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Research Article

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Modeling of Experimental Adsorption Isotherm Data for Chlorothalonil by Nairobi River Sediment

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Abstract

The present study deals with modeling of experimental adsorption data of chlorothalonil by Nairobi River sediment. Effects of initial concentration, different shaking time and contact time were investigated. The concentration of chlorothalonil in the clear aqueous solution (C_e) was determined by reversed phase HPLC. Determinations were made using the 15 cm MCH-5- N-CAP C_{18} column and 85% HPLC grade acetonitrile in distilled water as the mobile phase. Adsorption isotherm study indicated that the Quasi Langmuir (Scatchard plot) fitted the experimental data with heist regression values range of 99.8 to 100. Thermodynamic study calculations shows that the Gibbs free energy for chlorothalonil was -9.2687 kj/mol calculated using Freundlich and Langmuir constants. The maximum adsorption capacity of Nairobi river sediment was 33.389 mg/ml. Finally, Kinetics study revealed that the adsorption of chlorothalonil onto Nairobi river sediment falled a pseudo second order kinetics.

Keywords: Adsorption; Chlorothalonil; Isotherms; Kinetics; Thermodynamics

Introduction

Use of pesticide residues is accompanied by environmental pollution. When a pesticide molecule is applied, it undergo leaching, vaporization, adsorption, degradation, hydrolysis among other processes. Adsorption/desorption phenomenon is one of the most effective technologies used to remove persistent pesticide molecules in the environment. To effectively use adsorption/desorption process in environmental protection, scientist apply adsorption isotherm models. Adsorption isotherm is generally a curve describing the phenomenon governing the mobility and the retention of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [1,2]. The ratio between the adsorbed amount with the remaining in the solution (adsorption equilibrium) is established when an adsorbate containing phase and adsorbate concentration in the bulk solution has been contacted with the adsorbent for sufficient time [3,4]. Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration [5]. Its physicochemical parameters together with the underlying thermodynamic assumptions which provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents [6]. Scientist have constantly formulated equilibrium isotherm models which include Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherms in terms of three fundamental approaches [7] Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [8]. Thermodynamics is the second approach which provide a framework of deriving numerous forms of adsorption isotherm models [9,10]. Thirdly potential theory is the third approach which conveys the main idea in the generation of characteristic curve [10]. The trend of the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [11,12]. This paper focusses on modelling of adsorption isotherms of chlorothalonil onto Nairobi River sediment as a subject of initial concentration and shaking time.

Experimental Materials and Reagents

Chlorothalonil (IOBA Chemmie, 99% pure) acetone (Panreac quimica, 95%) and Acetonitrile (HPLC analytical grade 85% from Fisher Scientific Co. (Fairlawn, NJ). were used as received. An orbital shaker fitted stopwatch was used for all timing purposes. Distilled water was used for all preparations. The sediments used in these experiments were collected from the Nairobi River which is about 200 m from the Department of Chemistry, University of Nairobi.

Instrumentation

All UV-Visible spectrophotometric measurements were taken on UV-Visible spectrophotometer (1700 model, Shimadzu Corporation, Kyoto Japan). All reversed phase chromatographic measurements were done using a HPLC instrument (Shimadzu Corporation, Kyoto Japan) fitted with a tunable SPD-20A Prominence UV-Vis detector and a Prominence LC and CTO-10-AS VP Shimadzu column oven. A 15 cm MCH-5-N-CAP C_{18} column was employed. A Fischer scientific A-160, analytical balance was used for all weight measurements.

Procedure

Solutions of chlorothalonil in acetone in the concentration range 0-100 ppm were prepared. Each of the 20, 40, 60, 80, 100 ppm solutions prepared was scanned using the UV-Vis spectrophotometer on a wavelength range of between 200-900 nm.

