

## Discrimination of rival isotherm equations for aqueous contaminant removal systems

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**Abstract.** Two different model selection indices, the Akaike information criterion (AIC) and the coefficient of determination ( $R^2$ ), are used to discriminate competing isotherm equations for aqueous pollutant removal systems. The former takes into account model accuracy and complexity while the latter considers model accuracy only. The five types of isotherm shape in the Brunauer-Deming-Deming-Teller (BDDT) classification are considered. Sorption equilibrium data taken from the literature were correlated using isotherm equations with fitting parameters ranging from two to five. For the isotherm shapes of types I (favorable) and III (unfavorable), the AIC favors two-parameter equations which can easily track these simple isotherm shapes with high accuracy. The  $R^2$  indicator by contrast recommends isotherm equations with more than two parameters which can provide marginally better fits than two-parameter equations. To correlate the more intricate shapes of types II (multilayer), IV (two-plateau) and V (S-shaped) isotherms, both indices favor isotherm equations with more than two parameters.

**Keywords:** adsorption isotherm; Akaike information criterion; equilibrium data; modeling

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### 1. Introduction

Sorption-based technologies are now widely used as a key method to remove trace quantities of toxic, non-biodegradable contaminants from aqueous streams. For these applications, a key task is to characterize the equilibrium behavior of a given contaminant-sorbent system, usually by using the well-established batch technique. The resultant data describe the equilibrium relationship between the uptake concentration in the sorbent phase and the residual concentration in the liquid phase, which is usually a function of various environmental factors such as pH and temperature. To transform the experimentally measured equilibrium relationship into a practical form, isotherm equations are commonly used to correlate the discrete data points. The calibrated isotherm equations may be used to compare different sorbents on a quantitative basis, elucidate mechanistic relevance or used as part of a process model for design and optimization studies.

A multitude of isotherm equations of varying complexity, especially for single contaminant systems, may be used to correlate measured sorption equilibrium data. Most of these isotherm equations have their origins in the gas sorption literature (Do 1998). To test the correlative ability of rival isotherm equations, a common practice is to use some form of goodness-of-fit measures.

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For example, Maurya and Mittal (2006) tested 16 isotherm equations with different numbers of adjustable parameters in the correlation of dye sorption on fungal sorbents and isotherm comparisons were based on indices such as the correlation coefficient and  $t$ -test. Hamdaoui and Naffrechoux (2007) presented a similar study in which 13 isotherms with fitting parameters ranging from three to five were tested. Yet another two studies in a similar vein fitted 21 isotherm equations to the equilibrium data of heavy metal sorption on seaweed sorbents (Basha and Jha 2008, Basha *et al.* 2008). The isotherms with adjustable parameters ranging from one to five were compared using the correlation coefficient, sum of squared errors, standard error and  $F$ -ratio. In general, these studies found that the best isotherm equations tended to be those with a high number of fitting parameters. This finding is however trivial because a model can always be made to fit the data better by adding complications. For example, adding an adjustable parameter to an isotherm equation will almost always improve fit to some degree. Ranking competing isotherm equations with different numbers of fitting parameters solely in terms of goodness-of-fit measures is therefore a simplistic approach.

Several statistical tests that address the tradeoff between gain in fit and addition of parameters have been developed in a branch of statistics called model selection (Burnham and Anderson 2002, Motulsky and Christopoulos 2004). For example, the Akaike information criterion (AIC) is a commonly implemented test in several fields of science and engineering. The AIC, first developed in information theory in the 1970's (Akaike 1974), is a model discrimination technique that considers both model accuracy and complexity. Recently, an increasing number of studies have recommended or employed the AIC test to discriminate rival isotherm equations for a variety of aqueous contaminant removal systems (Bolster and Hornberger 2007, Matott *et al.* 2009, Zamil *et al.* 2009, El-Khaiary and Malash 2011, Akpa and Unuabonah 2011, Kah *et al.* 2011, Bianchi Janetti *et al.* 2012, Çoruh and Geyikçi, 2012, Marešová *et al.* 2012, Wang 2012, Copello *et al.* 2013). However, the experimental isotherms reported in these studies are largely of the favorable or convex type, which can be adequately correlated by using the popular Langmuir and Freundlich isotherm equations or their variants.

This contribution aims at applying for the first time the AIC test to the discrimination of isotherm equations for the five types of isotherm shape described in the Brunauer-Deming-Deming-Teller (BDDT) classification. Besides the ubiquitous favorable isotherm shape, the other four types of isotherm shape in the BDDT classification (unfavorable, multilayer, two-plateau and S-shaped) have been reported for some aqueous contaminant removal systems. The analysis will be illustrated with experimental data taken from the literature. Each type of isotherm shape will be correlated with a selection of rival isotherm equations with varying numbers of parameters and ranked according to the AIC test as well as a goodness-of-fit measure based on the coefficient of determination.

## 2. Sorption isotherms

### 2.1 Classification of isotherm shapes

In 1940, Brunauer *et al.* (1940) introduced a systematic scheme to classify sorption isotherms for gas-solid equilibria. This identification, referred to as the BDDT classification, divides experimentally observed sorption isotherms into five classes, as illustrated in Fig. 1. A modern IUPAC classification of sorption isotherms is based on the BDDT classification (Sing *et al.* 1985).

