

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

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## ABSTRACT

The investigated adsorption data of chlorothalonil on Nairobi River sediment using different models. 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 15cm MCH-5- N-CAP C18 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 showed 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. Kinetic studies revealed that the adsorption of chlorothalonil onto Nairobi river sediment followed a pseudo-second order kinetics.

**Keywords:** *Adsorption, Chlorothalonil, Isotherms, Kinetics, Thermodynamic.*

## I. INTRODUCTION

Use of pesticides is accompanied by environmental pollution. When a pesticide molecule is applied, it undergoes leaching, vaporization, adsorption, degradation, hydrolysis among other processes. Adsorption/desorption phenomenon is one of the most effective processes used to remove persistent pesticide molecules in the environment. To effectively use adsorption/desorption process in environmental protection, adsorption isotherm models are used.

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.<sup>1,2</sup> The ratio between the adsorbed amount and the remaining in the solution (adsorption equilibrium) is established when an adsorbate in the bulk solution has been contacted with the adsorbent for sufficient time.<sup>3,4</sup>

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 graphically by expressing the solid-phase against its residual concentration.<sup>5</sup> 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.<sup>6</sup>

Scientists 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.<sup>7</sup> Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined as a state of dynamic equilibrium with both adsorption and desorption rates equal.<sup>8</sup> Thermodynamics is the second

approach which provides a framework of deriving numerous forms of adsorption isotherm models.<sup>9,10</sup> Potential theory is the third approach and conveys the main idea in the generation of the characteristic curve.<sup>10</sup> 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.<sup>11,12</sup> This paper focuses on modeling of adsorption isotherms of chlorothalonil onto Nairobi River sediment as a subject of initial concentration and shaking time.

## II. METHODS AND MATERIAL

### A. MATERIALS AND REAGENTS:

Chlorothalonil (IOBACemie, 99% pure) acetone (PanreacQuimica, 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 timing purposes. Distilled water was used for preparation of reagents. 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.

### B. INSTRUMENTATION:

All UV-Visible spectrophotometric measurements were taken on a 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 C18 column was employed. A Fischer scientific A-160, an analytical balance was used for all weight measurements.

### C. 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 in a wavelength range of between 200-900 nm.

### D. 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 sediment was then allowed to settle for 12 hours, after which the water phase was decanted, and 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 C18 column and 85% HPLC grade acetonitrile in distilled water as the mobile phase. An assumption made in arriving at the modeling 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.<sup>13</sup> Adsorption kinetics constants were determined using Pseudo first order, Pseudo second order and intraparticle diffusion model.<sup>14,15,16, 17</sup>

The amount adsorbed (mg/g) was calculated using the expression reported by Vanderborght and van Greikenm.<sup>18</sup>

$$Q_e = \frac{V(C_i - C_e)}{W} \dots \dots \dots (1)$$

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.

## III. 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.

### A. Langmuir isotherms:

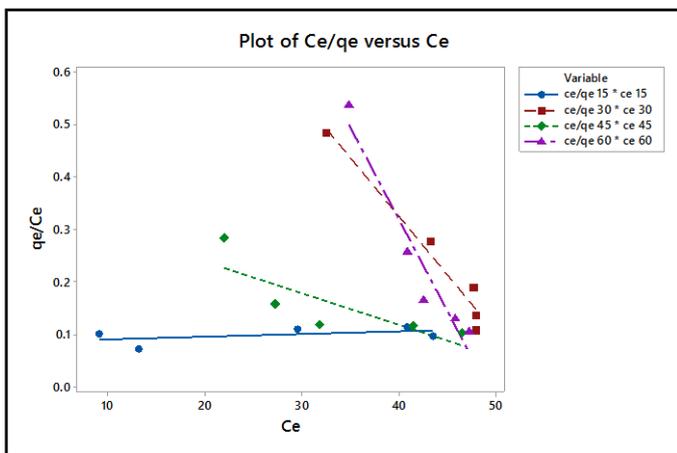
The Langmuir<sup>19</sup> model assumes that uptake of pesticide molecule occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules and uniform energies of adsorption. The Langmuir equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots \dots \dots (2)$$

Where  $q_e$  is the amount adsorbed (mg/g),  $C_e$  is the equilibrium concentration of the pesticide molecule (mg/L),  $q_m$  (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:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \dots \dots \dots (3)$$

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).



