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The Effect of Mass Transfer Resistance on the Adsorption Rate of Phenol in Soil Sediments

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Abstract: This study was aimed at evaluating the effect of mass transfer resistance to the transport of phenol in soil sediments. Batch adsorption experiments were conducted using phenol in homogenous soil sediments (clay and sand). The Physico-chemical properties of the soil sediments were determined and sorption behaviour kinetically modelled using the Pseudo-first order, Pseudo-second order, Intra-particle, Elovich, and Power function models. The sorption behaviour was best modelled with the intra-particle model ($R^2 > 0.9628$). The rate limiting step and mass transfer resistance were determined by the Boyd plot, Homogenous pore diffusion model (HPDM) and the modified Furusawa -Smith equation. The Boyd plots indicated external mass transfer as the rate-determining step for the phenol/clay and phenol/sand systems; the HPDM model gave a poor fit ($R^2 \approx 0.6$) for the phenol sorbate systems, corresponding with projections from the Boyd plots. From the results of the study, the rate controlling step for phenol sorption in the sediments was predominantly due to external mass transfer resistance. A comparative analysis between the two sediments using the Furusawa -Smith equation gave the mass transfer coefficients for clay and sand to be 2.09205E-14 m s^{-1} and 4.17537E-12 m s^{-1} respectively, showing that as the particle size decreased, the more significant the effect of external mass transfer effect on the sorption rate.

Keywords: Contaminants, Adsorption, Sediment, Adsorbate, Adsorbent, Resistance

1. Introduction

The soil environment serves as a sink for hydrophobic organic contaminants such as phenols, due to intended, accidental, industrial or naturally occurring events which have led to the introduction of these chemicals into the soil environment [1]. Therefore, because of the ecological risks associated with sediment contamination and the ubiquitous nature of the problem, the assessment and remediation of polluted soil presents a major research issue for the environmental community.

Research has shown that efficient remediation of contaminated soil is predicated on the accurate technical assessment of the mobility, toxic potency, mass transfer parameters and availability of contaminants in a given matrix [2]; and currently much focus is directed at the resistance posed by soil sediments to the transport of organic pollutants, as time required to reach sorption equilibrium or complete desorption in field contaminated sites can be months to years, therefore posing a challenge to remediation efforts. The evaluation of slow sorption and sorbent resistance effects are an important aspect to the science of environmental resource remediation, due to the influence of slow sorption on the fate and behaviour of sediment-sorbed organic compounds, with respect to their bioaccumulation, biodegradation and transport.

Several control mechanisms have been adduced for slow sorption: the limiting processes are hypothesized to be the retarded diffusion in the intra-particle pore space or the diffusion into the soil organic matter (SOM) [1, 2-4]. Studies on mass transfer effects for the evaluation of bioavailability and biodegradation parameters of contaminant solutes in aqueous solid/sediment matrix applicable for biodegradation of the environmentally persistent and recalcitrant chemicals have been extensively investigated using models [5], which

incorporate two-site sorption/desorption kinetics. But largely the mechanisms governing sorption resistance are still largely unknown, and it is also necessary to distinguish between the processes in pores and in SOM in accounting for the differential influence of these factors on mass transfer resistance to contaminant solutes [6]. Against this background, this study intends to determine mass transfer resistance of phenol in soil sediments by studying the rate limiting steps and the associated resistance to the transport of phenol in soil matrix using established models.

It is considered that an elucidation of these complex mechanisms in heterogenous matrix could be better understood by kinetic modelling in homogenous soil fractions. Therefore, this study evaluates the mass transfer effects described in the sorption of a priority pollutant phenol [7] in two homogenous soil sediments: clay and sand, with a view to determining the effect of sorbent-posed resistance to the transport of dissolved organics.

Batch experiments were conducted and the kinetic data tested with pseudo first-order, pseudo second-order, Elovich, Fractional Power (Power function), and intraparticle diffusion models to determine the rate of adsorption and process mechanism. The rate limiting step and mass transfer resistance were evaluated and comparatively analyzed from the sorption kinetics, using the Weber-Morris equation, the Boyd plot and the Homogenous pore diffusion model (HPDM). Subsequently the effect of mass transfer resistance on adsorption rate was analysed using the Furusawa and Smith model [8].