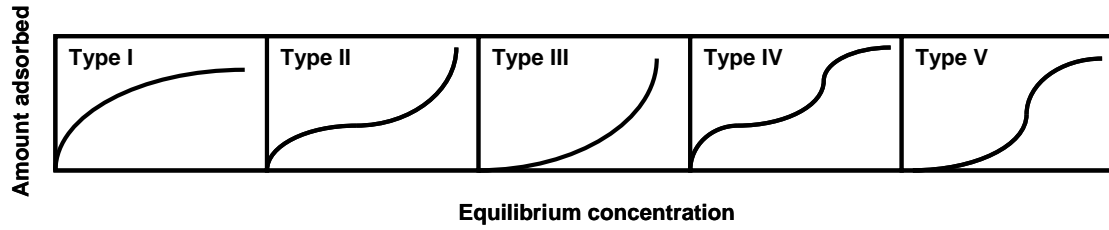


Fig. 1 Isotherm shapes in the BDDT classification

Table 1 Summary of the considered isotherm equations

	Isotherm model	Expression	Equation number	Fitting parameters	Number of parameters
	Langmuir <sup>a</sup>	$q = \frac{q_m bC}{1 + bC}$	(1)	$q_m, b$	2
Rational functions	Two-step Langmuir <sup>b</sup>	$q = \frac{a_1 b_1 C}{1 + b_1 C} + \frac{a_2 b_2 [(C - c_2) + \text{abs}(C - c_2)]}{2 + b_2 [(C - c_2) + \text{abs}(C - c_2)]}$	(2)	$a_1, b_1, a_2, b_2, c_2$	5
	BET <sup>c</sup>	$q = \frac{q_m b_s C}{(1 - b_L C)(1 - b_L C + b_s C)}$	(3)	$q_m, b_s, b_L$	3
	Freundlich <sup>d</sup>	$q = K_F C^n$	(4)	$K_F, n$	2
	Langmuir-Freundlich <sup>e</sup>	$q = \frac{q_m b C^n}{1 + b C^n}$	(5)	$q_m, b, n$	3
Power functions	Fritz-Schlunder <sup>f</sup>	$q = \frac{\alpha_1 C^{\beta_1}}{1 + \alpha_2 C^{\beta_2}}$	(6)	$\alpha_1, \alpha_2, \beta_1, \beta_2$	4
	BDDT <sup>g</sup>	$q = \left[ \frac{q_m v w}{1 - w} \right] \left[ \frac{1 + n[(g - 1)z + gy - (2g - 1)x] - x}{1 + (v - 1)w + v[(g - 1)x - gy]} \right]$ $v = b_s/b_L; w = b_L C; x = (b_L C)^n$ $y = (b_L C)^{n+1}; z = (b_L C)^{n-1}$	(7)	$q_m, b_s, b_L, g, n$	5
	Jovanović <sup>h</sup>	$q = q_m [1 - \exp(-a_J C)] [\exp(b_J C)]$	(8)	$q_m, a_J, b_J$	3
Transcendental functions		$q = K_L \ln [1 + (b_0 C)^{1/M}]$			
	Li <sup>i</sup>	$\frac{1}{M} = \frac{1 + \ln [1/(1 - b_L C)]}{M_0}$	(9)	$K_L, b_0, M_0, b_L$	4

<sup>a</sup> Langmuir (1918); <sup>b</sup> Czinkota *et al.* (2002), Konda *et al.* (2002); <sup>c</sup> Brunauer *et al.* (1938), Gritti *et al.* (2002); <sup>d</sup> Freundlich (1926); <sup>e</sup> Sips (1948); <sup>f</sup> Fritz and Schlunder (1974); <sup>g</sup> Brunauer *et al.* (1940); <sup>h</sup> Jovanović (1969); <sup>i</sup> Li (1985)

An alternative classification scheme suggested by Giles *et al.* (1974) divides sorption isotherms into four main types based on their initial slopes and curvatures. These curves are called the high affinity (H) isotherm, Langmuir (L) isotherm, constant partition (C) isotherm, and sigmoidal-shaped (S) isotherm (Hinz 2011). In the BDDT classification of sorption isotherms for physical adsorption of gases (Fig. 1), types I, II, and IV curves correspond to ‘favorable’ sorption isotherms while types III and V represent ‘unfavorable’ isotherms at low concentrations. Interestingly, examples of all five types of sorption isotherms have been reported for liquid-solid systems of contaminant removal.

## 2.2 Classification of isotherm equations

Although there are only five major classes of isotherm shape in the BDDT classification, numerous theoretical and empirical isotherm equations for data fitting abound in the literature. As noted earlier, as many as 21 isotherm equations were used to fit the equilibrium data of metal sorption on seaweed sorbents (Basha *et al.* 2008, Basha and Jha 2008). Hinz (2011) pointed out that the mathematical forms of most of the isotherm equations can be classified into three major classes: rational, power law, and transcendental. Listed in Table 1 are the isotherm equations tested in this study which are classified according to Hinz (2011). The selected isotherm equations have fitting parameters that range from two to five. Virtually all the equations in Table 1 can fit the type I isotherm shape while some have been formulated to fit a particular type of isotherm shape. In Table 1,  $q$  is the sorbed concentration in equilibrium with the solution concentration  $C$ .

## 3. Parameter estimation

Optimal parameter estimates were obtained by fitting the nonlinear isotherm equations in Table 1 to equilibrium data taken from the literature. In this work a genetic algorithm based on a scheme with a floating-point representation was used as the parameter estimation method. The genetic algorithm optimization method is a type of stochastic global optimization method based on an iterative procedure that mimics the process of biological evolution. The genetic algorithm method seeks to minimize the sum of the squared errors (SSE) between measured and calculated  $q$  values

$$\text{SSE} = \sum_{j=1}^m (q_{\text{exp},j} - q_{\text{cal},j})^2 \quad (10)$$

where  $m$  is the number of observations, and  $q_{\text{exp},j}$  and  $q_{\text{cal},j}$  are, respectively, the measured and model-calculated values for observation  $j$ .

## 4. Criteria for isotherm discrimination

### 4.1 Coefficient of determination

The following coefficient of determination ( $R^2$ ) is used as an indicator of goodness-of-fit

$$R^2 = 1 - \frac{\sum_{j=1}^m (q_{\text{exp},j} - q_{\text{cal},j})^2}{\sum_{j=1}^m (q_{\text{exp},j} - \bar{q}_{\text{exp}})^2} \quad (11)$$

where  $\bar{q}_{\text{exp}}$  is the mean of measured values and all other variables are as defined above. An  $R^2$  of 1 indicates a perfect fit to the data. Rival models may be ranked according to the  $R^2$  test statistics, with the one having the highest  $R^2$  being the best. When the sample size is small compared to the number of parameters, one should use a more conservative statistic to compensate for possible bias to parameter-rich models. Ranking candidate models solely in terms of the  $R^2$  test is a simplistic approach because it does not consider model complexity. We note, in passing, that another definition of  $R^2$ , called adjusted  $R^2$ , may be used to compensate for possible bias to parameter-rich models

$$\text{Adjusted } R^2 = 1 - \frac{m-1}{m-p} (1 - R^2) \quad (12)$$

where  $m$  is the number of observations and  $p$  is the number of fitting parameters.

#### 4.2 Akaike information criterion

The AIC test is a quantitative way to rank competing models with different numbers of adjustable parameters and identify the model that is most justified by the data at hand. The AIC provides an implementation of Occam's razor, in which parsimony or simplicity is balanced against goodness-of-fit. For small numbers of data points or sample sizes, the AIC takes on the following form (Hurvich and Tsai 1989, Burnham and Anderson 2002, Motulsky and Christopoulos 2004)

$$\text{AIC}_c = m \ln \left( \frac{\text{SSE}}{m} \right) + 2(p+1) \left( 1 + \frac{p+2}{m-p-2} \right) \quad (13)$$

where  $\text{AIC}_c$  stands for corrected AIC for small sample size and  $p$ ,  $m$  and SSE are as defined in Eqs. (10) and (12). The  $\text{AIC}_c$  is used for model discrimination when the sample size is small, i.e., when  $m/p < 40$  (Burnham and Anderson 2002). To apply Eq. (13),  $m-p$  must be  $\geq 3$  although Bolster and Hornberger (2007) recommend  $m-p \geq 5$  to ensure meaningful model comparison. In Eq. (13) the first term measures fit, while the second term penalizes complex models, i.e., models with more adjustable parameters. The number of adjustable parameters is thus considered as a measure of model complexity in the  $\text{AIC}_c$  formula. Given a data set, multiple models with different numbers of parameters may be ranked according to their  $\text{AIC}_c$ , with the one producing the lowest value being the best. The  $\text{AIC}_c$  test is a statistically sound procedure for model discrimination and offers a valuable alternative to traditional goodness-of-fit measures.