Sorption experiment

In order to model the experimental data, 0.5 g of the dried sediment was shaken with 10 ml distilled water spiked at 100, 200, 300, 400 and 500 mg/ml levels of chlorothalonil. Each of the samples in quadruplicate was shaken for 15, 30, 45 and 60 minutes in an Orbital shaker. The

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sediment was then allowed to settle for 12 hrs, after which the water phase was decanted, and then filtered through Whatman A40 filter paper. The concentration of chlorothalonil in the clear aqueous solution (C_e) was determined by reversed phase HPLC. Determinations were made using the 15 cm MCH-5- N-CAP C_{18} column and 85% HPLC grade acetonitrile in distilled water as the mobile phase. An assumption made in arriving at the modelling data was that the addition of sediment to the solution does not alter the volume of the solution significantly. The data was fitted into Freundlich, Langmuir, Quasi Langmuir 1, Temkin, Dubinin-Radushkevich and Scatchard isotherm models [13]. Adsorption kinetics constants was determined using Pseudo first order, Pseudo second order and intraparticle diffusion model [14-17]. The amount adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and van Greikenm [18].

$$Q_e=V(C_i-C_e) \qquad 1$$

Where Q_e is the amount of solute adsorbed from the solution, V is the volume of the adsorbate, C_i is the concentration before adsorption, C_e is the concentration after adsorption, and w is the weight in gram of the adsorbent.

Results and Discussion

The sorption isotherms of chlorothalonil by Nairobi River sediment were studied by fitting the obtained data to Freundlich, Langmuir, Quasi Langmuir 1, Quasi Langmuir 2**,** Temkin, Dubinin-Radushkevich and Scatchard isotherm models.

Langmuir isotherms

The Langmuir [19] model assumes that uptake of pesticide molecule occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules and uniform energies of adsorption. The Langmuir equation

$$q_e=q_m bC_e/1+bC_e \qquad 2$$

where qe is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the pesticide molecule (mg/L), qm (mg/g) is the maximum amount of adsorbed molecules per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, K_L (L/mg) is the Langmuir constant related to the energy of adsorption. This can further be written as:

$$C_e/q_e=1/b\ Q^0+C_e/Q^0 \qquad 3$$

A plot of C_e/q_e versus C_e gives a straight line with intercept of 1/ b Q^0 and slope of 1/ Q^0 (Figure 1)

The regression values obtained for the Langmuir adsorption isotherm model ranged from 65.8 to 93.3. The Langmuir constant b increases with shaking time. The Langmuir constant b is 44.8504 (Table 1).

Quasi Langmuir isotherm 1

A special case of Langmuir is described in the following equation [20]

$$q_e=Q_o K_L C_e/1+K_L C_e \qquad 4$$

Equation 4 can be linearized as follows

$$1/q_e=(1/K_L Q_0)\ 1/C_e+1/Q_0 \qquad 5$$

This means a plot of $1/q_e$ versus $1/C_e$ is linear with 1/ $K_L Q_0$ as the slope and intercept as $1/Q_0$ and is shown by Figure 2. Being a modified Langmuir isotherm, the data for quasi Langmuir model fitted well into t (R ≥ 0.87.4) (Table 2). The Langmuir constant values, K_L ranges from 0.00219 to 0.02051. The isotherm can be explained by a dimensionless constant separation parameter given below

$$R=1/[1+K_L C_o] \qquad 5$$

If the value of R_L lies between 0 and 1, the adsorption process is favorable, if R_L is greater than 1, the adsorption process is unfavorable [21]. The RL values obtained in this study is greater than 1 indicating low affinity of chlorothalonil to Nairobi River sediment.

Quasi Langmuir 2

Langmuir adsorption isotherm has been modified by many scientist. In the following modification, the Langmuir adsorption has been modified linearly as shown in equation 6 below

$$q_e=q_m-q_e/K_L C_e \qquad 6$$

A plot of q_e versus Q_e/C_e is linear and is indicated in the Figure 3 below.