2. Materials and Methods

2.1. Preparation of the Adsorbent

We sourced the clay and sandy soil samples used for this study from Ikpoba River, Benin City, Edo State, Nigeria. The clay and sandy soil samples were kept separately in a black polythene bags and stored in a refrigerator to ensure anaerobic conditions. Pre-treatment of the samples was carried out by removing stones and other heavy particles. A 220 μm mesh was used to remove the large non-clay fractions from the clay. A mesh size of 2.5 nm was used to sieve the sandy soil. The soils were dried overnight at 383 K in a vacuum oven and stored in an air tight container covered with a black polythene bag prior to the adsorption experiments [9].

2.2. Removal of Possible Presence of Organic Compounds in Soil Sediments

The soil samples were soaked in distilled water for two days while continuously stirring using a manual stirrer so as to loosen possibly present contaminants from the soil matrix. After which the mixture was drained, and then dried in a furnace. The dried soil samples were kept in black plastic bags. Physico-chemical properties of the clay and sandy soil samples such as moisture content, pH, specific gravity, bulk density, surface area, particle density and porosity were then analysed. The results are shown in Table 1.

2.3. Phenol

The adsorbate; phenol was procured at a Chemical Laboratory in Benin City, Edo State, Nigeria. 200mg, each of phenol were weighed separately into two beakers; 1000ml of water was added to the beakers. 100 g of each of the sediments (clay and sand) were weighed and mixed with 500 ml of the solution taken from the beakers, to form two different slurry solutions, at room temperature following the procedure of Owabor et al., 2013 [1]. After stirring the solutions, 25 ml of the sample-solution was placed into 50ml capacity volumetric flask, and the pH of the solution was adjusted to 7.0. 1ml of ammonia solution was added, 10ml of nitroprussia buffer solution was also added, then mixed properly. Promptly Hydrochloric reagent was added to fill the volumetric flask to the mark. The flask was stopped, and mixed well by inversion. The mixture was left for 45 minutes for complete development of the indo-phenol column. Measurements at an absorbance were carried out against reagent blank. The slurry suspensions were sampled at intervals of 3 hours using Gas Chromatogram Flame Ionization deflector.

2.4. Adsorption Studies

The rate of adsorption of phenol unto the various soil samples was determined from the uptake levels from aqueous solution in batch experiments before and after contact until adsorption equilibrium was attained in the soil samples. The slurry suspensions were sampled at intervals of 3 hours for a period of 3 days; and GC-FID was used for sample analyses. The uptake of the adsorbates at time t: q_t(mg/g) was calculated using the expression below;

$$q_t = \frac{(c_o - c_t)0.5L}{100g} \qquad (1)$$

Where q_e and q_t (mg/l) are the amount of adsorbate adsorbed per gram of adsorbent at equilibrium and at time t; C_0 and C_t (mg/l) are the initial concentration, equilibrium and concentration at time t of phenol.

2.5. Kinetic Modelling

Adsorption kinetics describes the relationship between the rate of solute uptake and adsorption time. In order to verify the adsorption kinetic models, the pseudo-first order, the pseudo-second-order, the Elovich and intra-particle diffusion models were applied to the experimental raw data.

2.5.1. Pseudo First-Order Model

$$In(Q_e - Q_t) = InQ_e - k_f t \qquad (2)$$

Where $Q_e(\frac{mg}{g}) = (C_o - C_e) \times \frac{0.5L}{100g} \qquad (3)$

2.5.2. Pseudo-Second Order

$$\frac{t}{Q_t} = \frac{1}{K_s q_e^s} + \frac{t}{Q_e} \qquad (4)$$

2.5.3. Elovich Model

$$Q_t = In\left(\propto b\right)/b + In\,t/b \qquad (5)$$

2.5.4. Intra-Particle Diffusion Model

The intra-particle diffusion model equation can be written as follows [10]:

$$Q_t = K_{id}t^{1/2} + C \qquad (6)$$

Where K_{id} the intra-particle rate constant (mg.g^{-1}.min$^{-1/2}$) and C is is the intercept on the Q_t axis. By plotting Q_t (mg.g^{-1}) versus t $^{1/2}$ one should obtain a linear graph if the intra-particle diffusion is involved in the adsorption process.

If the straight line passes through the origin, the intra-particle diffusion is the rate limiting step.

2.5.5. The Fractional Power Model

The fractional power known as power function model can be expressed as:

$$Q_t = Kt^v \qquad (7)$$

The above is linearized as:

$$Log\,Q_t = \log K + v\log t \qquad (8)$$

The parameters v and k are determined from slope and intercept of a linear plot of log Q_t versus log t [11].

2.6. Validity of the Kinetic Data

The suitability, agreement and best fit among the kinetic models is adjudged using the statistical validity models such as sum of square error (SSE), Chi-square test (χ^2) and normalized standard deviation (Δq).

