Errors in Parameters Estimation Using Linearized Adsorption Isotherms: Sulfadimethoxine Adsorption onto Kaolinite Clay

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

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ABSTRACT

In this work, an isothermal investigation of the adsorption of sulfadimethoxine from aqueous solution onto clay mineral (kaolinite) using batch equilibration method is reported. The equilibrium data were modelled using five linear forms of Langmuir equation, linear Freundlich and Temkin isotherm models and their corresponding non-linear equations. It is demonstrated that the linear Langmuir equations underestimated the maximum adsorption capacity of the sorbent. Linearization of adsorption isotherms is shown to induce errors that may lead to unreliable conclusions. The equilibrium data was best modeled by the non-linear Langmuir equation with a maximum adsorption capacity of 4.59 mg/g.

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1. INTRODUCTION

Removal of pharmaceutical ingredients from effluents and drinking water is a major emerging environmental concern today [1]. Though used for beneficial purposes, the presence of antibiotics in surface waters has been shown to detrimental to aquatic life and human health [2,3]. The occurrence of pharmaceutical compounds in effluents emerging wastewater treatment facilities indicates their resistance to conventional water treatment processes that mostly apply activated carbon as an industrial adsorbent [4,5]. The search for alternative adsorbents for removal of these compounds is a subject of continuing research [6,7]. Adsorption still remains the widely used method for pollutants removal from wastewater and drinking water. As such equilibrium adsorption isotherms are fundamentally important in the design and prediction of the operational conditions and performance of sorption systems. Adsorption isotherm studies generate the sorbent adsorption capacity and insights on the nature of the sorption mechanism depending on the calculated isotherm constants values [8]. Several non-linear isotherm models have been proposed to describe the relationship between the amount of adsorbate adsorbed onto the solid surface and the amount in bulk solution. In the process of statistically analyzing the empirical data, errors resulting to unreliable conclusions may occur. Possible sources of such errors include linearization of non-linear equations [9]. This is because the underlying assumptions of non-linear isotherms indicate the dependent variables do not depend linearly on the independent variable. Nevertheless, linear regression and the use of the coefficient of determination (R^2) remains the widely used method for determination of isotherms of best fit in adsorption experiments. The objective of this study was to evaluate the variances in the estimation of isotherm parameters using linear and nonlinear isotherms for removal of sulfadimethoxine, an antibiotic and water contaminant from aqueous solution using kaolinite clay at constant environmental conditions of temperature and pH.

2. MATERIALS AND METHODS

2.1 Isotherm Experiments

The clay was identified as kaolinite and the chemical composition determined by XRF analysis was SiO_2(43.8 %), Al_2O_3(16.9 %),

Fe_2O_3(6.67 %), K_2O (1.61 %), MgO (0.89 %), TiO_2 (0.84 %), Na_2O (0.62 %) and CaO (0.55 %) among other oxides [7]. The homogenized sample was passed through 220 μm sieves to control the particle size. Batch adsorption experiments were carried out in sealed 250 mL Erlenmeyer flasks with 0.1 g of clay dispersed in 50 mL of different concentrations (1.0, 1.25, 1.50, 1.75, 2.0 mg L^{-1}) of SDM. The sealed flasks were agitated at 200 rpm at 303 ±1 K and a working pH of 5.9 ±0.2. After equilibration, 0.5 mL aliquots were extracted from the flasks and sieved through 0.2 μm syringe filters into glass vials for analysis of the residual SDM concentrations using HPLC-DAD Varian (Palo Alto, CA, USA) at 270 nm. The mobile phase was a mixture of water (1% acetic acid) and acetonitrile (90:10 v/v), with a flow rate of 1.0 mL min^{-1}. The injection volume was 50 μL [7]. The amount of solute adsorbed per unit mass of adsorbent (q_e) was calculated using the mass balance equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

2.2 Isotherm Modeling

2.2.1 Langmuir isotherm

Langmuir [10] derived an empirical model that postulated a monolayer adsorption of molecules onto a morphologically homogeneous adsorbent surface containing at a fixed number of active adsorption sites, with no lateral interactions. Langmuir hypothesized that all the adsorption sites are identical in affinity and energy. The model further assumes that the intermolecular attractive forces diminish steadily with increased distance. The original non-linear form of the Langmuir equation is expressed as:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{2}$$

Where q_e is the amount of solute adsorbed per unit mass of the adsorbent at equilibrium (mg/g), C_e is the residual metal ion concentration in the solution at equilibrium (mg/L), Q_0 is the maximum adsorption capacity (mg/g) and *b* is the Langmuir constant related to the free energy of adsorption (L/g). Equation (2) can be linearized and the five linear forms of the Langmuir equation are presented in Table 1. Langmuir isotherm is also described in terms of the dimensionless

parameter known as the separation factor (R_L) [11] expressed as:

$$R_L = \frac{1}{1 + K_L C_i} \qquad (3)$$

2.2.2 Freundlich isotherm

The Freundlich model [12] postulates a multilayer adsorption process, with non – uniform distribution of adsorption enthalpy and affinities onto the heterogeneous adsorbent surface without lateral interaction. The energetically favoured binding sites are theorized to be occupied first and the binding strength decreases sequentially with increased coverage of the binding sites. The non-linear Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

The exponential relation indicates that the amount of adsorbate migrating onto the adsorbent surfaces increases with rise in solute concentration. According to Halsey [13], the Freundlich maximum adsorption capacity is given by the equation:

$$K_F = \frac{q_m}{C_i^{1/n}} \qquad (5)$$

Where C_i is the initial concentration of the solute in the bulk solution (mg/L) and q_m is the Freundlich maximum adsorption capacity (mg/g). The linearized Freundlich equation is given in Table 1.