Freundlich equation

The Freundlich [22] equation is an empirical equation based on

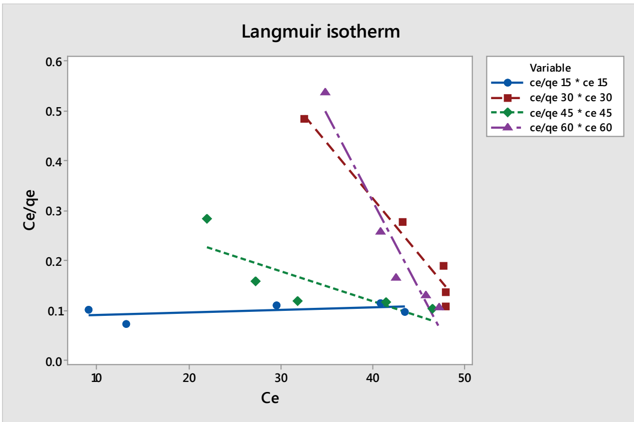

Figure 1: Lanngmuir isotherm model Assumption made is that the adsorbed chemical species do not react with one another. From Figure 1 above, the following constants are calculated.

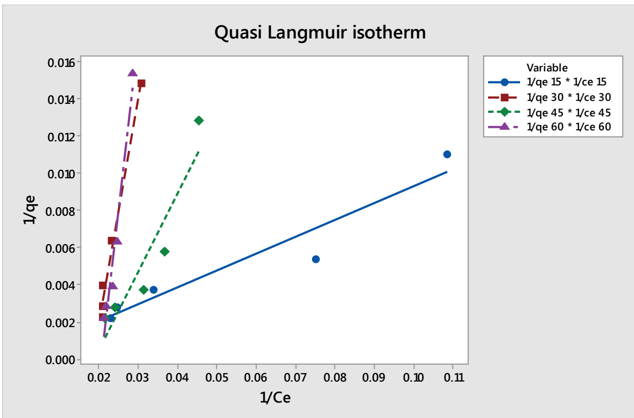

Figure 2: Quasi Langmuir adsorption isotherm model The parameters of Quasi Langmuir adsorption isotherm are stipulated in Table 2.

Time in minute	1/ Q^0	1/ b Q^0	b	R_2	ΔG
15	0.000528	0.08384	15.8787	94.3	-12.4032
30	0.02229	1.218	54.6433	95.8	-9.7923
45	0.005989	0.3583	59.8264	65.8	-10.0141
60	0.03540	1.737	49.0678	93.3	-9.5289

Table 1: Langmuir adsorption isotherm parameters.

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adsorption on a heterogeneous surface. The equation is commonly represented as:

$q_e = K_F Ce^{1/n}$ 7

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed pesticide molecule per unit mass of the adsorbent. The constant n (measure of adsorption non-linearity between solution solute concentration and adsorption) is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface [23] K_F (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (Table 3).

Taking the logarithm on both sides

$\ln q_e = \ln K_F + 1/n \ln C_e$ 8

This means that a plot of $\ln q_e$ against $\ln C_e$ is linear with slope of 1/n and is shown in Figure 4.

The Freundlich isotherm model is seen to fit strongly in the adsorption of chlorothalonil unto Nairobi River sediment at all contact times investigated ($R^2 \geq 0.89$) (Table 4)

From the above parameters, the values of K_{OC} was calculated from K_d values. The percentage organic carbon for Nairobi River sediment was 0.85%.