**Figure 1:** Langmuir Isotherm Model

The assumption made is that the adsorbed chemical species do not react with one another. From Figure 1 above, the following constants were calculated.

Table 2: Langmuir adsorption isotherm parameters

Time in minute	$1/Q_0$	$1/b Q_0$	b	$R^2$	$\Delta G$
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

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 44.850

## B. Quasi Langmuir isotherm 1:

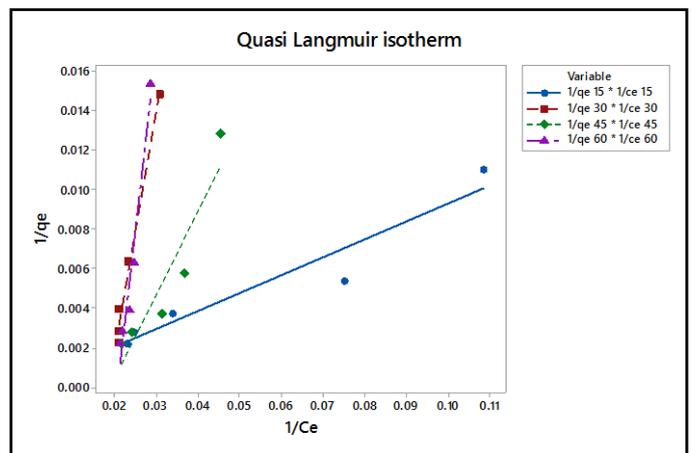
A special case of Langmuir is described in the following equation.<sup>20</sup>

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \dots \dots \dots (4)$$

Equation 4 can be linearized as follows:

$$\frac{1}{q_e} = \frac{1}{K_L Q_0} \cdot \frac{1}{C_e} + \frac{1}{Q_0} \dots \dots \dots (5)$$

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 in Figure 2.



**Figure 2:** Quasi Langmuir adsorption isotherm model

The parameters of Quasi Langmuir adsorption isotherm are stipulated in Table 2 below.

Table 2: Quasi-Langmuir isotherm parameters

Time in minute	$1/K_L Q_0$	$1/Q_0$	$K_L$	$R_L$	$R^2$
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

Being a modified Langmuir isotherm, the data for quasi Langmuir model fitted well into t ( $R \geq 0.87.4$ ), Table 2. The Langmuir constant values,  $K_L$  ranges from 0.00219 to 0.021. The isotherm can be explained by a dimensionless constant separation parameter given below:

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots (6)$$

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.<sup>21</sup> The  $R_L$  values obtained in this study is greater than 1 indicating low affinity of chlorothalonil to Nairobi River sediment.

### C. Quasi Langmuir 2:

Langmuir adsorption isotherm has been modified by many scientists. In the following modification, the Langmuir adsorption has been modified linearly as shown in equation 7 below:

$$q_e = q_m \left( \frac{q_e}{K_L C_e} \right) \dots \dots \dots (7)$$

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

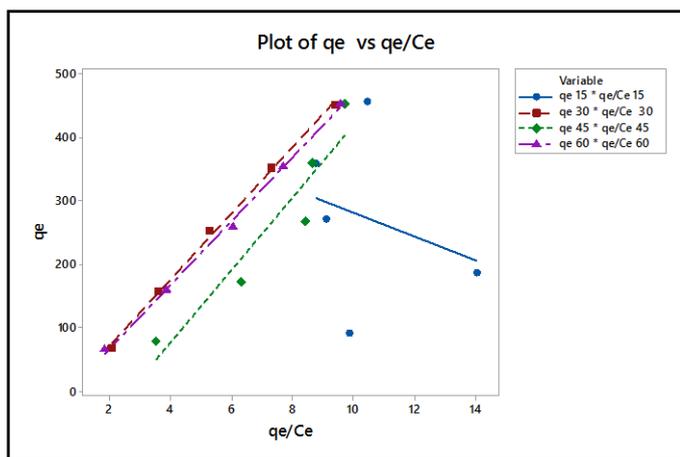


Figure 3: quasi Langmuir isotherm model 2

From 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 below.

