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Is the Frumkin (Fowler–Guggenheim) adsorption isotherm a two- or three-parameter equation?

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ABSTRACT

The Frumkin or Fowler–Guggenheim isotherm, which has three fitting parameters, is often converted to a linear form with two fitting parameters to facilitate parameter estimation by linear regression. This conversion is made possible by way of replacing the unknown capacity parameter of the Frumkin isotherm with a surrogate value. The capacity parameters of certain simple isotherms (e.g., Dubinin–Radushkevich) are often used as surrogates. However, such surrogates have never been evaluated for validity or accuracy. In this paper, the three-parameter Frumkin isotherm was fit to previously published isotherm data to identify all three unknown parameters, including the capacity parameter. In the cases examined, the fitted capacity values were found to differ rather significantly from the surrogate capacity values used in the two-parameter Frumkin isotherm. The dubious practice of transforming the three-parameter Frumkin isotherm into the two-parameter Frumkin isotherm for linear estimation of parameters should be discarded in favor of estimating all three parameters by nonlinear regression.

1. Introduction

Several theoretical and empirical isotherm equations are available to correlate adsorption isotherms of water contaminants, most of which are of type I in the IUPAC classification. Such isotherms can be effectively described by the two-parameter equations of Freundlich and Langmuir. Some other commonly used isotherms are those of Dubinin and Radushkevich, Temkin, and Frumkin. Unfortunately, it is not uncommon to find examples of isotherm misuse in this field of research. A pertinent example is the Dubinin–Radushkevich (D–R) isotherm, which has been incorrectly used to identify the adsorption mechanism at the liquid-solid interface [1].

The purpose of the present study is to call attention to the misuse of the Frumkin isotherm [2] in the area of adsorptive water decontamination. Specifically, this paper dissects some questionable methods adopted by researchers to fit a linear form of the Frumkin isotherm to experimental isotherm data. Many studies have shown that adsorption of water contaminants by porous materials obeys the Frumkin isotherm, of which the celebrated Langmuir isotherm is a special case. For aqueous adsorption systems the Frumkin isotherm relates the fractional loading θ to the bulk concentration c with which it is in equilibrium according to Eq. (1), where b and w are constants, R is the gas constant, and T is the temperature.

$$c = \frac{1}{b}\frac{\theta}{1-\theta}\exp\left(\frac{2w\theta}{RT}\right) \tag{1}$$

The parameter θ in Eq. (1) is given by q/q_m, where q is the amount adsorbed and q_m is the specific saturation capacity of the adsorbent. Mathematically, the Fowler–Guggenheim isotherm [3] derived from statistical thermodynamics is analogous to the Frumkin isotherm. In some publications, Eq. (1) is known as the Frumkin–Fowler–Guggenheim or FFG isotherm. In addition, Eq. (1) can be derived from the vacancy solution theory of adsorption [4] or adsorption-desorption kinetic argument [5,6]. It should be mentioned that several different versions of the Frumkin isotherm exist in the adsorption literature. For example, a popular version includes a negative sign in the argument of the exponential term (the parameter w can be a positive or negative value). Very recently, Barbero et al. [7] have presented a generalized FFG isotherm. Eq. (1) is based on the Fowler–Guggenheim version given in Ruthven's book [8].

To correlate isotherm data of water contaminants, Eq. (1) is frequently rearranged to the following linear form:

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$$\ln\left[\frac{\theta}{(1-\theta)c}\right] = \ln(b) - \frac{2w}{RT}\theta \tag{2}$$

If Eq. (2) is obeyed, plots of the left side of the equation against θ should yield a straight line. Linear regression can then be used to estimate the two free parameters b and w. Eq. (2) therefore implies that the linearized Frumkin isotherm is an expression with two undetermined parameters. However, this is only true if q_m is known [9]. We can see this more clearly if we replace θ in Eq. (2) with q/q_m:

$$\ln\left[\frac{q}{(q_m-q)c}\right] = \ln(b) - \frac{2w}{RT}\frac{q}{q_m} \tag{3}$$