$K_O = K_d/\%OC$ 9

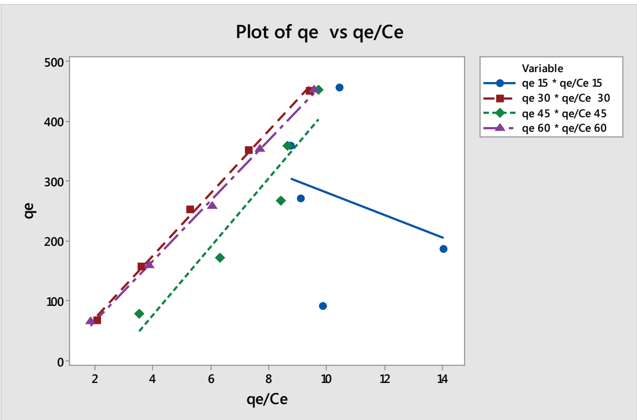

Figure 3: Quasi Langmuir isotherm model 2 Form Figure 3 above, it is evident that the slight modification of the Langmuir model does not bring any difference to the values of the Langmuir constants. The regression values obtained in this special Langmuir model ranges from 0.78 to 0.98. This is shown in Table 3.

Time in minute	$1/K_LQ_0$	$1/Q_0$	K_L	R_L	R_2
15	0.09070	0.000199	0.00219	0.219	92.1
30	1.204	0.02196	0.01822	3.644	98.4
45	0.420	0.007885	0.01877	5.631	87.1
60	1.803	0.03698	0.02051	8.204	95.9

Table 2: Quasi-Langmuir isotherm parameters.

Time in minute	q_m	K_L	R_2
15	472.5	19.10	7.9
30	33.41	52.23	99.8
45	153.6	57.24	90.3
60	34.57	50.21	99.8

Table 3: Quasi Langmuir 2 parameters.

$K_d = q/c$ 10

From the above equations, $K_d = 10.4631$

$K_{OC} = 10.4631/0.85 = 12.3095$

Temkin isotherm equation

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [24]. The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} Ln(K_T C_e) \quad (11)$$

Where, T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol. K), K_T is the equilibrium binding constant (L/mg), and b_T is the variation of adsorption energy (kJ/mol). B_T is Temkin constant related to the heat of adsorption (kJ/mol). This can be rearranged linearly as:

$$q_e = B_T ln(K_T C_e) + B_T LnC_e \quad (12)$$

Therefore a plot of q_e against $\ln C_e$ is linear (Figure 5). From the plots, the data in Tables 5 and 6 was obtained

Like in Freundlich isotherm, the curve fits better at higher contact times. This is expected since at higher contact times, equilibration is achieved and thus the adsorbents interaction has equilibrated, i.e., the rate of forward and backward reactions are equal. At lower contact times, this has not been achieved and therefore the points are more diverse (Figure 6). Dubinin-Radushkevich (D-R) Isotherm was applied to the obtained data to deduce the heterogeneity of the apparent adsorption energy on the adsorption site [24]. The equation linear form is given as

$\ln q_e = \ln q_D - B_D \varepsilon^2$ 13

Time in minute	1/n	ln K_F	K_F	R_2	ΔG
15	0.8753	2.724	15.2412	93.2	-6.6672
30	4.237	3.7690	43.337	89.5	-9.2249
45	2.219	2.314	10.1148	93.9	-5.6637
60	6.438	3.142	23.1501	98.7	-7.0294

Table 4: Freundlich isotherm parameters.

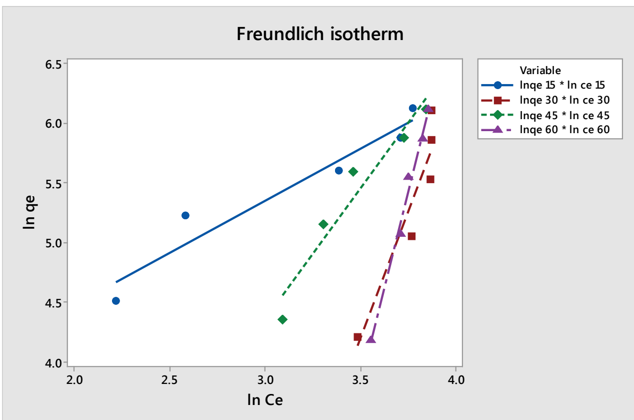

Figure 4: Adsorption isotherm from Figure 4 above, the following apparent thermodynamic parameters were calculated Table 4.