Strictly speaking, the  $\text{AIC}_c$  expression is not a valid equation because the first term on the right of Eq. (13) has the units of SSE which are adsorbed concentration squared while the second term is dimensionless (Motulsky and Christopoulos 2004). The numerical value of  $\text{AIC}_c$  is thus dependent on the units of SSE. The effect of SSE units vanishes when a model is compared to the best model within a cohort of candidate models based on the difference in their  $\text{AIC}_c$  values ( $\Delta_i$ ), as follows (Burnham and Anderson 2002, Motulsky and Christopoulos 2004)

$$\Delta_i = \text{AIC}_{c,i} - \text{AIC}_{c,\min} \quad (14)$$

where  $i$  is an index corresponding to the number of models,  $\text{AIC}_{c,i}$  is the  $\text{AIC}_c$  value for model  $i$  and  $\text{AIC}_{c,\min}$  is the  $\text{AIC}_c$  value of the model with the lowest  $\text{AIC}_c$  value calculated from Eq. (13).

As a rule of thumb, a  $\Delta_i < 2$  indicates substantial support from the data for model  $i$ ,  $3 < \Delta_i < 7$  suggests weak support, and a  $\Delta_i > 10$  suggests model  $i$  receives essentially no support (Burnham and Anderson 2002). Additionally, these  $\Delta_i$  values can be used to compute another measure termed the Akaike weight. For a set of  $R$  competing models, the Akaike weight for model  $i$  ( $w_i$ ) is calculated as (Burnham and Anderson 2002, Motulsky and Christopoulos 2004)

$$w_i = \frac{\exp(-0.5\Delta_i)}{\sum_{r=1}^R \exp(-0.5\Delta_r)} \quad (15)$$

$w_i$  can be interpreted as the probability that model  $i$  is the best model given the data at hand and the chosen set of competing models.

## 5. Results and discussion

Using data taken from the literature, we compare the ability of rival isotherm equations with different numbers of parameters to fit the five types of isotherm shape in the BDDT classification. Given the requirement of  $m-p \geq 3$  of the  $AIC_c$  formula, an important consideration in the selection of literature data is the number of data points reported in a data set. The results of this work are conveniently split into five groups according to the BDDT classification. We discuss these sequentially.

### 5.1 Type I isotherm shape

The shape of this isotherm is convex upward (cf. Fig. 1). This isotherm shape is the most ubiquitous one reported in the literature of contaminant sorption in aqueous systems. Countless systems involving the sorption of contaminants such as heavy metals and dyes to a broad cohort of sorbents exhibit this type of equilibrium relationship. For example, this type of favorable isotherms can be found in the work of Barka *et al.* (2009) who investigated the sorption of methylene blue and basic yellow 28 on natural phosphate rock. The equilibrium data of the two dyes, shown in Fig. 2, exhibit similar saturation capacities but vastly different isotherm slopes. The slope of the methylene blue sorption curve is much steeper than that of the basic yellow 28 sorption curve. Indeed, the methylene blue isotherm is highly favorable and may thus be approximated by a rectangular isotherm. Here, we will fit some of the isotherm equations listed in Table 1 to the two data sets and use the  $R^2$  and  $AIC_c$  tests as guides to select the best isotherm equation for each data set.

Although most of the isotherm equations in Table 1 are able to describe the type I isotherm shape, we restrict our interest to the following three rational and power-law equations: the two-parameter Langmuir (Eq. (1) in Table 1), the three-parameter Langmuir-Freundlich (Eq. (5) in Table 1), and the four-parameter Fritz-Schlunder (Eq. (6) in Table 1). For the two data sets, the derived parameters and associated  $R^2$  and  $AIC_c$  scores are summarized in Tables A1-A2 of Appendix A. To compare fits in visual terms, parity plots of the calculated  $q$  values versus observed  $q$  values are given in Fig. 3. For the methylene blue data, Fig. 3(a) shows that the three equations provide satisfactory fits to the data points in the plateau region, as judged by the closeness of the calculated  $q$  values to the 1:1 line. However, all three equations performed rather poorly in tracking the data points in the ascending part of the sorption curve. The calculated  $q$

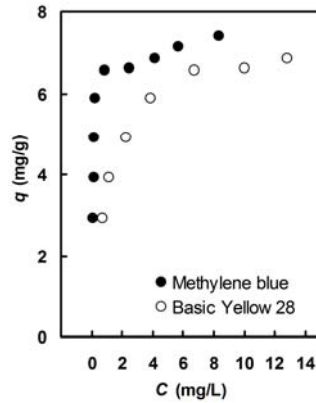
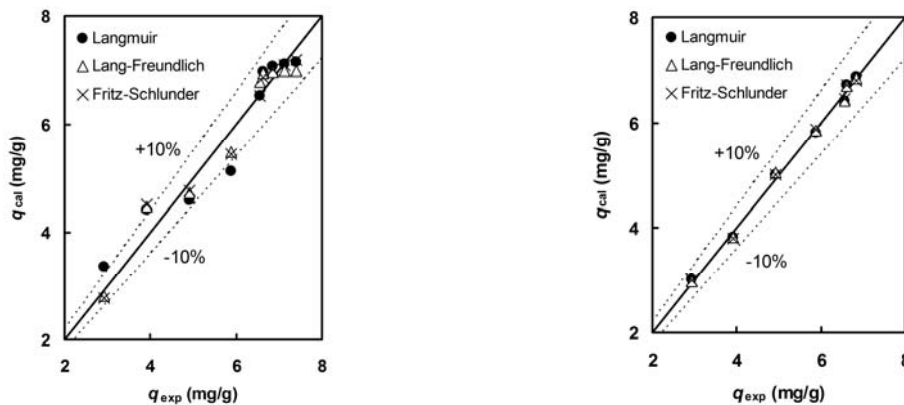


Fig. 2 Type I isotherms of the sorption of methylene blue and basic yellow 28 on natural phosphate rock (Data of Barka *et al.* (2009))



(a) Comparison between the methylene blue data of Fig. 2 and  $q$  values calculated from the Langmuir, Langmuir-Freundlich and Fritz-Schlunder equations with the parameters given in Table A1

(b) Comparison between the Basic Yellow 28 data of Fig. 2 and  $q$  values calculated from the Langmuir, Langmuir-Freundlich and Fritz-Schlunder equations with the parameters given in Table A2

Fig. 3 Type I isotherms of the sorption of methylene blue and basic yellow 28 on natural phosphate rock (Data of Barka *et al.* (2009))

values lie very close to or beyond the lines of  $\pm 10\%$  errors, revealing limitations of the rational or power-law equations to correlate this type of highly favorable sorption curve. In contrast, Fig. 3(b) shows that all three isotherm equations provide excellent fits to the entire range of the basic yellow 28 data set. The moderate steepness of the isotherm slope poses no significant challenge to the correlative power of the isotherm equations.