2.7. The HPDM and Boyd Plot Modelling

A comparison was made between the homogeneous pore diffusion model and Boyd's model, so as to ascertain the adsorption rate-controlling step.

2.8. Homogenous Particle Diffusion Model (HPDM)

In order to evaluate the rate limiting step, the *Homogenous Particle Diffusion Model* was applied. In this model, the sorption mechanism involves the diffusion of solute molecules from the aqueous solution into the sorbent phase through a number of possible resistances. The sorption of the organic compound molecules can be rigorously described by Fick's equation. This applies to the diffusion of organic compounds in a quasi-homogeneous media such as that under study:

The homogenous particle diffusion model is given below;

$$X(t) = 1 - \frac{6}{\pi^2}\sum_{z=1}^{\infty}\frac{1}{z^2}\exp\left[\frac{-z^2\,\pi^2\,D_{eff}t}{r^2}\right] \qquad (9)$$

Where $X(t)$ is the fractional attainment of equilibrium at time t, D_{eff} the effective diffusion coefficient of sorbate in the sorbent phase (m^2 s^{-1}), $r(m)$ the radius of the sorbent particle assumed to be spherical in shape (m), and z is an integer.

$X(t)$ values could be calculated by using the following equation:

$$X(t) = \frac{q_t}{q_e} \qquad (10)$$

Where q_t and q_e are solute loading on the solid phase at time t and when equilibrium is attained (mg g−1), respectively. Vermeulen's (1953) [12], approximation of the Eq. (2.16) fits the whole range $0 < X(t) < 1$, for sorption on spherical particles:

$$X(t) = \left[1 - \exp\left[-\frac{\pi^2\,D_e^2\,t}{r^2}\right]\right]^{1/2} \qquad (11)$$

This equation could be further simplified to cover most of the data points for calculating effective particle diffusivity by using the following expression:

$$-In\left(1 - X^2(t)\right) = 2Kt, \qquad (12)$$

$$where\ K = \frac{\pi^2\,D_e}{r^2} \qquad (13)$$

2.9. Boyd Plot

The slow step involved in the adsorption process was predicted by Boyd plot. The Boyd kinetic expression is given by Vadivelan et al., 2005 [14].

$$F = 1 - (6/\pi(22)2)\exp\left(-B_t\right) \qquad (14)$$

and

$$F = {Q_t}/{Q_0} \qquad (15)$$

where

$$B_t = -0.4977 - In(1 - F) \qquad (16)$$

Where Q_0 is the amount of adsorbate adsorbed at infinite time (mg/g), which equates with the amount adsorbed at equilibrium and Q_t represents the amount of adsorbate adsorbed at any time t (min), B_t is a mathematical function of F, and F represents the fraction of solute adsorbed at any time t.

2.10. The Modified Furusawa and Smith Model

Furusawa and Smith model was used to analyse the effect of external mass transfer resistance on adsorption rate. The mass transfer coefficient, k_f (ms^{-1}), of phenol at the adsorbent solution interface was determined by using:

$$\left(\frac{1}{1+1/mK_L}\right)In\left(\frac{C_t}{C_0} - \frac{1}{mK_L}\left(1 - \frac{C_t}{C_0}\right)\right) = -kAt \qquad (17)$$

Where k_L is a constant (L/g) and m and A are the mass and outer surface of the adsorbent particle per unit volume of particle free slurry (g/L and m−1), respectively. A linear plot of f(t) $= In\left(\frac{C_t}{C_0} - \frac{1}{mK_L}\left(1 - \frac{C_t}{C_0}\right)\right)$ versus t was plotted and the coefficient k_f was found. The value of k_L was determined from previous studies [7, 15].

$$A = \frac{6M}{V d_p \rho (1-\varepsilon_p)} \qquad (18)$$

Where V is the volume of solution (L), M is the adsorbent mass (g), ε_p is bed porosity, and ρ is bulk density (g/cm^3)

# 3. Results and Discussion

3.1. Characterization of Soil Sediments

Presented in Table 1 are the results from the physico-chemical analysis of clay and sand.