$$\acute{\varepsilon}=RT\ln[1+1/C_e] \quad 14$$

Where q_D is adsorption capacity of the adsorbent, B_D is the D-R isotherm constant related to energy, $\acute{\varepsilon}$ is the Polanyi potential. The plot of ln qe against ε^2 is shown in Figure 7. The D-R isotherms parameters are given in Table 6 below. The mean adsorption energy E (kj/mol) can be obtained from the value of B_D by using the formula. q_D and B_D were obtained by a plot of ln qe against ε^2 as shown above (Figure 8). The energy of chlorothalonil adsorption to Nairobi River sediment was calculated according to equation 15. The parameters are recorded in Tables 7 and 8.

$$E=1/[2\,B_D]^{1/2} \quad 15$$

When the adsorption energy is less than 8 kj/mol the sorption process is said to be dominated by physisorption (physical attachment of pesticide molecule to the soil surface), if E is between 8 and 16 kj/mol, the process is dominated by chemical ion exchange mechanism and if the value of E is greater than 16 kj.mol the process is dominated by chemical particle diffusion [24]. The value of E obtained in this work is 4.4445 kj/mol which indicates that the adsorption of chorothanil is dominated by physisorption as earlier noted by James et al. [25]. The scatchard plot analysis is applied to obtain comprehensive information on the affinity of of binding sites and to analyze the result of the adsorption isotherms [26]. The equation is given below

$$Q_e/C_e=Qb-q_e b \quad 16$$

Where Q and b are the Scatchard adsorption isotherm constants, if the plot of q_e/C_e versus qe gives a straight line, the adsorbent consist

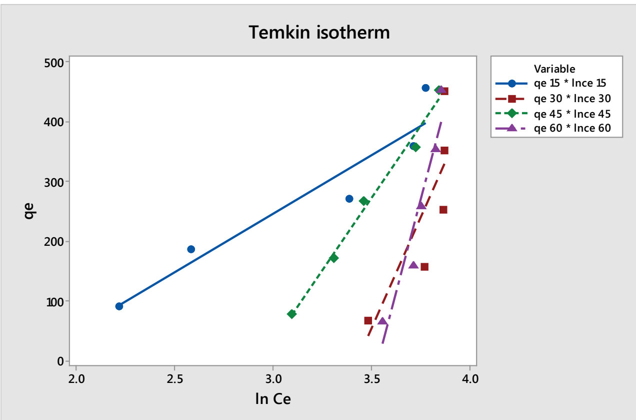

Figure 5: Temkin adsorption isotherm. The obtained values from the plots of the adsorption data obtained subject to Temkin equation are recorded in Table 5.

Time in minute	B_T	$B_T\ln K_T$	K_T	R_2
15	195.7	-341.1	0.17499	91.1
30	746.0	-2558	0.03862	66.7
45	485.1	-1425	0.05299	98.8
60	1235.0	-4361	0.02927	90.8

Table 5: Temkin isotherm parameters.

Time	Ln q_D	B_D	q_D	R^2	E(kj/mol)
15	5.974	0.000023	393.0748	93.9	3.7438
30	7.137	0.000535	1257.6498	85.1	3.5709
45	6.607	0.000185	740.2589	99.3	5.9875
60	8.382	0.000874	4367.7357	97.8	2.9187

Table 6: D-R isotherm parameters.

