of solvent, volume of solvent and extraction time. Before extraction, pestle and mortar was used to pound samples to get fine texture, pebbles and stones were also removed.

Hydrocarbons in the soil samples were then determined using Agilent 6890 Gas Chromatograph fitted with a split injection auto sampler. Samples were injected and separated on a HP-5MS/DB-5MS column of 0.25 mm diameter, 30 m long and is 0.25 µm film thick while placed in a 2 ml chromatographic vial. Carrier gas was Nitrogen with a makeup flow of 25 ml/min while temperature throughout the chromatographic operation was 80°C for 3minutes, 20°C/minute until 280°C was obtained and hold for 20 minutes and the detector flame was set at 300°C.

KINETICS OF FIELD PILOT EXPERIMENTAL DATA

Reaction controlled kinetic models such as pseudo-first order and pseudo-second order model were used to ascertain the exact nature and chemical reaction that occurs during land farming treatment of crude petroleum hydrocarbon contaminated soil. The main focus was to monitor the change in the concentration of total petroleum hydrocarbon (TPH), with treatment time. Intra-particle diffusion model was employed to assess whether diffusion process is the dominant step in the land farming process.

The pseudo first-order rate expression of Lagergren based on the solid capacity have been given as in Equation 1:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (1)$$

Where:

q_e and q_t ; are the amount of crude petroleum hydrocarbon removed at equilibrium in time t (mg·g⁻¹),

K_1 is the rate constant of pseudo first-order.

TABLE 1. Physical and Chemical Properties of the soil used in the study

Properties	Value
pH (1:1 soil-water)	5.72
Nitrogen (mg kg ⁻¹)	8.83
Phosphorus (mg kg ⁻¹)	11.73
Organic Carbon (g kg ⁻¹)	47.8
Gradation Analysis	
Sand (%)	79.4
Silt (%)	14.5
Clay (%)	6.1
Textural Class	Sandy Loam
Specific Gravity	2.5

TABLE 2. Summary of Total Petroleum Hydrocarbon Found in Spiked Samples

TPH Concentration	Before Treatment (mg/kg)	After Treatment (mg/kg)
Low	1016.82±19.96	59.24±9.53
Medium	3029.87±14.39	105.56±5.22
High	5033.67±146.89	260.32±32.34

TABLE 3. Physical and Chemical Properties of the Crude oil used in the study

Parameters	Value
Water (% Vol.)	0.50
Specific Gravity @ 15/150c	0.8966
Dry Specific Gravity @ 15/150c	0.8961
*API@ 15/150c	26.4
Kinematic Viscosity	10.45
Appearance	Dark Brown Liquid

* API- American Petroleum Institute

TABLE 4. Properties of Organic and Inorganic Fertilizers used in the Study

Parameters	Cow Dung	NPK Fertilizer
pH	8.27	9.62
Organic Carbon (%) *10-1	137.40	463.23
Total Nitrogen (%)	40.65	58.40
Calcium (mg/kg)	1.42	37.55
Phosphate (mg/kg)	23.68	26.07
Potassium (mg/kg)	17.49	7.83
Magnesium (mg/kg)	5.88	11.35
Sodium (mg/kg)	1.94	1.06

The organic and inorganic fertilizers used have high Nitrogen content which makes them suitable for remediation operations.

The linear plots of $\text{Log} [q_e - q_t]$ versus time (t) shows the appropriateness of the above equation and also first order nature of land farming treatment procedure. For the first order kinetic computation, the value of q_e was taken as the amount of total petroleum hydrocarbon removed after (150 days) of remediation (measured in terms of TPH content) while q_t represent amount of total petroleum hydrocarbon removed with time.