Table 1. *Physico-chemical analysis of clay and sand.*

Parameters	Clay	Sand
Bulk density (g/cm^3)	1.16	1.58
Surface area (mm^2)	6.25 x 10^{-8}	7.65 x 10^{-5}
Particle density (g/cm^3)	2.837	2.659
Moisture content (%)	4.25	2.35
Effective diameter (cm)	2 x 10^{-4}	0.026
Ph	7.1	7.1
Porosity (%)	45.9	39

3.2. Equilibrium Time for Adsorption

The time dependent plot of the concentration of solute as shown in figure 1, shows that at the 21st hour the phenol/sand system attained equilibrium while phenol in clay system attained equilibrium after 27 hours, which gives an early indication that the nature (physical properties) of the soil sediment affect the rate of adsorption of the solute. As the hindrance to diffusion is more in the clay soil with a comparable smaller particle size to that of the sandy soil.
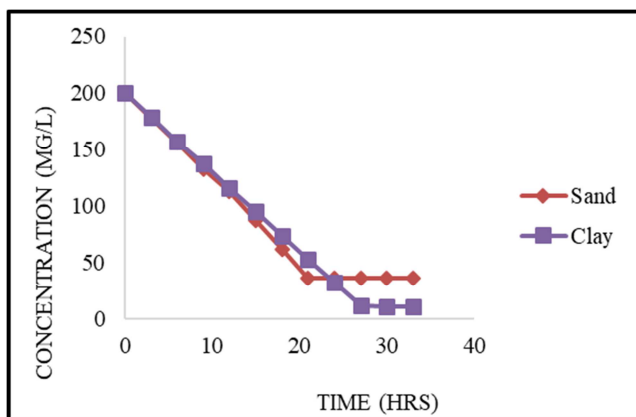
Figure 1. *Variation of concentration with time for phenol in soil sediments.*

3.3. Adsorption Kinetics and Mechanism of Reaction

The results of the kinetic modelling using the pseudo first-order, pseudo second-order, Elovich, intraparticle diffusion and fractional power plots are shown in table 2.

Table 2. *Kinetic parameters from the different kinetic model.*

Kinetics model parameters	PHENOL	
	Sand	Clay
Pseudo first order		
R^2	0.6875	0.6067
q_e(mg/g)	1.5401	0.8049
k_1(min^{-1})	0.0025	0.0011
SSE	0.519	0.02
χ^2	0.337	0.025
$\Delta q\%$	87.9	14.9
R^2	0.6875	0.6067
Pseudo Second order		
R^2	0.3063	0.4628
q_e(mg/g)	6.605	7.037
k_2(g/mg/min)	1.5E-5	1.257E-5
SSE	33.473	37.09
χ^2	5.06	5.207
$\Delta q\%$	706	543.16
Elovich model		
R^2	0.9325	0.9367
α(g min^2/mg)	2.64E-3	2.12E-3
β(g min/mg)	2.51	2.726
q_e(mg/g)	0.8442	0.8936
SSE	6.15E-4	2.84E-3
χ^2	7.29E-4	3.18E-3
$\Delta q\%$	3.02	0.056
Intra-particle diffusion model		
R^2	0.9731	0.9817
q_e(mg/g)	0.8776	1.00
C	-0.3258	-0.357
k_p(mg/g/min$^{0.5}$)	0.0297	0.0305
SSE	3.387E-3	2.83E-3
χ^2	3.86E-3	0.17
$\Delta q\%$	7	0.435
Power		
R^2	0.9898	0.9936
v(min^{-1})	0.9585	0.9537
k_p(mg/g)	3.11E-3	7.79E-4
q_e(mg/g)	1.164	1.5417
SSE	0.119	0.354
χ^2	0.102	1.229
$\Delta q\%$	0.42	62.8

Applying the regression coefficient (R^2), the chi square test(χ^2) and the SSE parameters, the adsorption kinetics data were generally best described by the intra-particle ($R^2 > 0.9731$). The regression coefficients obtained from the Pseudo-first order and the pseudo-second order modelling was generally low and the chi square test(χ^2) and the SSE parameters gave a very large error margin.