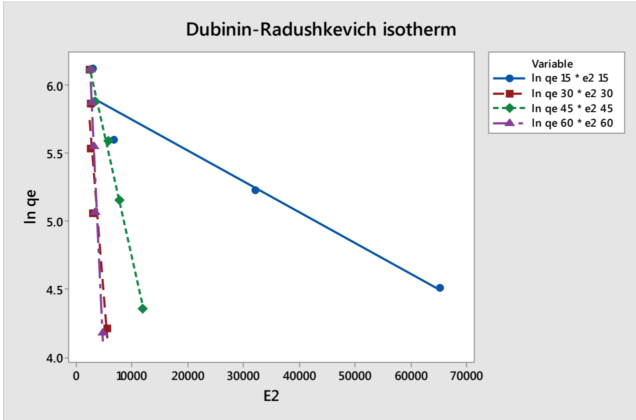

Figure 6: D-R adsorption isotherm model.

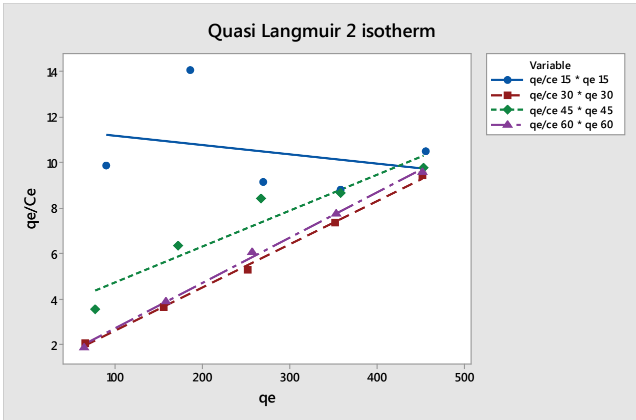

Figure 7: Scatchard adsorption isotherm model. The isotherm parameters obtained from the plots in Figure 7 are shown in Table 7 below whereby the regression ranges from 0.903 to 0.998.

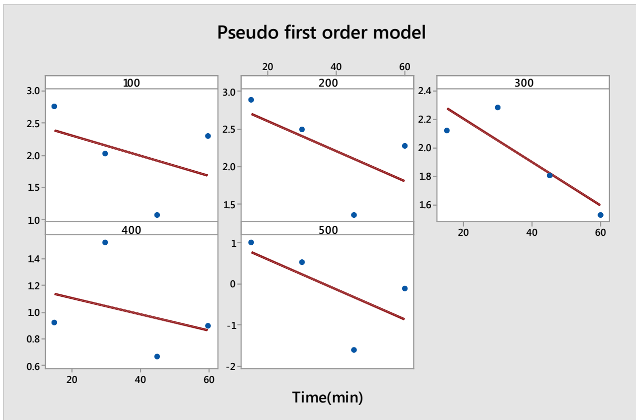

Figure 8: Pseudo first order model plot.

Time in minute	bQ_0	b	Q_0	R_2
15	2.6010	0.01416	183.6864	97.9
30	0.6499	0.01578	41.18501	90.3
45	3.133	0.01910	164.0314	99.8
60	0.7004	0.01987	35.24911	99.8

Table 7: Scatchard plot analysis parameter.

Initial Conc	Inq_e	k_f	R^2
100	2.625	0.01559	18.0
200	2.996	0.01975	35.0
300	2.502	0.01511	75.1
400	1.231	0.00613	10.5
500	1.334	0.03671	38.8

Table 8: Indicates the data obtained from the plot of ln(qe-qt) versus t.

of one type of binding site (homogeneous surface). However, if the plot deviates from linearity, then the adsorbent consists of more than one type of binding site. The regression value obtained is 0.903 which show high adsorption of chlorothalonil. Based on the higher regression values in Quasi-Langmuir isotherms (Scatchard plot), the experiment was found to follow this model. Since the data obtained in this study has the highest regression in this model, it's evident that the adsorbent consist of only one type of binding site (homogeneous surface) [26].

Adsorption kinetics

Kinetics is the major approaches used to evaluate biosorption dynamics whereby the constants are used to optimize the biosorption time. To examine the controlling mechanism of the biosorption process, various kinetic models were used to test the experimental data. In order to obtain the rate constants and order of sorption reaction, pseudo-first-order and pseudo-second-order kinetics model were applied to the kinetic data obtained at 298K at an optimize pH of 7 and initial pesticide residue concentration of 100, 200, 300, 400, 500 mg/L and at 15, 30, 45, 60 minutes shaking time.