To plot Eq. (3) using a linear regression procedure (left side member vs. q), knowledge of q_m is required to calculate the left side member of the equation. Therefore, the plateau value of an experimental isotherm must be estimated in some way. Because there is no consensus in the literature, different methods have been used to estimate q_m. A method used by Hamdaoui and Naffrechoux [10] assumes that q_m corresponds to a theoretical maximum adsorption capacity which can be calculated using the BET surface area of the adsorbent and the molecular cross-sectional area of the adsorbate. Another approach assumes that q_m in the Frumkin isotherm can be replaced by a surrogate capacity parameter. For example, the capacity parameters that appear in different isotherm models such as the equations of Langmuir [10], Freundlich [10–12], and D–R [13–21] have been inserted into the linearized Frumkin isotherm to calculate θ. In particular, the D–R capacity parameter is a popular surrogate, probably owing to the fact that it has been featured in a review article [22]. The simplest approach assumes that the Frumkin capacity parameter is given by the plateau of an experimental isotherm [23] but it is prone to subjective interpretation when the isotherm exhibits no apparent saturation region. We mention in passing that many studies have applied the two-parameter Frumkin isotherm to experimental data without disclosing how the Frumkin capacity parameter was estimated [24–35].

To our knowledge, no previous studies have examined the implications of using a surrogate capacity parameter in the Frumkin isotherm. The research reported here fills this gap. In our approach, the Frumkin isotherm is treated as an equation with three fitting parameters. Because the three-parameter Frumkin isotherm is implicit in solid phase concentration, a data fitting procedure based on orthogonal distance regression (ODR) is used for parameter estimation. In the cases studied, the Frumkin q_m values extracted directly from published isotherm data are compared with the surrogate q_m values, and conclusions are reached regarding the applicability of the two-parameter Frumkin isotherm. To facilitate parameter estimation, Eq. (1) is rewritten as Eq. (4) or (5), where $a = 2w/RT$. When $a = 0$, Eq. (5) reduces to Eq. (6), which is the familiar Langmuir isotherm.

$$c = \frac{1}{b}\frac{q}{q_m-q}\exp\left(a\frac{q}{q_m}\right) \tag{4}$$

$$q = \frac{q_m bc\exp(-aq/q_m)}{1+bc\exp(-aq/q_m)} \tag{5}$$

$$q = \frac{q_m bc}{1+bc} \tag{6}$$

2. Parameter estimation

The Solver add-in bundled with Excel provides a convenient way to estimate the unknown parameters of an isotherm by nonlinear least-squares fitting [36]. The conventional nonlinear regression approach treats q and c as the dependent and independent variables, respectively. To obtain best-fit parameter estimates, the sum of squared residuals (SSR) is calculated and minimized using a fitting algorithm. The most common SSR is defined as the difference between the measured and calculated q values, given here by Eq. (7), where $q_{i,obs}$ is the ith observed q value, $q_{i,fit}$ is the ith q value calculated from the chosen isotherm, and m is the number of data points.

$$\mathrm{SSR} = \sum\nolimits_{i=1}^{m}\left(q_{i,obs} - q_{i,fit}\right)^2 \tag{7}$$

Unfortunately, it is somewhat difficult to use Eq. (7) as the objective function for least-squares fitting because the Frumkin isotherm defined by Eq. (5) is implicit in solid phase concentration. It is necessary to incorporate a numerical routine within the fitting algorithm in order to calculate $q_{i,fit}$ at each iteration. Such an approach was used by Pennanen et al. [37]. A more practical approach is to use Eq. (4), which is explicit in solution phase concentration, in lieu of Eq. (5) as the regression equation. It is straightforward to minimize the SSR based on the solution phase concentration c, given here by Eq. (8), where $c_{i,obs}$ is the ith observed c value and $c_{i,fit}$ is the ith c value calculated from Eq. (4).

$$\mathrm{SSR} = \sum\nolimits_{i=1}^{m}\left(c_{i,obs} - c_{i,fit}\right)^2 \tag{8}$$

The SSR defined by Eq. (8) has been used by several researchers to evaluate the Jossens isotherm, which is also implicit in solid phase concentration [38–40]. From a statistical perspective Eq. (8) is considered superior to Eq. (7) for the nonlinear least-squares fitting of explicitly defined isotherm models such as the Langmuir and Freundlich equations. The parameter estimation procedure requires that the values of $c_{i,fit}$ be obtained from the solution of the mass balance equation for a batch adsorber [41]. In this treatment, c becomes the dependent variable and the other measured quantities in the mass balance equation (initial concentration, adsorbent mass, solution volume) become the independent variables.