The observed good approximations of the correlation co-efficient obtained from the intra-particle model for phenol was consistent for both clay and sand sediments which affirms the suitability of the model. The experimental quantity adsorbed at equilibrium and the calculated quantity adsorbed at equilibrium (qe$_{exp}$ and qe$_{cal}$) from the model were in close agreement given the low values for the chi square test(χ^2) and the SSE parameters, further confirming good experimental fit.
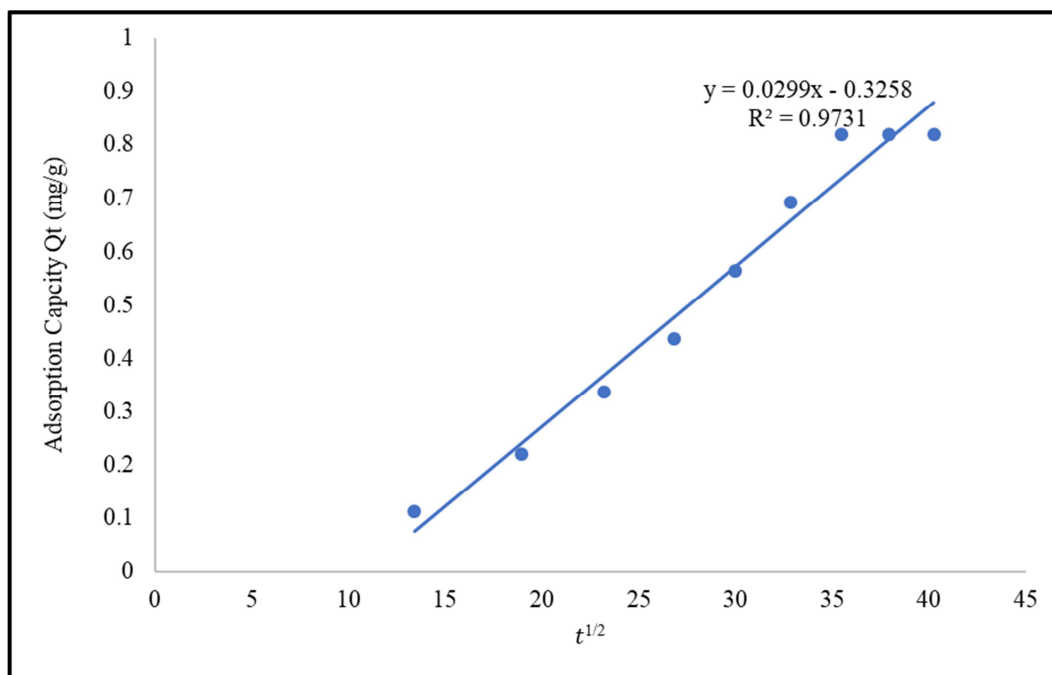
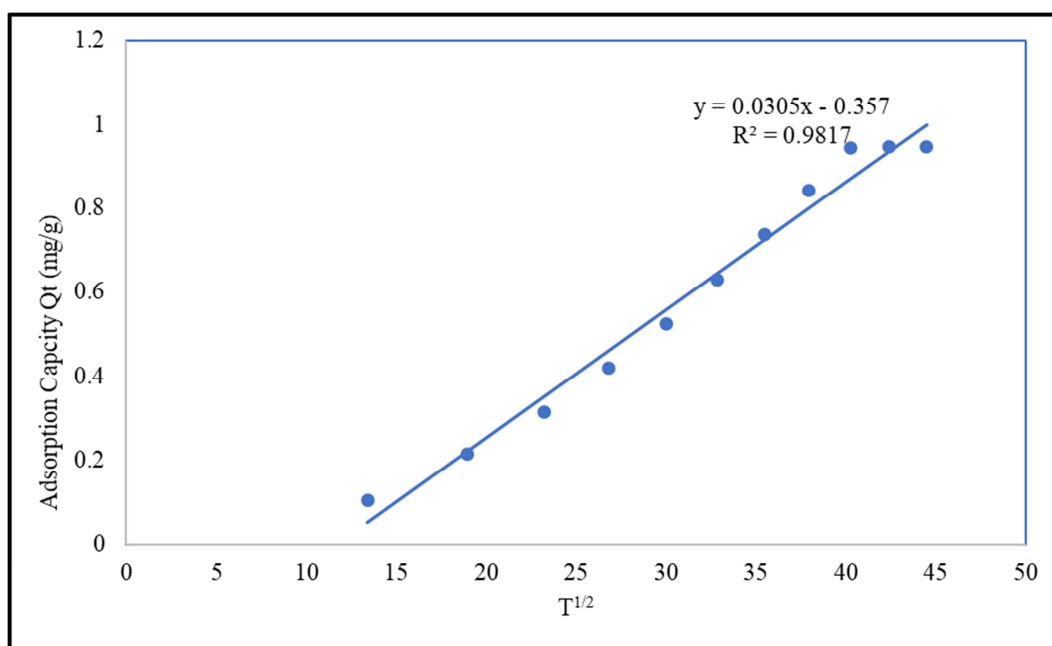*Figure 2. Intra-particle / Weber-morris modelling for phenol/ sand adsorbate system.*

Figure 3. Intra-particle/ Weber-morris kinetic modelling for phenol/ clay adsorbate system.