For the methylene blue data, Table A1 indicates that the  $R^2$  score of the four-parameter Fritz-Schlunder fit is 3.5% and 0.9% higher than the respective  $R^2$  score of the two-parameter

Langmuir and three-parameter Langmuir–Freundlich fits. This indicates that the four-parameter Fritz-Schlunder equation with the highest  $R^2$  score is the best isotherm for this data set. As for the basic yellow 28 data, although differences in the  $R^2$  scores of the three fits appear trivial (cf. Table A2), the four-parameter Fritz-Schlunder equation still comes out on top. These results confirm the general perception that a model can always be made to fit the data better by adding more parameters and that the  $R^2$  approach tends to select a parameter-rich model as the best one among a group of competing models.

Next, we assess the relative performance of the three equations in terms of  $AIC_c$  statistics. Table A1 indicates that the Langmuir equation with the lowest  $AIC_c$  score (−6.28) is well supported by the methylene blue data compared to the other two equations. The three-parameter Langmuir-Freundlich equation with a  $\Delta_i$  of 3.41 and a  $w_i$  of 0.15 receives some limited support from the data. The four-parameter Fritz-Schlunder with a  $\Delta_i > 10$  and a  $w_i$  of zero receives no support from the data. Likewise, the Langmuir equation is well supported by the basic yellow 28 data whereas the Langmuir-Freundlich and Fritz-Schlunder equations with  $\Delta_i$  values  $> 10$  receive no support from the data. It is evident that the improvement in fit provided by the parameter-rich Fritz-Schlunder equation, especially in the methylene blue case, is deemed by the  $AIC_c$  test to be insufficient to justify the use of four fitting parameters.

Given that the  $R^2$  and  $AIC_c$  tests differ in their selection of the best isotherm equation for the dye data sets, which approach should we follow? If the aim of correlating the dye data is to find the best-fit isotherm equation, it is obvious that one should opt for the four-parameter Fritz-Schlunder equation recommended by the  $R^2$  approach. However, because the  $R^2$  indicator tends to favor parameter-rich models, one should be mindful of the issue of parameter inter-correlation in such models. Note that parameter correlation is common in power-law models; it is even present in the simple two-parameter Freundlich isotherm (Schwaab and Pinto 2008). When multiple parameters are to be simultaneously identified, it is important to assess the degree of correlation between the parameters being estimated. This is because strong correlations may result in non-unique estimates of each parameter or hamper convergence when gradient-based regression methods are used for parameter identification.

To explore the possible presence of parameter correlation in the four-parameter Fritz-Schlunder equation, we used a rapidly converging regression method based on a combination of Gauss-Newton and Levenberg-Marquardt algorithms for parameter estimation. We found that the nonlinear regression method required initial parameter guesses that were in the vicinity of the optimal values determined by the genetic algorithm method in order to avoid convergence difficulties. The regression method was especially sensitive to the starting values of  $\beta_1$  and  $\beta_2$ . Note that the genetic algorithm makes use of a population of individuals (parameter estimates), so good initial guesses are not required. The convergence problem of the gradient-based regression method suggests that the parameters in the Fritz-Schlunder equation are closely correlated.

One means of assessing the degree of parameter correlation is to look at the correlation matrix of the derived parameters (Bolster and Hornberger 2007). First, the covariance matrix of the derived parameters (**cov**) is estimated from the Jacobian matrix, as follows

$$\mathbf{cov} = \left( \frac{\text{SSE}}{m-p} \right) (\mathbf{J}^T \mathbf{J})^{-1} \quad (16)$$

where  $\mathbf{J}$  and  $\mathbf{J}^T$  are the Jacobian matrix and its transpose, respectively. The relation between a coefficient of the covariance matrix ( $\theta_{ij}$ ) and a coefficient of the correlation matrix ( $\theta_{ij}^*$ ) is given by



$$\theta_{ij}^* = \theta_{ij} / \sqrt{\theta_{ii}\theta_{jj}} \quad (17)$$

The resulting correlation matrix will contain 1's in the diagonal, reflecting that each parameter is perfectly correlated with itself. The off-diagonals are filled with  $\theta_{ij}^*$  between  $-1$  and  $+1$ . A  $\theta_{ij}^*$  with value near  $-1$  or  $+1$  reflects highly correlated parameter estimates, and a value close or equal to  $0$  indicates that parameters  $i$  and  $j$  are not correlated. The correlation matrix containing correlation coefficients calculated at the optimal values of the four Fritz-Schlunder parameters is given below.

	$\alpha_1$	$\beta_1$	$\alpha_2$	$\beta_2$
$\alpha_1$	1			
$\beta_1$	0.989	1		
$\alpha_2$	0.000	0.987	1	
$\beta_2$	0.984	0.999	0.981	1

The above correlation matrix clearly shows that, with the exception of the  $\alpha_1$ - $\alpha_2$  pair, the four parameters are strongly correlated. In particular,  $\beta_1$  and  $\beta_2$  with a correlation coefficient of  $0.999$  are highly interrelated. As a result, without knowing the genetic algorithm-derived parameter values, simultaneous identification of the Fritz-Schlunder parameters using gradient-based regression methods will require a careful search for a set of initial parameter guesses in order to attain convergence and/or unique estimates.

If the aim of correlating the dye data is to obtain an isotherm equation for use as part of a dynamic process model (e.g., fixed bed model) for design or optimization studies, one should follow the  $AIC_c$  recommendation and opt for the two-parameter Langmuir equation. For this purpose, simpler is better because in dynamic process studies, using a simple isotherm equation reduces computational requirements considerably.