Pseudo-first-order model

Different kinetic models have been used to describe the experimental data of heavy metals adsorption on biomass [13,14]. Pseudo first order Kinetic model of Lagergren [13] is based on the solid capacity for sorption analysis and expressed as follows,

$$dqt/dt=kf(qe-qt) \qquad 17$$

where qt is the amount of adsorbate adsorbed at time t (mg/g), kf is the rate constant of pseudo-first-order kinetics (min) and t is the time (min). The integration of Eq. (3) with the initial condition, qt=0 at t=0 leads to the pseudo first-order rate equation:

$$\ln(qe-qt)=\ln qe-kft \qquad 18$$

A straight line of ln(qe-qt) versus t suggests the applicability of this kinetic model. Pseudo first order rate constant (*kf*) (1/min) can be determined from the slope of the plot. This equation is, however, valid only for the initial adsorption period. The following figure and table shows the data obtained from the plot of experimental data.

Pseudo-second-order model

The pseudo-second order reaction kinetic model based on the sorption equilibrium capacity can be expressed as [15],

$$dqt/dt=ks\,(qe-qt) \qquad 19$$

where *k*S is the pseudo-second-order rate constant (g/mg min). Integrating Eq. (4) and noting that *qt*=0 at *t*=0, the following equation is obtained:

$$t/qt=1/ksqe+1/qet \qquad 20$$

The plot *t*/*qt* versus *t* should give a straight line if second-order kinetics are applicable, and *qe* and *ks* can be determined from the slope and intercept of the plot, respectively. The initial sorption rate, *h* (mg/g min), as *t*→0 can be defined as

$$h=ksqe^2 \qquad 21$$

The straight line plot for the pseudo first order sorption kinetic model between ln(qe−qt) vs. t was plotted (Figure 9) for sorption of chlorothalonil. The value of the rate constant calculated from the slope of plot with the correlation coefficient ranged from 0.00028 to 0.07347. The linear plot of pseudo second order kinetic model was also plotted between t/qt. vs. t, and sorption capacity and pseudo second order rate constants qe and ks were calculated from the slope and intercept of the plot (Figure 10). The pseudo second order kinetic constant ks and sorption capacity qe were 0.3236 g/mg min to 10.6346 mg/g. A high coefficient of determination, i.e., 0.998, was obtained for the pseudo second order kinetic model, and these results were good in comparison to pseudo first order model, indicating that process of uptake of chlorothalonil followed pseudo second order rate expression (Table 9). In addition to this initial sorption rate (h) were also calculated by using Eq. 21. The initial sorption rate were 0.0136, 0.079, 0.6329, 3.021 and 4.807 mg/min for 100, 200, 300, 400 and 500 mg/ml respectively (Table 10).

Intraparticle diffusion model

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model,

$$q_t=k_{id}t^{1/2}+I \qquad 22$$

where *k*id is the intra-particle diffusion rate constant. According

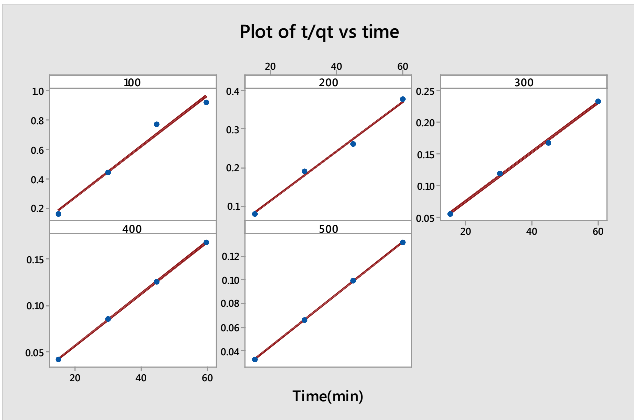

Figure 9: Pseudo second order model plot.