The remediation ability of solid phase using pseudo second order is given as in Equation 2:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t) \quad (2)$$

Where: K_2 is the rate constant of pseudo-second order ($\text{gm}g^{-1}\text{min}^{-1}$)

The plot of $\left(\frac{t}{q_t}\right)$ against (t) gives straight line graph in which q_e and K_2 can be evaluated using the gradient and intercept derived from the plotting. For the second order kinetic computation, the value of q_t was taken as the amount of total petroleum hydrocarbon removed with time (measured in terms of TPH content)

Intra-particle diffusion model was employed to investigate whether diffusion process is the dominant step during the land farming treatment of crude petroleum hydrocarbon. Although, intra particle diffusion kinetics was suggested for the procedure of heavy metals ion adsorption, it was adopted in this study to test if the diffusion step is rate limiting. Intra-particle diffusion equation as recommended in Weber and Chakravorti (1974) report; Scheckel and Sparks, 2001 is given in Equation 3;

$$q_t = K_{ad} t^{\frac{1}{2}} + I \quad (3)$$

Where

K_{ad} is intra-particle diffusion rate constant (mg/g min)

Plotting (q_t) against $\left(\frac{t}{t^{\frac{1}{2}}}\right)$ gave a slope equal to (K_{ad}) and intercept equal to (I). Values of (I) gave an insight into

the thickness of the boundary layer. Higher values indicate greater boundary layer effects.

RESULTS AND DISCUSSION

To select the kinetic model that best define the experimental data obtained from the field pilot study, linear and non-linear regression analysis was done and results obtained are presented as follows:

KINETIC OF TPH REMOVAL AT LOW, MEDIUM AND HIGH CONCENTRATIONS

The kinetic computations and the linear least square regression of TPH based on intra particle diffusion, pseudo-first order and pseudo-second order kinetic models are presented in Tables 5-7

On the kinetic model that best explain the experimental data generated from the use of land farming treatment for the removal of TPH at low, medium and high concentrations of crude petroleum hydrocarbon, linear coefficient of determination (R^2) was first employed as bases for judgment. Results of Tables 8 shows the computed R^2 value for pseudo-first order kinetic model, pseudo-second order kinetic model and intra-particle diffusion model.

From the result in Tables 8, it was observed based on the computed value of r^2 that intra-particle diffusion model had the best fit for the experiment data set. Determination of R^2 value including its subsequent application in the selection of best fit kinetic model is not satisfactory owing to the alteration in the error structure associated by transforming non-linear equation into linear form. In addition, R^2 value only account for the difference associated with each individual point fitted by the model in relation to the overall average of the fitted curve. Therefore, to have an accurate judgement in the selection of best fit kinetic model, non-linear regression using selected error functions was employed.

Non-linear regression analysis is an optimization procedure that demands the selection of an error function that will aid in evaluating the fit of the kinetic model to the experiment equilibria datasets. This study

TABLE 5. Kinetic model computation for the removal of TPH at LOW crude petroleum concentration

Time (days)	q _e	q _t	q _e - q _t	Log(q _e - q _t)	(t/qt)	(t ^{0.5})
0	q _e	q _t	q _e - q _t	Log(q _e - q _t)	(t/qt)	0
0	957.58	0	957.58	2.9812	0	2.2361
30	957.58	356.6	600.98	2.7789	0.0561	5.4772
60	957.58	602.2	355.38	2.5507	0.0830	7.7460
90	957.58	702.3	255.28	2.4070	0.1139	9.4868
120	957.58	866.4	91.18	1.9599	0.1270	10.9545
150	957.58	947.6	9.98	0.9991	0.1477	12.2474

TABLE 6. Kinetic model computation for the removal of TPH at MEDIUM crude petroleum concentration

Time (days)	q _e	q _t	q _e - q _t	Log(q _e - q _t)	(t/qt)	(t ^{0.5})
0	0	2924.31	3.4660	0	0	0
30	1302.28	1622.03	3.2101	0.0230	1302.28	5.4772
60	1993.61	930.7	2.9688	0.0301	1993.61	7.7460
90	2399.15	525.16	2.7203	0.0375	2399.15	9.4868
120	2680.44	243.87	2.3872	0.0448	2680.44	10.9545
150	2924.31	0	0	0.0513	2924.31	12.2474

TABLE 7. Kinetic model computation for the removal of TPH at HIGH crude petroleum concentration