Table 3: quasi Langmuir 2 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 above indicates that the maximum adsorption of chlorothalonil by Nairobi River sediment is 33.54 mg/ml from the regression values for 30 and 60 minutes.

### D. Freundlich Equation:

The Freundlich<sup>22</sup> equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$q^e = K^F C_e^{\frac{1}{n}} \dots \dots \dots (8)$$

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  $n$  (a measure of adsorption non-linearity between solution solute concentration and adsorption) is the Freundlich equation exponent that represents the parameter characterizing the quasi-Gaussian energetic heterogeneity of the adsorption surface.<sup>23</sup>  $K_F$ (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent.

Taking the logarithm on both sides:

$$\ln q^e = \ln K^F + \frac{1}{n} \ln C_e \dots \dots \dots (9)$$

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.

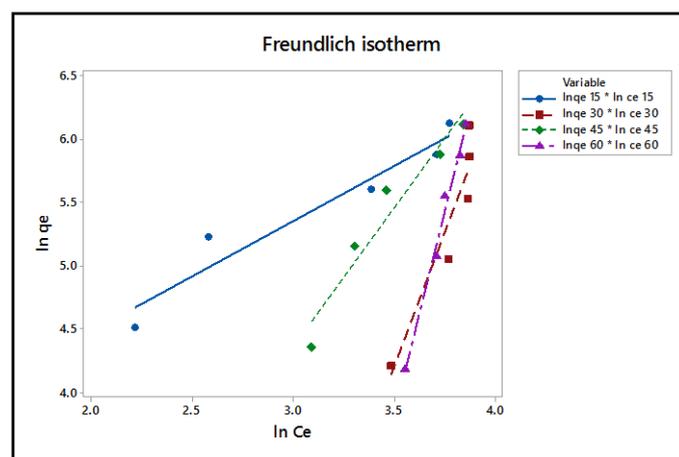


Figure 4: Freundlich adsorption isotherm

From Figure 4 above, Freundlich isotherm apparent thermodynamic parameters were calculated as shown in Table 4 below.

Table 4: Freundlich isotherm parameters

Time in minute	1/n	ln K <sup>F</sup>	K <sub>F</sub>	R <sup>2</sup>	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

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

$$K_{OC} = \frac{K_d}{\%OC} \dots \dots \dots (10)$$

$$K_d = \frac{q}{c} \dots \dots \dots (11)$$

From the above equations,  $K_d = 10.4631$ ,  $K_{OC} = 10.4631/0.85 = 12.3095$ .

**E. 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.<sup>24</sup> The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \dots \dots \dots (12)$$

Where,  $T$  is the absolute temperature (K),  $R$  is the universal gas constant (8.314J/mol. K),  $K_T$  is the equilibrium binding constant (L/mg), and  $bT$  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:

$$q_e = B_T \ln K_T + B_T \ln C_e \dots \dots \dots (13)$$

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

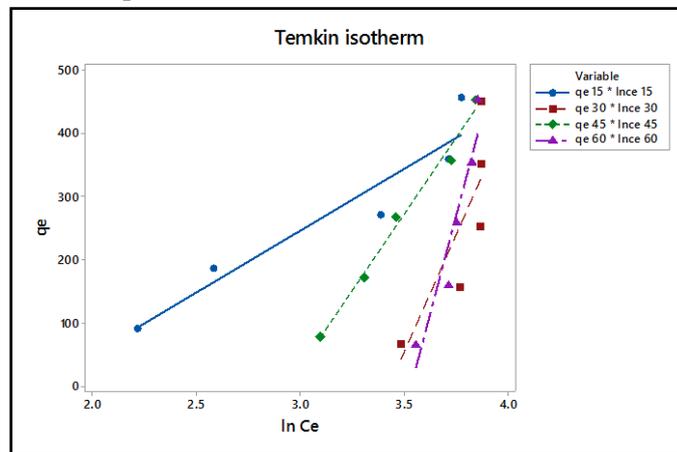


Figure 5: Temkin adsorption isotherm

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

Table 5: Temkin isotherm parameters

Time in minute	B <sup>T</sup>	B <sub>T</sub> lnK <sub>T</sub>	K <sub>T</sub>	R <sup>2</sup>
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

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.