Additionally, there is evidence that the performance of a dynamic process model is not particularly sensitive to the type of isotherm equation used. For example, simulation results obtained from a dynamic model for a membrane-based biosorption system were found to be insensitive to the type of isotherm equation used (Pagnanelli *et al.* 2003). Lua and Yang (2009) also reported that different types of nonlinear isotherms used in a kinetic model of  $SO_2$  sorption on activated carbon exerted little effect on the overall particle uptake kinetics. Consequently, from a practical standpoint, no useful purpose is served in using an isotherm equation with more than two parameters to fit equilibrium data exhibiting the type I isotherm shape if the resulting equation is to be embedded in a dynamic process model.

## 5.2 Type II isotherm shape

This class of isotherm shape is found in gas-solid systems that display multilayer adsorption behavior. The shape of these isotherms is favorable at low concentrations. At high concentrations the isotherms have an inflection point due to a change from a plateau to an unfavorable shape (cf. Fig. 1). Examples of aqueous systems manifesting this type of isotherm shape include the sorption of phenolic compounds (Miller and Clump 1970, Edgehill and Lu 1998, Juang and Shiau 1999) and methyl tert-butyl ether (Ebadi *et al.* 2007) on a variety of sorbents. We chose the data set of Miller and Clump (1970) for analysis because it contains an unusually large number of data points. We fit the following isotherm equations to their data of phenol sorption on activated carbon: the two-parameter Langmuir (Eq. (1) in Table 1), the three-parameter BET (Eq. (3) in Table 1), the

three-parameter Jovanović (Eq. (8) in Table 1), and the four-parameter Li (Eq. (9) in Table 1). Note that the functional form of the Langmuir equation does not permit it to fit the type II isotherm shape. It is included here as an example of a misspecified model.

The BET, Jovanović and Li equations are originally developed to fit type II isotherms of gas-solid systems. For example, the original BET equation for multilayer adsorption (Brunauer *et al.* 1938) has the form

$$q = \frac{q_m b P/P_S}{(1 - P/P_S)(1 - P/P_S + b P/P_S)} \quad (18)$$

where  $q_m$  is the monolayer capacity,  $b$  is the adsorption-desorption equilibrium constant and  $P$  and  $P_S$  are, respectively, the partial pressure and the saturation pressure of the adsorbate. Application of the BET equation to liquid-solid systems requires the following modifications (Gritti *et al.* 2002, Ebadi *et al.* 2009)

$$P = C; \quad b = b_s/b_L; \quad P_S = 1/b_L \quad (19)$$

where  $b_s$  is the equilibrium constant for the first layer and  $b_L$  is the equilibrium constant for subsequent layers. Substituting Eq. (19) in Eq. (18) leads to Eq. (3).

The original Jovanović and Li equations require similar modifications before they can be applied to liquid-solid systems. The original Jovanović equation for multilayer adsorption (Jovanović 1969) is given by

$$q = q_m [1 - \exp(-\varepsilon_1 P/P_S)] [\exp(\varepsilon_2 P/P_S)] \quad (20)$$

where  $\varepsilon_1$  and  $\varepsilon_2$  are two constants which describe adsorption in the first and in the second and higher layers, respectively. The parameter  $P_S$  can be absorbed in the constants  $\varepsilon_1$  and  $\varepsilon_2$

$$q = q_m [1 - \exp(-a_J P)] [\exp(b_J P)] \quad (21)$$

where  $a_J = \varepsilon_1/P_S$  and  $b_J = \varepsilon_2/P_S$ . We obtain Eq. (8) by replacing  $P$  in Eq. (21) with  $C$ .

The original Li equation for multilayer adsorption (Li 1985) is given by

$$q = K_L \ln \left[ 1 + (b_0 P)^{1/M} \right] \quad \text{with} \quad \frac{1}{M} = \frac{1 + \ln[1/(1 - P/P_S)]}{M_0} \quad (22)$$

where  $K_L$ ,  $b_0$  and  $M$  are constants with physical meanings. Eq. (9) is obtained when  $P$  and  $P_S$  in Eq. (22) are replaced by  $C$  and  $1/b_L$ , respectively.

The equilibrium data of Miller and Clump (1970) are shown in Fig. 4. It is evident that the data conform to the type II isotherm shape. Tabulated in Table A3 of Appendix A are the derived parameters obtained by fitting the four equations to the Fig. 4 data. The results of the model fits are grouped together in Fig. 4 (lines). It is obvious that the BET, Jovanović and Li equations can track the data well. The Langmuir equation, by contrast, performed poorly. The lack-of-fit displayed by the Langmuir equation is expected in that its functional form limits its correlative ability to the type I isotherm shape. With four parameters the Li equation provides the best fit to the data, as indicated by the highest  $R^2$  given in Table A3. The  $R^2$  score of the four-parameter Li fit is 3.2% and 4.5% higher than the respective  $R^2$  score of the three-parameter BET and Jovanović fits. The AIC<sub>c</sub> statistics in Table A3 also suggest that the Li equation is well supported by the data

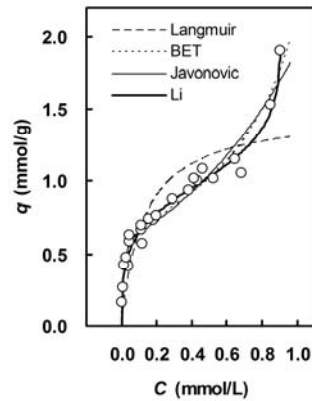


Fig. 4 Type II isotherm of the sorption of phenol on activated carbon showing comparison between the experimental trend and the theoretical curves calculated from the Langmuir, BET, Jovanović and Li equations with the parameters given in Table A3 (Data of Miller and Clump (1970))

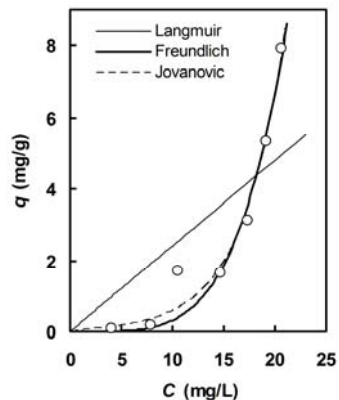


Fig. 5 Type III isotherm of the sorption of reactive yellow 125 on natural phosphate rock showing comparison between the experimental trend and the theoretical curves calculated from the Langmuir, Freundlich and Jovanović equations with the parameters given in Table A4 (Data of Barka *et al.* (2009))

and is superior to the BET and Jovanović equations. It is apparent that both the  $R^2$  indicator and the  $AIC_c$  test endorse the use of the four-parameter Li equation to fit the type II isotherm data of Miller and Clump.