As is observed, the plot of q_t versus $t^{1/2}$ did not pass through the origin, indicating that intraparticle pore diffusion is not the rate-determining step [16, 17], which suggests that other steps like external diffusion and liquid film diffusion may be involved in the rate-determining steps.

Since, the aim of this kinetic study is to evaluate the effect of resistance to mass transfer of phenol in the different sediments, the intercept of the intra-particle plots: figure 2 and 3; which defines the thickness of the surface and provides an insight into the transfer of contaminant solute within the boundary layer (i.e. contribution of the surface adsorption in the rate-determining step) was evaluated at -

0.3258 and -0.357 for sand and clay respectively, which were very low, indicating that boundary layer effect on sorption is minimal.

3.4. Results for HPDM and Boyd Modelling

Figures 4-5 shows the results for the HPDM model; and figures 6-7 show the Boyd plots. It can be observed that HPDM model gave a poor fit ($R^2 \approx 0.6$) for the both sediment system which negates resistance due to intrapore diffusion mechanism as the controlling step; but indicates film and external diffusion mechanisms in the rate-limiting step..
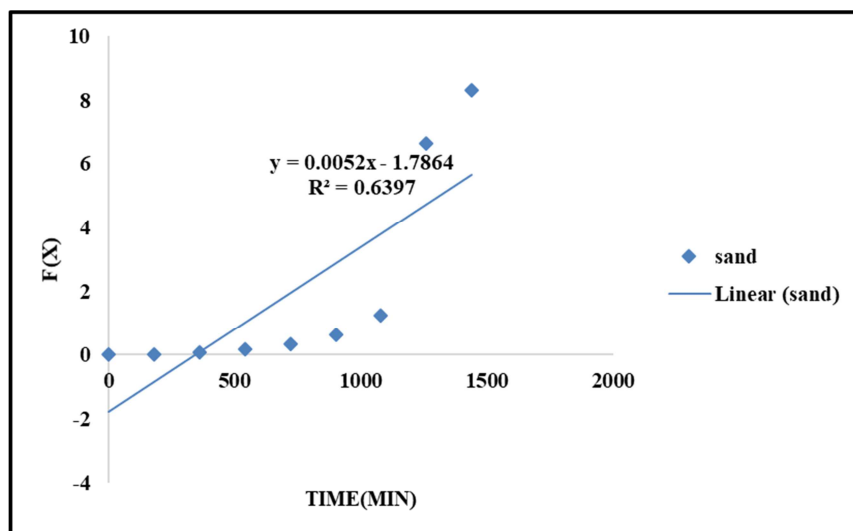
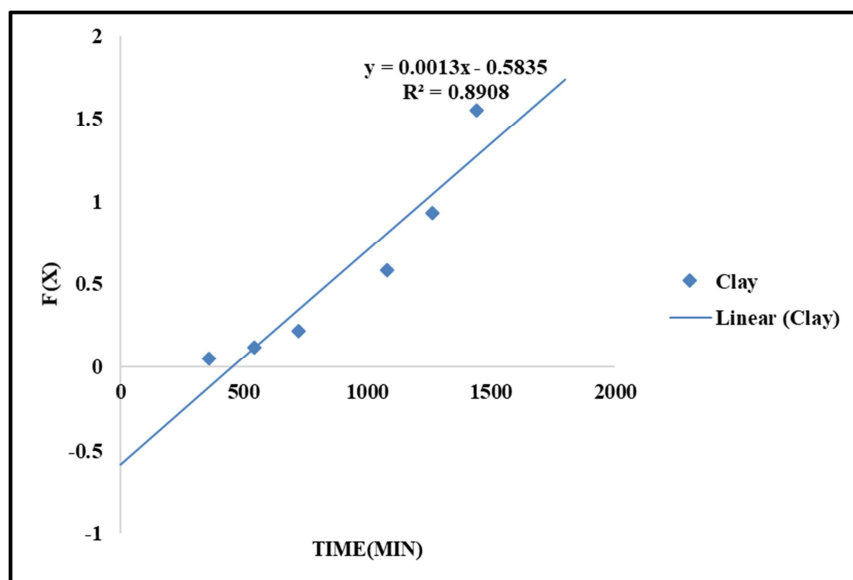***Figure 4.*** *Test of kinetic model equation of HPDM for Phenol/sand system.*