2.2.3 Temkin isotherm

The Temkin isotherm model [14] postulates that the heat of adsorption of all the molecules in the layer reduces linearly rather than logarithmically with surface coverage due to adsorbent–adsorbate interactions. The adsorption is considered a uniform distribution of the binding energies, up to some maximum binding energy. The non-linear Temkin isotherm equation is given by:

$$q_e = \frac{RT}{b_T} \ln\left(A_T C_e\right) = B \ln\left(A_T C_e\right) \qquad (6)$$

Where T is temperature (K), R is the universal gas constant (8.314 J/mol.K), A_T is the equilibrium binding constant (L/mg), b_T represents the variation in adsorption energy (kJ/mol) and B is Temkin constant associated with the parameter b_T by the relation:

$$b_T = \frac{RT}{B} \qquad (7)$$

The linear form of Temkin isotherm is given in Table 1.

Table 1. Linear isotherm model parameters

Isotherm model	Equation	Parameters	Plot
Langmuir-1	$\dfrac{1}{q_e} = \dfrac{1}{Q_o} + \dfrac{1}{Q_o K_L C_e}$	Q_o (mg g^{-1}) K_L (L g^{-1})	$\dfrac{1}{q_e}$ vs $\dfrac{1}{C_e}$
Langmuir-2	$\dfrac{C_e}{q_e} = \dfrac{C_e}{Q_o} + \dfrac{1}{Q_o K_L}$	Q_o (mg g^{-1}) K_L (L g^{-1})	$\dfrac{C_e}{q_e}$ vs C_e
Langmuir-3	$q_e = -\dfrac{q_e}{K_L C_e} + Q_o$	Q_o (mg g^{-1}) K_L (L g^{-1})	q_e vs $\dfrac{q_e}{C_e}$
Langmuir-4	$\dfrac{q_e}{C_e} = -K_L q_e + K_L Q_o$	Q_o (mg g^{-1}) K_L (L g^{-1})	$\dfrac{q_e}{C_e}$ vs q_e
Langmuir-5	$\dfrac{1}{C_e} = \dfrac{K_L Q_o}{q_e} - K_L$	Q_o (mg g^{-1}) K_L (L g^{-1})	$\dfrac{1}{C_e}$ vs $\dfrac{1}{q_e}$
Freudlich	$\ln q_e = \ln K_f + \dfrac{1}{n} \ln C_e$	K_f, n	$\ln q_e$ vs $\ln C_e$
Temkin	$q_e = B \ln A_T + B \ln C_e$	A_T, B	q_e vs $\ln C_e$

3. RESULTS AND DISCUSSION

3.1 Langmuir isotherm

Three mathematical models were tested to describe the equilibrium data, namely; Langmuir (five linear forms), Freundlich and Temkin and the applicability of each model evaluated using the coefficient of determination (R^2) and the values of calculated parameters as listed in Table 2.

The equilibrium data were linearly regressed using five linear expressions of Langmuir equation shown in Table 1 and the calculated Langmuir constants are listed in Table 2. Despite their wide usage, owing to their best error distribution, Langmuir-2, Langmuir-3 and Langmuir-4 had the least coefficients of determination. It is noteworthy that Langmuir-3 and Langmuir-4 had equal and very low coefficients of determination (R^2=0.069) yet the theoretical Langmuir maximum adsorption capacity (Q_o) estimated using Langmuir-4 equation was more than five-fold higher than Langmuir-3 maximum adsorption capacity. The induced errors and discrepancy between the parameters is evidently large. Similarly, Langmuir-1 and Langmuir-5 had a similar coefficient of determination yet the calculated constants were widely dissimilar. Here, the maximum adsorption capacity varied by a magnitude of two. Furthermore, if the Langmuir constants (K_L) are to be used to estimate the thermodynamic functions related to the adsorption process the wide variance between the calculated K_L values from the linear forms of the Langmuir would lead to serious errors in both values and interpretation. In the present work, coefficients of determination values (R^2) could not by themselves determine the best fit model. This is compelling evidence that coefficient of determination should not be the sole criteria to determine the best-fitting model for linearized equations due to the error structures accompanying transformation of non-linear functions to linear models [9]. Instead, other error analysis functions should be considered.