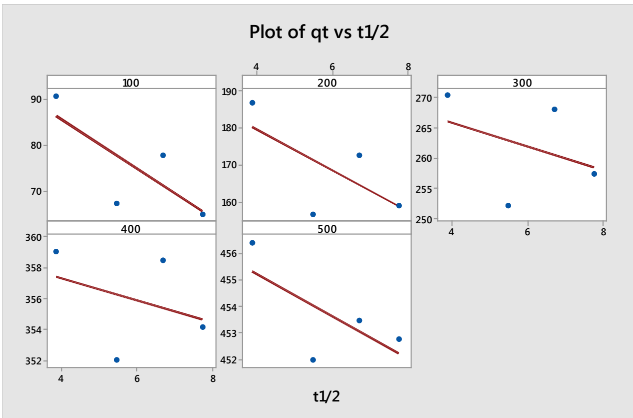

Figure 10: Intra-particle diffusion model the data obtained from the plots in Figure 10 above are given in Table 10.

Initial Conc	$1/k_s q_e^2$	$1/q_e$	k_s	H	R^2
100	0.07347	0.01734	0.23602	13.6109	98.0
200	0.01254	0.006399	0.51029	79.7448	99.1
300	0.001580	0.003877	2.45379	632.9113	99.7
400	0.000331	0.002822	8.52568	3021.1480	100
500	0.000208	0.002212	10.6346	4807.6923	100

Table 9: Pseudo second order kinetic parameter.

Initial Conc	I	k_{id}	R^2
100	107.3	5.382	58.3
200	201.6	5.522	43.9
300	273.7	1.958	14.2
400	360.2	0.719	12.2
500	458.5	0.806	47.6

Table 10: Intra-particle diffusion model parameters.

to equation 22, a plot of qt ½ versus t should be a straight line with a slope k_{id} and intercept I when adsorption mechanism follows the intra-particle diffusion process as shown in Figure 10. Low regression values were obtained with the plots not passing the origin. The values for k_{id} and I were in a range of 5.382 to 0.806 and 107 to 458.5 respectively. The value of I gives an insight about the thickness of the boundary layer. The larger the intercept, the greater is the boundary layer effect [27]. Deviation from the lines from the origin may have resulted from difference in the rate of mass transfer in the initial and final stages of adsorption. This is an indication that pore diffusion is not the sole rate controlling step.

Thermodynamic study

Thermodynamic properties of a adsorption/desorption process are necessary to conclude whether the process is spontaneous or non-spontaneous. The Gibbs free energy change, ΔG, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG is a negative quantity. The free energy of a biosorption reaction, considering the biosorption equilibrium constant Kc is given by the following equation,

$$\Delta G = -RT \ln Kc \text{ or } K_F \quad (23)$$

where ΔG is the standard free energy change (kJ/mol), R the universal gas constant, 8.314 J/mol K, and T is absolute temperature (K). Kc is the equilibrium constant, which is calculated from following equation,

$$Kc = C_{Ae}/C_e \quad (24)$$

where C_{Ae} is the equilibrium concentration of metal ion on the sorbent (mg/L) and C_e is the equilibrium concentration of metal ion in bulk solution (mg/L).

Conclusion

In this study, investigation of equilibrium sorption was carried at 298K. the sorption data of chlorothalonil adsorption onto Nairobi river sediment was fitted to Freundlich, Langmuir, Quasi Langmuir 1, Temkin, Dubinin-Radushkevich and Scatchard isotherm models out of which the data fitted the quasi Langmuir (Scatchard plot) best with highest regression values of 99.8-100. From the kinetics study, the adsorption of chlorothalonil obeyed pseudo second order kinetics. It's therefore in conclusion that different models should be used to fit adsorption experimental data to evaluate the best model to explain adsorption of different pesticide molecule.

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