**F. Dubinin- Radushkevich (D-R) Isotherm:**

Dubinin- Radushkevich (D-R) isotherm was applied to the obtained data to deduce the heterogeneity of the

apparent adsorption energy on the adsorption site.<sup>24</sup> The equation linear form is given as:

$$\ln q_e = \ln q_D - B_D \epsilon^2 \dots \dots \dots (14)$$

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \dots \dots \dots (15)$$

Where  $q_D$  is adsorption capacity of the adsorbent,  $B_D$  is the D-R isotherm constant related to energy,  $\epsilon$  is the Polanyi potential. The plot of  $\ln q_e$  against  $\epsilon^2$  is shown in Figure 6 below.

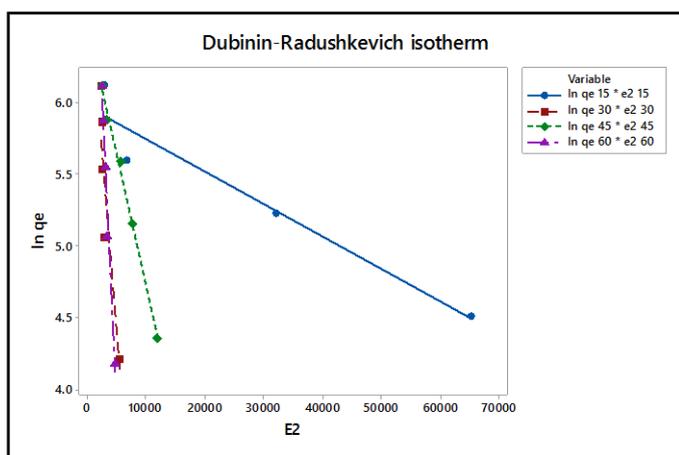


Figure 6: D-R adsorption isotherm model

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  $\ln q_e$  against  $\epsilon^2$  as shown above. The energy of chlorothalonil adsorption to Nairobi River sediment was calculated according to equation 15.

$$E = \frac{1}{(2B_D)^{1/2}} \dots \dots \dots (16)$$

The calculated parameters are recorded in Table 6.

Table 6: D-R isotherm parameters

Tim e	Ln $q_D$	$B_D$	$q_D$	$R^2$	E (kj/mo l)
15	5.97 4	0.0000 23	393.074 8	93. 9	3.7438
30	7.13	0.0005	1257.64	85.	3.5709

	7	35	98	1	
45	6.60 7	0.0001 85	740.258 9	99. 3	5.9875
60	8.38 2	0.0008 74	4367.73 57	97. 8	2.9187

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.<sup>24</sup> The value of  $E$  obtained in this work is 4.4445 kJ/mol which indicates that the adsorption of chlorothanil is dominated by physisorption as earlier noted by James et al.<sup>25</sup>

### F. Scatchard plot analysis:

The Scatchard plot analysis is applied to obtain comprehensive information on the affinity of binding sites and to analyze the result of the adsorption isotherms.<sup>26</sup> The equation is given in equation 17:

$$\frac{Q_e}{C_e} = QB - q_e b \dots \dots \dots (17)$$

Where  $Q$  and  $b$  are the Scatchard adsorption isotherm constants, if the plot of  $q_e/C_e$  versus  $q_e$  gives a straight line, the adsorbent consist 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 showed high adsorption of chlorothalonil (Figure 7).