Figure 5. *Test of kinetic model equation of HPDM for Phenol/clay system.*
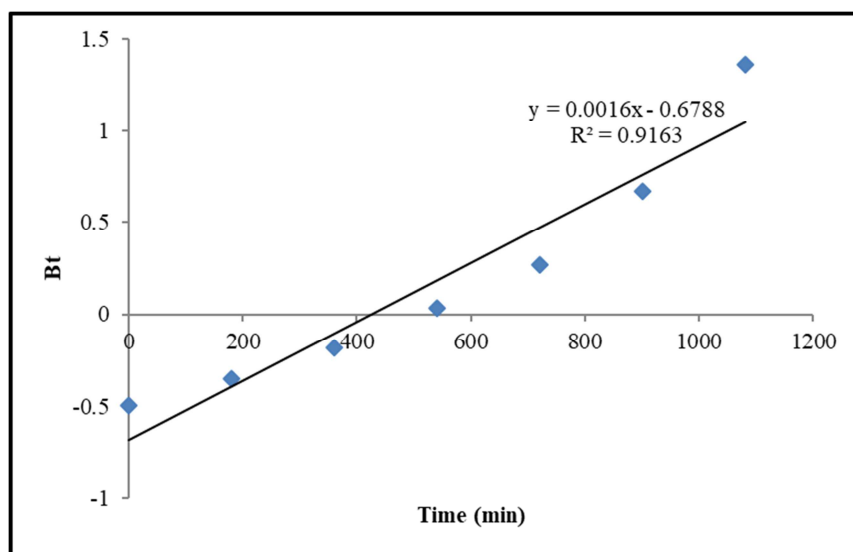

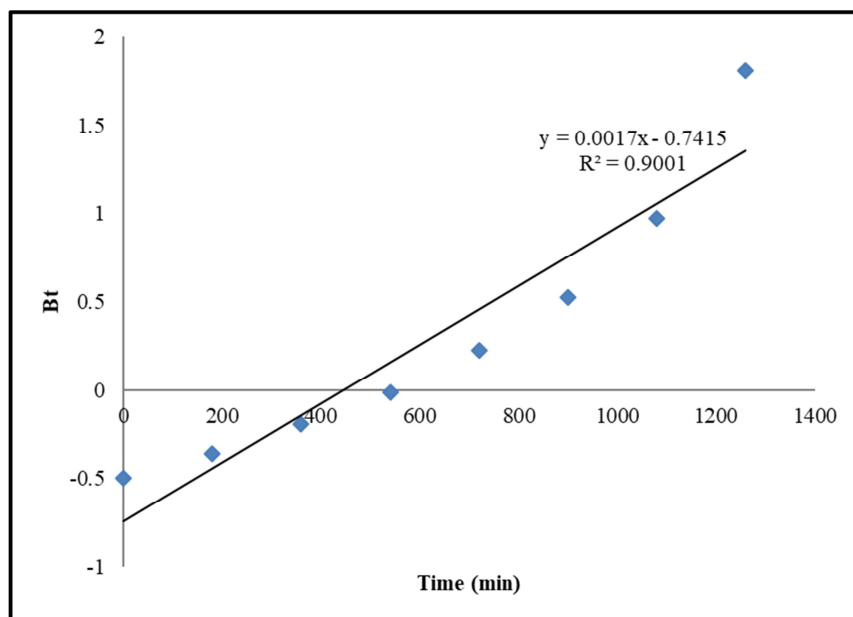***Figure 6.*** *Boyd plot for phenol/sand.*

***Figure 7.** Boyd plot for phenol/clay.*

The results obtained from the HPDM corresponded with projections from the Boyd plots. The Boyd plots for phenol showed straight lines which did not pass through the origin indicating external diffusion as the rate limiting step [18], which may explain why phenol sorption could not be modelled in the HPDM.

In summary, phenol transport in the sediments was limited by resistance due to external and film diffusion.