Another way to handle implicit isotherms is by using a regression technique called orthogonal distance regression (ODR) [42], which is also known as errors-in-variables modeling and total least squares. The ODR method has been applied to the evaluation of explicitly defined isotherm models, including the Langmuir and Freundlich equations [43,44]. In these cases, ODR was used to provide more accurate regression parameters by accounting for the measurement errors in both c and q. The solution phase concentration c is not error-free because it is a measured quantity, while q is calculated from the mass balance equation that contains several measured quantities, including c. The errors in the independent variable c and the dependent variable q may be comparable. As a result, fitting such data using standard least-squares methods can lead to bias in the solution. This problem is solved in the ODR treatment, which makes no distinction between dependent and independent variables. The ODR method for fitting explicit isotherm models to experimental equilibrium data has been implemented in a freely available Excel spreadsheet [45]. It should be mentioned that ODR does not address the statistical problem of correlation that exists between c and q [41,46].

In addition to being applicable to explicit models, ODR can handle implicit functions [47,48]. Several software packages including the freely available ODRPACK package [47] support fitting to such functions. In this work, OriginPro 2019 was used to evaluate the implicit Frumkin isotherm given by Eqs. (4) and (5). To use the software's ODR procedure to fit implicit expressions, Eqs. (4) and (5) must be designated as an implicit function and expressed as Eqs. (9) and (10), respectively:

$$c - \frac{1}{b}\frac{q}{q_m-q}\exp\left(a\frac{q}{q_m}\right) = 0 \tag{9}$$

$$q - \frac{q_m bc\exp(-aq/q_m)}{1+bc\exp(-aq/q_m)} = 0 \tag{10}$$

The two overall fit indicators used in this work are given by Eqs. (11) and (12), where R^2 is the coefficient of determination, $q_{av,obs}$ is the mean of all $q_{i,obs}$ values, RRMSE is the residual root mean square error, and p is the number of fitting parameters.

$$R^2 = 1 - \frac{\sum_{i=1}^{m}\left(q_{i,obs} - q_{i,fit}\right)^2}{\sum_{i=1}^{m}\left(q_{i,obs} - q_{av,obs}\right)^2} \tag{11}$$

$$\text{RRMSE} = \sqrt{\frac{\sum_{i=1}^{m}\left(q_{i,obs} - q_{i,fit}\right)^2}{m-p}} \tag{12}$$

3. Results and discussion

In the work reported here, the ODR procedure is used to fit the three-parameter Frumkin isotherm to previously published isotherm data, which have been analyzed using the two-parameter Frumkin isotherm. The fitted values of q_m are compared with the values of surrogate q_m used in the two-parameter expression.

3.1. Surrogate q_m based on theoretical capacity parameter

Hamdaoui and Naffrechoux [10] have conducted an experimental and modeling study of the adsorption of five phenolic compounds by activated carbon. They assumed monolayer surface coverage and used a theoretical method based on the BET surface area of the adsorbent and the molecular cross-sectional area of the adsorbate to calculate q_m. The resulting theoretical values of q_m were used to calculate θ in the two-parameter Frumkin isotherm given by Eq. (2), which was fit to the isotherm data of the five phenolic compounds. Fig. 1A presents a representative data set for 2-chlorophenol (2-CP), which exhibits a typical type I curve shape. The theoretical value of q_m for 2-CP was found to be 594.76 mg g^{-1} [10], to which the value of q_m extracted from the data of Fig. 1A will be compared.

Four data fitting strategies were used to fit the three-parameter Frumkin isotherm to the 2-CP data, the first of which used the ODR method to handle the implicit equation defined by Eq. (10). The resulting parameter estimates and statistical metrics (R^2 and RRMSE) are given in Table 1, column 2. Second, the ODR procedure was applied to Eq. (9), the resulting parameter estimates (Table 1, column 3) are identical to those of the first procedure. Third, we tested the use of Eq. (4), which is explicit in c, as the regression equation for the ODR procedure, again obtaining the same parameter estimates (Table 1, column 4). The final procedure applied the ordinary least-squares method based on the Levenberg-Marquardt algorithm to Eq. (4). In this case, Eq. (8) was used as the objective function. Column 5 of Table 1 reveals that the resulting parameter estimates are somewhat different from those of the previous three ODR cases. The parameter a has the least dependable estimate because of its very large standard error. The R^2 and RRMSE scores are also inferior to those of the three ODR procedures.