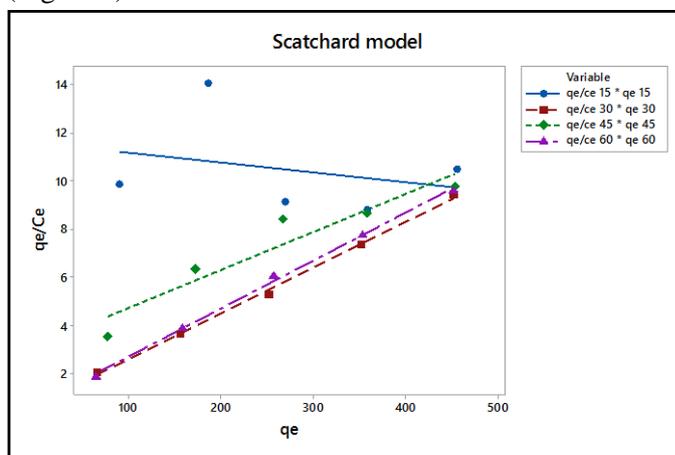


Figure 7: Scatchard adsorption isotherm model

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.

Table 7: Scatchard plot analysis parameter

Time in minute	bQ <sub>0</sub>	b	Q <sub>0</sub>	R <sup>2</sup>
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

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).<sup>26</sup>

### G. 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 298 K 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.

### H. Pseudo-First-Order Model:

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

$$\frac{dq_t}{dt} = kf(q_e - q_t) \dots \dots \dots (18)$$

Where  $q_t$  (mg/g) is the amount of adsorbate adsorbed at time  $t$ ,  $kf$  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,  $q_t=0$  at  $t = 0$  leads to the pseudo first-order rate equation:

$$\ln(q_e - q_t) = \ln q_e - kft \dots \dots \dots (19)$$

A straight line of  $\ln(q_e - q_t)$  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. Figure 8 and Table 8 below show the data obtained from the plot of experimental data.

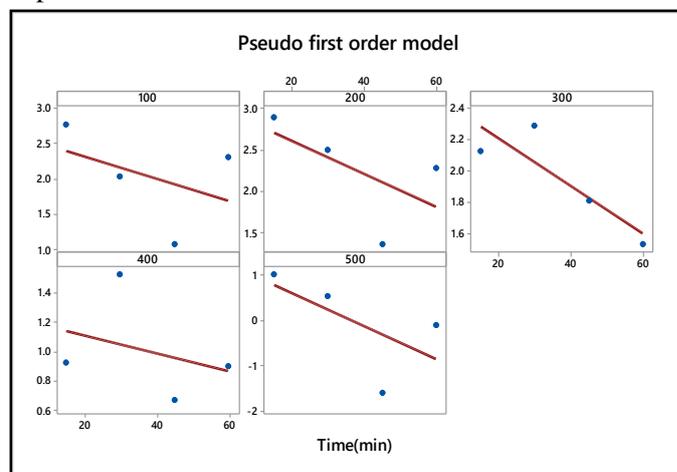


Figure 8: Pseudo-first order model plot

Table 8 below indicates the data obtained from the plot of  $\ln(q_e - q_t)$  versus  $t$ .

Table 8: Pseudo-first order data

Initial Conc.	$\ln q_e$	K <sub>F</sub>	R <sup>2</sup>
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

### I. Pseudo-Second-Order Model:

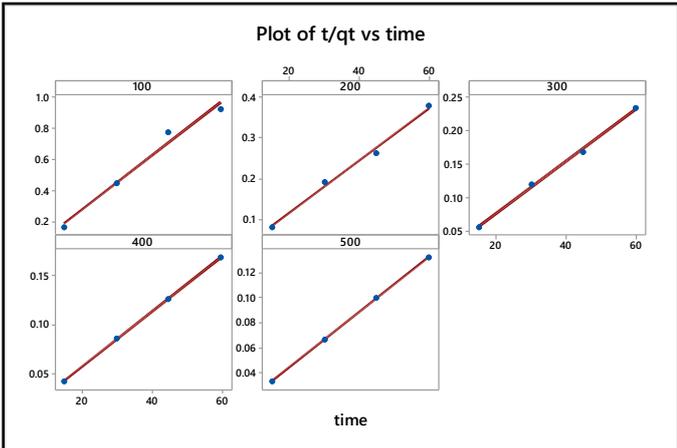
The pseudo-second order reaction kinetic model based on the sorption equilibrium capacity can be expressed as shown in Equation 21:<sup>15</sup>

$$\frac{dq_t}{dt} = ks(q_e - q_t) \dots \dots \dots (20)$$

Where  $K_s$  is the pseudo-second-order rate constant (g/mg min). Integrating Eq. (4) and noting that  $q_t=0$  at  $t = 0$ , the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{ksq_e} + \frac{1}{q_e t} \dots \dots \dots (21)$$

The plot  $t/q_t$  versus  $t$  should give a straight line if second-order kinetics are applicable, and  $q_e$  and  $ks$  can be determined from the slope and intercept of the plot, respectively (Figure 9).