3.5. Evaluation of the Effect of External Mass Transfer Resistance on Adsorption Rate Using the Furusawa-Smith Model

External mass transfer resistance is generally correlated in terms of a mass transfer coefficient (k_f). An increase in the k_f value indicates a decrease in the external mass transfer resistance. The furusawa- smith model for external film diffusion is developed based on external film diffusion being predominant during the initial sorption period and controlling the sorption rate, [19] which is the case for phenol sorption in the sediments. The furusawa-smith plot for phenol in the sediments is given in figures 8 and 9.
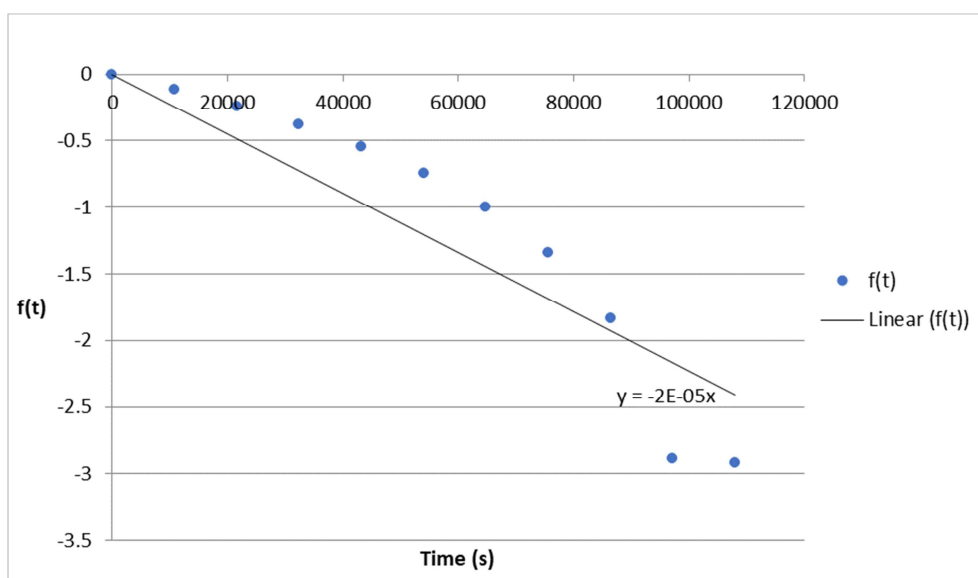

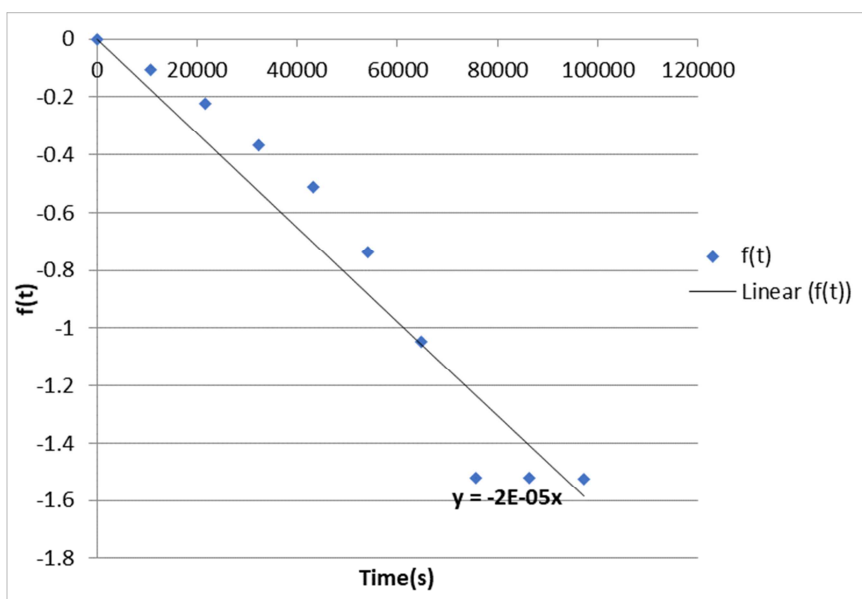***Figure 8.** Furusawa-smith plot for phenol in clay.*

Figure 9. Furusawa-smith plot for phenol in sand.

From the above plots the value for the slopes are approximately the same. Given that A (surface area of sediment particle per unit volume of solution for clay and sand respectively are 9.56E8 m^{-1} and 4.79E6m^{-1}, the value of k_f for the sediments are 2.09205E-14 m s^{-1} and 4.17537E-12 m s^{-1} which are very low values of k_f indicating that the change in fluid phase concentration, C; with respect to time, t; is related to the fluid phase concentration at the external surface, Cs and that external mass transfer resistance on adsorption rate increases with time i.e. external mass transfer resistance is generally correlated in terms of mass transfer coefficient (kf), as an increase in the k_f value indicates a decrease in the external mass transfer resistance.

4. Conclusion

From the results of the study it is clear that the rate controlling step for phenol sorption in the sediments was due to external mass transfer resistance. A comparative analysis between the two sediments showed that as the particle size decreased, the external mass transfer effect on the sorption rate became more significant which was also reported in Erdogan., 2011 [19]. Increasing the particle size resulted in a greater time to reach equilibrium. As the particle size increased, the distance for diffusion of solute molecule in the particle become longer and thus the solute required more time to diffuse to the interior of the particle.

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