Time (days)	q _e	q _t	q _e - q _t	Log(q _e - q _t)	(t/qt)	(t ^{0.5})
0	4773.35	0	4773.35	3.6788	0	0
30	4773.35	1707.09	3066.26	3.4866	0.0176	5.4772
60	4773.35	2212.51	2560.84	3.4084	0.0271	7.7460
90	4773.35	3566.11	1207.24	3.0818	0.0252	9.4868
120	4773.35	4211.62	561.73	2.7495	0.0285	10.9545
150	4773.35	4773.35	0	0	0.0314	12.2474

TABLE 8. Selection of best fit kinetic model for TPH removal at Various concentrations of crude using R²

S/No	Kinetic Model	R-Square (Low Conc.)	R-Square (Medium Conc.)	R-Square (High Conc.)
1	Pseudo-first order	0.7898	0.6776	0.6131
2	Pseudo-second order	0.9337	0.9467	0.7867
3	Intra-particle diffusion	0.9940	0.9821	0.9589

utilized two non-linear error functions were selected, namely; normalized standard deviation (NSD) and root mean square error (RMSE). Since each of the selected error function produced non-identical sets of kinetic parameters, an overall optimum kinetic parameter set was difficult to identify directly. To overcome this limitation and make a more meaningful comparison between the kinetic parameter sets, a procedure of normalizing the computed error functions was adopted to produce a single combination of the minimized error called sum of normalized error (SNE) for each selected kinetic parameter. The sum of normalized error, (SNE) was thereafter employed to select the kinetic model that best described the removal of TPH using the method of land farming treatment. The lower the sum of normalized error the better the ability of the kinetic model to described the

experimental data. The results of the non-linear regression optimization employed in computing the selected error functions are presented in Tables 9.

From the result in Table 9, it was observed that pseudo-first order kinetic model had the lowest sum of normalized error followed by intra-particle diffusion model and pseudo-second order. Hence, pseudo-first order kinetic model was selected as the kinetic model that best explain the pilot study data for the removal of TPH at low, medium, and high concentrations of crude petroleum hydrocarbon by method of land farming treatment. Maletić et al, (2009) had a similar result when they investigated the degradation mechanism of aged petroleum hydrocarbon polluted soil; pseudo first order was adjudged the best model for the degradation kinetics of aged PAHs in contaminated soils.

TABLE 9. Result of Non-linear Regression Optimization Employed in Computing the Selected Error Functions

Kinetic Model	Sum of Normalized Error (Low Concentration)	Sum of Normalized Error (Medium Concentration)	Sum of Normalized Error (High Concentration)
First Order	0.000270	0.000815	0.000278
Second Order	2.4517	2.2992	2.3029
Intra-Particle	0.5332	0.5114	0.5101

CONCLUSION

The application of land farming treatment on the artificially spiked samples at different concentrations (low, medium and high) was responsible for the significant reduction of TPH in the contaminated samples within a period of 150 days. Table 2 shows that low TPH concentration decreased by 94.17%, medium TPH concentration decreased by 96.52% while high TPH concentration decreased 94.83% respectively. The results of the degradation were fitted into the three kinetic equations that was used to determine the pattern of kinetic degradation. However, the complexities involved in the determination of the kinetics of biodegradation of TPH such as transporting through interfacing phases were described near accurately by intra particle diffusion. The introduction of non-linear regression was used to determine and sum minimal errors in the kinetic models and pseudo first order was more suitable. Other kinetic models can also be used and compared with already established results for validation of results.

ACKNOWLEDGMENTS

This article is part of my PhD research, my appreciation goes to the Federal Government of Nigeria for funding this work at the Federal University of Technology Akure through Tertiary Education Fund (tetfund). Great thanks to Mr. Nicholas Uwadia and Dr. R. Ilaboya for their assistance and contribution to the work.

DECLARATION OF COMPETING INTEREST

The Authors declare that there is no conflict of interest in this work.