3.2 Freundlich Isotherm

The data were also modeled using the linearized expression of Freundlich equation (Table 1) and the constants are listed in Table 3. Relative to the Langmuir linear equations, the R^2 value for the linearized Freundlich had comparable but slightly higher linearity than Langmuir-1 and Langmuir-5 equations. From the coefficient of determination perspective, the experimental data seems to follow the Freundlich model. Furthermore, the extremely low R^2 values for type 2, 3 and 4 Langmuir equations Langmuir necessitate rejection of these linearized forms. Therefore, Freundlich model was best suited for the experimental data over the Langmuir isotherm. According to Treybal [15], the magnitude of *n* depicts the favorability of the adsorption process. Values of *n* in the range 2-10 represent good, 1-2 moderately difficult, and less than 1 a poor adsorptive potential. The magnitude of *n* (1.28) in the present study indicates a moderately difficult adsorption process [7].

3.3 Temkin Isotherm

The calculated Temkin model parameters are presented in Table 3. The R^2 values reflect acceptable linearity though less than Langmuir-1, Langmuir-5 and linear Freundlich equations. The adsorption of SDM arguably does not follow the postulates of the Temkin model. Nevertheless, the positive value of the constant B (0.332) corresponds to a positive value of the variation of adsorption energy parameter b_T (7.588 kJ/mol) which suggests that the adsorption of SDM onto the kaolinite clay is exothermic in nature [16]. Further, the low b_T value indicates weak interactions between the SDM molecules and the adsorbent. However, the Langmuir constants (K_L) from the linear equations would lead to discrepancies in the estimation of the enthalpy of adsorption.

Table 2. Linear Langmuir Isotherm model parameters for SDM adsorption

Isotherm model	Q_0 mg/g	K_L L/g	R_L	R^2
Langmuir-1	1.389	0.744	0.402	0.857
Langmuir-2	2.289	0.384	0.565	0.244
Langmuir-3	0.693	2.827	0.150	0.069
Langmuir-4	4.117	0.195	0.719	0.069
Langmuir-5	2.274	0.390	0.562	0.857

Table 3. Linear Freundlich and Temkin isotherm model parameters for SDM adsorption

Isotherm model	Parameters		R^2
Freundlich	1/n	0.780	0.877
	K_F (L/g)	0.638	
Temkin	A_T (L/g)	6.256	0.835
	B	0.332	

3.4 Non-linear Analysis

Following the aforementioned problems associated with linearization of non-linear isotherm equations, the equilibrium adsorption data was fitted to the original non-linear Langmuir, Freundlich and Temkin equations to overcome the inherent challenges of linear regression analysis. Non-linear regression of equilibrium sorption data for each isotherm was performed by minimizing the regression sum of squares (RSS) error function (equation 8) using the *solver* add-in with excel's spreadsheet, Excel (Microsoft) and the calculated constants are presented in Table 4.

$$RSS = \sum_{1}^{N} \left(q_{e,\text{experimental}} - q_{e,predicted} \right)^2 \qquad (8)$$

Where *N* is the number of data points. In the non-linear regression, there was an appreciation in the R^2 value, corresponding to increased conformity, for the Langmuir isotherm from 0.857 to 0.882 for the linear and non-linear forms, respectively. Furthermore, the Langmuir monolayer maximum adsorption capacity increased to 4.590 mg/g in non-linear regression with R^2 values above those for both Freundlich and Temkin models. Unlike in linear regression, it is here concluded that the adsorption data follows the Langmuir model. It is further noted that while the linearized Langmuir isotherms underestimated the maximum adsorption capacity, Langmuir-4 type equation had comparable adsorption capacity (4.117 mg/g) with the original non-linear equation (4.590 mg/g) yet it yielded the least R^2 values. It is evident that while linear regression is widely used to model adsorption models due to their simplicity; non-linear regression is the best method of isotherm modeling and great care should be taken while using linearized adsorption isotherms. Noteworthy, the constants and R^2 values for the linear and non-linear Temkin isotherms were identical. On the other hand, while the R^2 values for the linear and non-linear Freundlich isotherms were identical, there was notable variance in the calculated constants.

Table 4. Linear Freundlich and Temkin isotherm model parameters for SDM adsorption

Isotherm model	Parameters		R^2
Langmuir	Q_o (mg/g)	4.590	0.882
	K_L (L/mg)	0.171	
Freundlich	1/n	0.780	0.877
	K_F (L/mg)	0.638	
Temkin	A_T (L/mg)	6.256	0.835
	B	0.332	

4. CONCLUSION

In this study, kaolinite clay was used as a sorbent for removal of sulfadimethoxine synthetic wastewater under constant temperature and pH. The equilibrium adsorption data were analyzed using five linear forms of the Langmuir isotherm, linear Freundlich and Temkin isotherms and their corresponding non-linear equations. The results show that linearization of adsorption isotherms induced serious variations in computed parameters that would significantly affect interpretation and conclusions. The linearized Langmuir equations underestimated the maximum adsorption capacity of the clay. On the contrary, there was a convergence of the parameters derived from the linear and non-linear Temkin isotherms. The adsorption data were best described by the non-linear Langmuir isotherm. Non-linear regression is demonstrated to be a suitable method for estimation of adsorption isotherm parameters and linear regression is to be applied with caution.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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