**Figure 9:** Pseudo second order model plot

The initial sorption rate,  $h$  (mg/g min), as  $t \rightarrow 0$  can be defined as:

$$h = ksq_e^2 \dots \dots \dots (22)$$

The results of calculation are shown in Table 9.

Table 9: Pseudo second order kinetic parameter

Initial Conc.	$1/ksq_e^2$	$1/q_e$	$k_s$	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

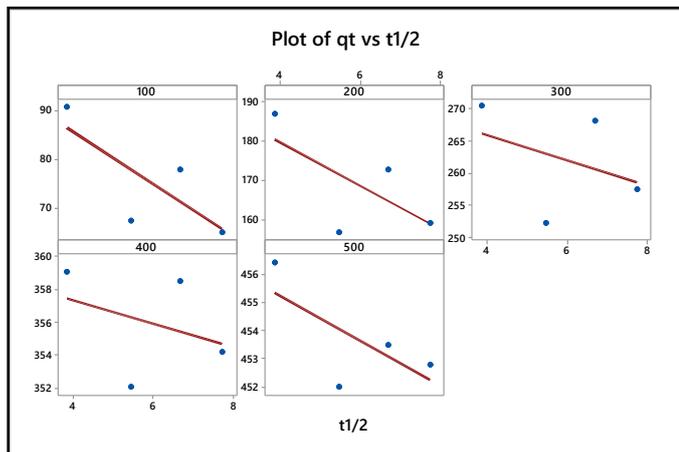
The straight line plot for the pseudo first order sorption kinetic model between  $\ln(q_e - q_t)$  vs.  $t$  was plotted (Figure 9) for sorption of chlorothalonil. The value of the rate constant calculated from the slope of plot with the correlation coefficient ranged from 0.00028 to 0.07347. The linear plot of pseudo second order kinetic model was also plotted between  $t/q_t$  vs.  $t$ , and sorption capacity and pseudo second order rate constants  $q_e$  and  $ks$  were calculated from the slope and intercept of the plot (Figure 10). The pseudo second order kinetic constant  $ks$  and sorption capacity  $q_e$  were 0.3236 g/mg min to 10.6346 mg/g. A high coefficient of determination, i.e 0.998, was obtained for the pseudosecond 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. 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.

**J. Intraparticle Diffusion Model:**

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

$$q_t = k_{id}t^{1/2} + I \dots \dots \dots (23)$$

where  $k_{id}$  is the intra-particle diffusion rate constant. According to equation 22, a plot of  $qt^{1/2}$  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.



**Figure 10:** intra-particle diffusion model

The data obtained from the plots in Figure 10 above are given in Table 10 below.

Table 10: intra-particle diffusion model parameters

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

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.<sup>27</sup> Deviation from the lines from the origin may have resulted from the 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.<sup>28</sup>

### K. 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,  $\Delta G$ , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for the 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  $\Delta G$  is a

negative quantity. The free energy of a biosorption reaction, considering the biosorption equilibrium constant  $K_c$  is given by the following equation:

$$\Delta G = -RT \ln K_C \text{ or } K_F \dots \dots \dots (25)$$

where  $\Delta G$  is the standard free energy change (kJ/mol),  $R$  the universal gas constant, 8.314 J/molK, and  $T$  is absolute temperature (K).  $K_c$  is the equilibrium constant, which is calculated from the following equation,

$$K_C = \frac{C_{Ae}}{C_e} \dots \dots \dots (26)$$

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).

## IV. CONCLUSION

The sorption data of chlorothalonil adsorption onto Nairobi river sediment was fitted to Freundlich, Langmuir, Quasi Langmuir 1, Quasi Langmuir 2, 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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