### 5.3 Type III isotherm shape

This isotherm shape, depicted in Fig. 1, is termed unfavorable because there is essentially no sorption at low concentrations. Very few aqueous systems exhibiting the type III isotherm shape have been reported. This is understandable because such sorbents are useless for the removal of trace quantities of contaminants from wastewaters. Examples of this class of isotherms include the

sorption of phenolic compounds on fly ash (Akgerman and Zardkoohi 1996) and of a reactive dye on natural phosphate rock (Barka *et al.* 2009). The latter data set with more data points is analyzed here. Fig. 5 shows the sorption data of reactive yellow 125 on natural phosphate rock reported by Barka *et al.* (2009). Although there is an outlier, it can be seen that the sorption isotherm resembles a type III isotherm shape. We fit the two-parameter Langmuir (Eq. (1) in Table 1), two-parameter Freundlich (Eq. (4) in Table 1) and three-parameter Jovanović (Eq. (8) in Table 1) equations to the Fig. 5 data. As in the case of the type II data fits, the Langmuir fit is meant to illustrate the application of a misspecified model.

The results of the model fits are grouped together in Fig. 5. From this figure, one may conclude that, with the exception of the obvious outlier, the data set is very well fitted by the Freundlich and Jovanović equations. The serious divergence of the Langmuir fit from the data is indicative of the limitations of its equation structure. The derived parameters and associated  $R^2$  and  $AIC_c$  scores are summarized in Table A4 of Appendix A. According to the  $R^2$  statistics, the three-parameter Jovanović equation provides a more accurate means of fitting the data as compared to the two-parameter Freundlich equation. However, the  $AIC_c$  statistics reveal that the improvement in fit is not sufficiently large enough to justify the use of three parameters to fit the data. Consequently, the  $AIC_c$  measure favors the use of the two-parameter Freundlich equation to describe this data set. It appears that two-parameter equations (e.g., Langmuir and Freundlich) are advocated by the  $AIC_c$  approach as the preferred models for fitting the relatively simple types I and III isotherm shapes.

#### 5.4 Type IV isotherm shape

This isotherm shape is characterized by two plateaus (cf. Fig. 1). Although not common, this type of isotherm is increasingly being reported for aqueous systems involving the sorption of pesticides on soil (Czinkota *et al.* 2002, Konda *et al.* 2002) as well as the sorption of heavy metals on citrus peels (Schiewer and Patil 2008) and solid waste from olive oil production (Martín-Lara *et al.* 2009, Blázquez *et al.* 2010). To describe the shape of these isotherms, equations with specific functional forms are needed. For example, the somewhat complex BDDT equation (Eq. (7) in Table 1) can deal with this isotherm shape. Originally developed for gas-solids systems, the BDDT equation (Brunauer *et al.* 1940) is an extension of the famous BET equation and has the form

$$q = \left[ \frac{q_m b X}{1 - X} \right] \left[ \frac{1 + n \left[ (g - 1) X^{n-1} + g X^{n+1} - (2g - 1) X^n \right] - X^n}{1 + (b - 1) X + b \left[ (g - 1) X - g X^{n+1} \right]} \right] \quad (23)$$

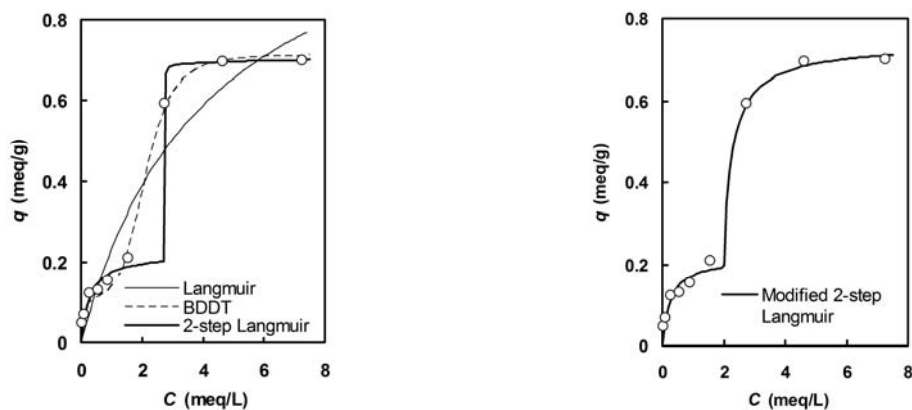
where  $g$  is a constant with physical meaning and  $X = P/P_s$ . Using Eq. (19), Eq. (23) can be converted to Eq. (7) for liquid-solids systems. Another equation developed for the type IV isotherm shape is the so-called two-step Langmuir (Czinkota *et al.* 2002, Konda *et al.* 2002). This equation (Eq. (2) in Table 1) uses two inter-connected Langmuir equations to capture the type IV isotherm shape.

We fit the BDDT (Eq. (7) in Table 1) and two-step Langmuir (Eq. (2) in Table 1) equations to the data of cadmium sorption on untreated lemon peels reported by Schiewer and Patil (2008). The Langmuir equation (Eq. (1) in Table 1) is also tested here. As before, it is used as an example of model misapplication. The fits are shown in Fig. 6(a). It is clearly seen in the figure that the Langmuir equation is unable to reproduce the isotherm shape whereas the BDDT and two-step Langmuir equations provide excellent fits to the data, the excellent fits coming at the expense of five adjustable parameters. These visual observations are reflected in the  $R^2$  statistics of the fits (cf.

Table A5 of Appendix A). On the basis of the  $R^2$  scores, the two-step Langmuir fit gives the best overall agreement with the data.

The  $AIC_c$  statistics on the other hand indicate that the Langmuir equation is the best model for describing this particular data set. The excellent fits of the BDDT and two-step Langmuir equations, whose  $R^2$  scores are respectively 7.3% and 7.2% higher than that of the Langmuir equation, are rejected by the  $AIC_c$  test largely because they rely on five fitting parameters. It appears that the low  $AIC_c$  score of the Langmuir equation relative to those of the BDDT and two-Langmuir equations is attributable to two factors: (a) a fortuitous fit to a majority of the data points resulted in a low SSE and hence a small first term on the right side of the  $AIC_c$  formula, and (b) two fitting parameters, compared to five in the BDDT and two-Langmuir equations, led to a very small second term in the  $AIC_c$  formula. As such, the  $AIC_c$  approach is not a panacea as it can lead to a mistaken preference for the Langmuir equation which is clearly inappropriate for correlating the type IV isotherm shape.