REFERENCES

- Abdul, A. S. and Gibson, T. L. 1991. Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyl from sand material. *Environment Science and Technology* 25(4): 665–670.
- Allen, S. J., Gan, Q., Matthews, R., Johnson, P. A. 2003. Comparison of optimized isotherm models for basic dye adsorption by kudzu, *Bioresource Technology* 88: 143–152.
- Bazin, M. J., Saunders, P. T., & Prosser, J. I. 1976. Models of microbial interactions in the soil. *CRC Critical Reviews in Microbiology* 4(4): 463–498.
- Cutright, T. J. (1995). Polycyclic Aromatic Hydrocarbon Biodegradation and Kinetics Using *Cunninghamella echinulata* var. *elegans*. *International Biodeterioration & Biodegradation*, 35(4), 397–408.
- Ehiorobo, J. O. 2010. Flood and Erosion Control in Edo State, Inception report submitted to NDDC on flood and erosion control in Niger Delta States
- Ho, Y. S., Porter, J. F., McKay, G. 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Pollution* 141: 1–31.
- Ivančev-Tumbas, I., Tričković, J., Karlović, E., Tamaš, Z., Rončević, S., Dalmacija, B., Petrović, O., & Klačnja, M. 2004. GC/MS-SCAN to follow the fate of crude oil components in bioreactors set to remediate contaminated soil. *International Biodeterioration & Biodegradation* 54(4): 311–318.
- Kumar, K. V. 2006. Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, *Dyes Pigments* 74: 595–597.
- Kumar, K. V., & Porkodi, K. 2007. Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, *Journal of Hazard Material* 146: 214–226.
- Maletić, S., Dalmacija, B., Rončević, S., Agbaba, J., & Petrović, O. 2009. Degradation kinetics of an aged Petroleum contaminated soil. *Water Air Soil Pollution* 202: 149–159. doi:10.1007/s11270-008-9965-8
- Morrow, N. R., Chatzis, I., & Taber, J. J. 1998. Entrapment and mobilization of residual oil in bead packs. *SPE Reservoir Engineering* 3(3): 927–934.
- Ng, J. C. Y., Cheung, W. H., & McKay, G. 2002. Equilibrium studies of the sorption of Cu (II) ions onto chitosan. *Journal of Colloid Interfaces and Science* 255: 64–74.
- Pala, D. M., de Carvalho, D. D., Pinto, J. C., & Sant'Anna Jr., G. L. 2006. A suitable model to describe bioremediation of a petroleum-contaminated soil. *International Biodeterioration & Biodegradation* 58(3–4): 254–260.
- Pennell, K. D., Pope, G. A., & Abriola, L. M. 1996. Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing. *Environment, Science and Technology* 30: 1328–1335.
- Porter, J. F., McKay, G., & Choy, H. K. 1999. The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory, *Chemical Engineering and Science* 54: 5863–5885.
- Priddle, M. W. & MacQuarrie, T. B. 1994. Dissolution of creosote in groundwater: an experimental and modeling investigation. *Journal of Contaminants and Hydrology* 15: 27–56.
- Renshaw, D. E., Zynda, G. D., & Fountain, J. C. 1997. Permeability reductions induced by sorption of surfactant. *Water Resources Research* 33(3): 371–378.
- Rončević, S., Dalmacija, B., Ivančev-Tumbas, I., Petrović, O., Klačnja, M., & Agbaba, J. 2005. Kinetics of degradation of

- hydrocarbons in the contaminated soil layer. *Archives of Environmental Contamination and Toxicology* 49(1): 27–36.
- Scheckel, G. K., & Sparks, D. L. 2001. Temperature Effects on Nickel Sorption Kinetics at the Mineral–Water Interface. *Soil Sci. Soc. AM. J.* 65: 719–728
- Weber, T. W., & Chakravorti, R. K. 1974. Pore and solid diffusion models for fixed-bed adsorbers. *AIChE Journal* 20(2): 228–238.
- Wong, Y. C., Szeto, Y. S., Cheung, W. H. & McKay, G. 2004. Adsorption of acid dyes on chitosan—equilibrium isotherm analyses. *Process Biochemistry* 39: 695–704