It should be noted that the genetic algorithm was unable to determine a unique value for the parameter  $b_2$  in the two-step Langmuir equation. The final value of  $b_2$  was found to vary with the upper limit used in the parameter estimation process. The  $b_2$  value given in Table A5 was obtained when the upper limit was set at 500. This problem is due in large part to a lack of data points in the region between the first and second plateaus. As can be seen in Fig. 6(a), the fit is characterized by a vertical line for this region as a result of a large  $b_2$ . One way to circumvent the problem caused by  $b_2$  is to assume that the two Langmuir components of the two-step Langmuir equation have the same  $b$ , i.e.,  $b_1 = b_2$ . This assumption effectively reduces the five-parameter two-step Langmuir equation to a four-parameter equation. As Fig. 6(b) shows, the modification provides an excellent fit to the data. All four parameters can now be uniquely determined. Listed in Table A6 of Appendix A is the  $R^2$  score for this new fit, which is slightly lower than the  $R^2$  score obtained



(a) Comparison between the experimental trend and the theoretical curves calculated from the Langmuir, BDDT and two-step Langmuir equations with the parameters given in Table A5

(b) Comparison between the experimental trend and the theoretical curve calculated from a modified form of the two-step Langmuir equation ( $b_1 = b_2$ ) with the parameters given in Table A6

Fig. 6 Type IV isotherm of the sorption of cadmium on untreated lemon peels (Data of Schiewer and Patil (2008))

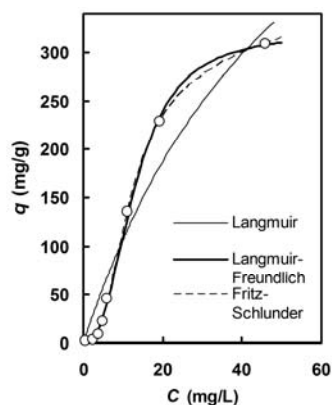


Fig. 7 Type V isotherm of the sorption of fluoride on MgAl-CO<sub>3</sub> layered double hydroxides showing comparison between the experimental trend and the theoretical curves calculated from the Langmuir, Langmuir-Freundlich and Fritz-Schlunder equations with the parameters given in Table A7 (Data of Lv *et al.* (2007))

with the original equation. Nevertheless, it is still higher than the  $R^2$  scores for the BDDT and Langmuir equations. A bonus of this modification is that the Akaike scores now agree with the  $R^2$  statistics, selecting the modified two-step Langmuir equation with four parameters as the best model (cf. Table A6).

### 5.5 Type V isotherm shape

As with the type III isotherm shape, this isotherm shape is unfavorable at low concentrations (cf. Fig. 1). This type of S-shaped isotherm seems to be rather rare for aqueous systems, a good example of which is the sorption of fluoride on MgAl-CO<sub>3</sub> layered double hydroxides reported by Lv *et al.* (2007), as shown in Fig. 7. Isotherm models best suitable for correlating this isotherm shape are the power-law functions. Accordingly, we fit the three-parameter Langmuir-Freundlich (Eq. (5) in Table 1) and four-parameter Fritz-Schlunder (Eq. (6) in Table 1) equations to the Fig. 7 data. As before, the Langmuir equation (Eq. (1) in Table 1) is used as an example of an inappropriate model fit. The derived parameters are summarized in Table A7 of Appendix A. As can be seen in Fig. 7, the data are well correlated by the two power-law equations, and, as expected, poorly fitted by the Langmuir equation. The Fritz-Schlunder equation with the highest  $R^2$  score delivers only slightly better fit than the Langmuir-Freundlich equation, but it has four fitting parameters. As a result, the AIC<sub>c</sub> test favors the three-parameter Langmuir-Freundlich equation, as indicated by the Akaike scores in Table A7.

## 6. Conclusions

A comparison of the AIC<sub>c</sub> and  $R^2$  indicators as guides in discriminating rival isotherm equations for the five types of isotherm shape in the BDDT classification is presented. The AIC<sub>c</sub> measure is perceived as more appropriate due to its ability to tradeoff between goodness-of-fit and

model complexity. The findings from this work indicate that for the simple isotherm shapes of types I and III the  $AIC_c$  test will pick two-parameter equations while the  $R^2$  approach will favor equations with more than two parameters. For these two types of isotherms, according to the premise of the  $AIC_c$  test, any improvement in the quality of fit that can be obtained from equations with more than two parameters is marginal. Given that most of the aqueous contaminant removal systems reported in the literature exhibit the type I (favorable) isotherm shape, the  $AIC_c$  measure will recommend that their equilibrium data be interpreted in terms of the simple two-parameter Langmuir or Freundlich equation. For the more intricate isotherm shapes of types II, IV and V, both indices favor equations with more than two parameters. This is due to the fact that two-parameter equations are unable to track these isotherm shapes. As a result, equations with more than two parameters can provide significantly better fits, justifying the need for parameter-rich equations.

As a final note, we present a caveat on using the  $AIC_c$  measure to discriminate rival isotherm equations for intricate isotherm shapes. It was shown that a fortuitous fit by the Langmuir equation to a majority of the data points of a type IV isotherm propelled the  $AIC_c$  measure to select it as the best model. Visual inspection of the fit revealed that the two-parameter Langmuir equation, originally intended as an example of a misspecified model, was unable to track the type IV isotherm shape. To avoid such pitfalls, one should ensure that the competing equations selected to interpret a complex isotherm shape have the correct functional form.

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## Appendix A

Results of model fits to the five types of isotherm shape in the BDDT classification.

Table A1 Results of model fits to type I isotherm of the sorption of methylene blue on natural phosphate rock

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	7.23 <sup>a</sup> , 10.71 <sup>b</sup>	0.9299	-6.28	0.00	0.85
Langmuir-Freundlich	6.99 <sup>a</sup> , 41.83 <sup>b</sup> , 1.64 <sup>c</sup>	0.9540	-2.87	3.41	0.15
Fritz-Schlunder	814.53 <sup>d</sup> , 122.56 <sup>e</sup> , 2.02 <sup>f</sup> , 1.98 <sup>g</sup>	0.9621	7.39	13.67	0.00

<sup>a</sup>  $q_m$  (mg/g); <sup>b</sup>  $b$  (L/mg) or (L/mg)<sup>n</sup>; <sup>c</sup>  $n$ ; <sup>d</sup>  $\alpha_1$  (mg<sup>(1- $\beta_1$ )</sup>L <sup>$\beta_1$</sup> )/g; <sup>e</sup>  $\alpha_2$  (L/mg) <sup>$\beta_2$</sup> ; <sup>f</sup>  $\beta_1$ ; <sup>g</sup>  $\beta_2$

Table A2 Results of model fits to type I isotherm of the sorption of basic yellow 28 on natural phosphate rock

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	7.47 <sup>a</sup> , 0.91 <sup>b</sup>	0.9960	-19.99	0.00	1.00
Langmuir-Freundlich	7.33 <sup>a</sup> , 0.93 <sup>b</sup> , 1.07 <sup>c</sup>	0.9965	-6.87	13.11	0.00
Fritz-Schlunder	5.49 <sup>d</sup> , 0.56 <sup>e</sup> , 0.87 <sup>f</sup> , 0.96 <sup>g</sup>	0.9968	34.55	54.53	0.00

<sup>a</sup>  $q_m$  (mg/g); <sup>b</sup>  $b$  (L/mg) or (L/mg)<sup>n</sup>; <sup>c</sup>  $n$ ; <sup>d</sup>  $\alpha_1$  (mg<sup>(1- $\beta_1$ )</sup>L <sup>$\beta_1$</sup> )/g; <sup>e</sup>  $\alpha_2$  (L/mg) <sup>$\beta_2$</sup> ; <sup>f</sup>  $\beta_1$ ; <sup>g</sup>  $\beta_2$

Table A3 Results of model fits to type II isotherm of the sorption of phenol on activated carbon

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	1.48 <sup>a</sup> , 7.72 <sup>b</sup>	0.7357	-67.97	49.26	0.00
BET	0.68 <sup>a</sup> , 83.20 <sup>c</sup> , 0.68 <sup>d</sup>	0.9617	-108.92	8.31	0.02
Jovanović	0.57 <sup>a</sup> , 69.86 <sup>e</sup> , 1.20 <sup>f</sup>	0.9481	-101.80	15.42	0.00
Li	1.73 <sup>g</sup> , 1.47 <sup>h</sup> , 1.10 <sup>i</sup> , 2.74 <sup>j</sup>	0.9920	-117.23	0.00	0.98

<sup>a</sup>  $q_m$  (mmol/g); <sup>b</sup>  $b$ , <sup>c</sup>  $b_S$ , <sup>d</sup>  $b_L$ , <sup>e</sup>  $a_J$ , <sup>f</sup>  $b_J$  (L/mmol); <sup>g</sup>  $K_L$  (mmol/g); <sup>h</sup>  $b_0$ , <sup>i</sup>  $b_L$  (L/mmol); <sup>j</sup>  $M_0$

Table A4 Results of model fits to type III isotherm of the sorption of reactive yellow 125 on natural phosphate rock

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	252.94 <sup>a</sup> , 0.001 <sup>b</sup>	0.6258	20.78	15.24	0.00
Freundlich	1.26E-5 <sup>c</sup> , 4.40 <sup>d</sup>	0.9576	5.54	0.00	1.00
Jovanović	0.05 <sup>a</sup> , 0.76 <sup>e</sup> , 0.24 <sup>f</sup>	0.9725	16.52	10.98	0.00

<sup>a</sup>  $q_m$  (mg/g); <sup>b</sup>  $b$  (L/mg); <sup>c</sup>  $K_F$  ((mg<sup>(1- $n$ )</sup>L <sup>$n$</sup> )/g); <sup>d</sup>  $n$ ; <sup>e</sup>  $a_J$ , <sup>f</sup>  $b_J$  (L/mg)

Table A5 Results of model fits to type IV isotherm of the sorption of cadmium on untreated lemon peels

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	1.20 <sup>a</sup> , 0.24 <sup>b</sup>	0.9298	-37.33	0.00	1.00
BDDT	0.113 <sup>a</sup> , 19.38 <sup>c</sup> , 0.14 <sup>d</sup> , 655.57 <sup>e</sup> , 6.31 <sup>f</sup>	0.9963	-20.56	16.77	0.00
Two-step Langmuir	0.22 <sup>g</sup> , 0.49 <sup>h</sup> , 3.69 <sup>i</sup> , 490.64 <sup>j</sup> , 2.75 <sup>k</sup>	0.9978	-25.26	12.07	0.00

<sup>a</sup>  $q_m$  (meq/g); <sup>b</sup>  $b$ , <sup>c</sup>  $b_S$ , <sup>d</sup>  $b_L$  (L/meq); <sup>e</sup>  $g$ ; <sup>f</sup>  $n$ ; <sup>g</sup>  $a_1$ , <sup>h</sup>  $a_2$  (meq/g); <sup>i</sup>  $b_1$ , <sup>j</sup>  $b_2$  (L/meq); <sup>k</sup>  $c_2$  (meq/L)

Table A6 Results of model fits to type IV isotherm of the sorption of cadmium on untreated lemon peels

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	1.20 <sup>a</sup> , 0.24 <sup>b</sup>	0.9298	-37.33	10.44	0.01
BDDT	0.113 <sup>a</sup> , 19.38 <sup>c</sup> , 0.14 <sup>d</sup> , 655.57 <sup>e</sup> , 6.31 <sup>f</sup>	0.9963	-20.56	27.21	0.00
Two-step Langmuir ( $b_1 = b_2$ )	0.22 <sup>g</sup> , 0.52 <sup>h</sup> , 4.01 <sup>ij</sup> , 2.00 <sup>k</sup>	0.9974	-47.77	0.00	0.99

<sup>a</sup>  $q_m$  (meq/g); <sup>b</sup>  $b$ , <sup>c</sup>  $b_S$ , <sup>d</sup>  $b_L$  (L/meq); <sup>e</sup>  $g$ ; <sup>f</sup>  $n$ ; <sup>g</sup>  $a_1$ , <sup>h</sup>  $a_2$  (meq/g); <sup>i</sup>  $b_1$ , <sup>j</sup>  $b_2$  (L/meq); <sup>k</sup>  $c_2$  (meq/L)

Table A7 Results of model fits to type V isotherm of the sorption of fluoride on MgAl-CO<sub>3</sub> layered double hydroxides

Isotherm model	Derived parameters	$R^2$	Akaike measures		
			AIC <sub>c</sub>	$\Delta_i$	$w_i$
Langmuir	736.17 <sup>a</sup> , 0.02 <sup>b</sup>	0.9322	65.76	23.12	0.00
Langmuir-Freundlich	320.72 <sup>a</sup> , 0.002 <sup>b</sup> , 2.50 <sup>c</sup>	0.9988	42.63	0.00	1.00
Fritz-Schlunder	0.23 <sup>d</sup> , 0.002 <sup>e</sup> , 2.98 <sup>f</sup> , 2.80 <sup>g</sup>	0.9995	54.08	11.45	0.00

<sup>a</sup>  $q_m$  (mg/g); <sup>b</sup>  $b$  (L/mg) or (L/mg)<sup>n</sup>; <sup>c</sup>  $n$ ; <sup>d</sup>  $\alpha_1$  (mg<sup>(1- $\beta_1$ )</sup>L <sup>$\beta_1$</sup> )/g; <sup>e</sup>  $\alpha_2$  (L/mg) <sup>$\beta_2$</sup> ; <sup>f</sup>  $\beta_1$ ; <sup>g</sup>  $\beta_2$