Table 1
Parameter estimates and statistical metrics for Frumkin fits of the Fig. 1 data.

Frumkin parameter and statistical metric	Nonlinear regression method			
	ODR/Eq. (10)	ODR/Eq. (9)	ODR/Eq. (4)	OLSR/Eq. (4)
a	0.51 (0.68)	0.51 (0.58)	0.51 (0.68)	0.29 (0.92)
b (L mg^{-1})	0.08 (0.02)	0.08 (0.02)	0.08 (0.02)	0.07 (0.03)
q_m (mg g^{-1})	330.4 (19.0)	330.4 (16.8)	330.4 (19.0)	324.3 (21.7)
R^2	0.993	0.993	0.993	0.989
RRMSE (mg g^{-1})	6.25	6.25	6.25	7.47

Bracketed values represent standard errors for parameter estimates. ODR: orthogonal distance regression; OLSR: ordinary least-squares regression.

It is evident that the three ODR procedures fit the 2-CP data better than the ordinary least-squares method. Of the three ODR procedures, the second approach based on Eq. (9) is not recommended because it was very sensitive to the initial values given to the three parameters. Convergence failures were sometimes encountered when the initial values used were far from the optimal values. In contrast, the mathematical form of Eq. (10) was far more tolerant to suboptimal initial values. The performance of the third ODR procedure based on Eq. (4) is identical to those of the first and second ODR procedures. Thus, a freely available Excel spreadsheet developed for the ODR treatment of isotherm models that are explicit in solid phase concentration [45] may be used to fit the Frumkin isotherm based on Eq. (4), which is explicit in solution phase concentration. Although the fourth procedure based on the ordinary least-squares method is inferior to the ODR method, its parameter estimates are quite acceptable. This finding suggests that the Solver add-in of Excel can be used to evaluate the three-parameter Frumkin isotherm by conventional nonlinear regression. Fig. 1 plots the fitted curves obtained from the ODR procedure based on Eq. (10) and the ordinary least-squares procedure based on Eq. (4). One can see that the two fitted curves are very effective in tracing the 2-CP data points.

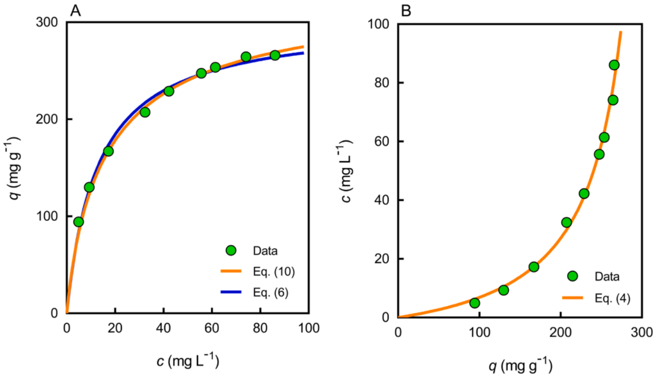

Fig. 1. (A) Three-parameter Frumkin fit [Eq. (10)] and Langmuir fit [Eq. (6)] compared to observed 2-CP isotherm data reported by Hamdaoui and Naffrechoux [10]. (B) Three-parameter Frumkin fit [Eq. (4)] compared to observed 2-CP isotherm data.

The theoretical value of q_m (594.76 mg g^{-1}) calculated by Hamdaoui and Naffrechoux [10] is significantly higher than the observed values of q ($<$ 300 mg g^{-1}) that correspond to the plateau of the experimental isotherm, as can be seen in Fig. 1A. Given the presence of the isotherm plateau, it is very unlikely that the type I isotherm could reach a maximum adsorption capacity of close to 600 mg g^{-1} with increasing solution phase concentration. The fitted value of q_m (330.4 mg g^{-1}) is in good agreement with the observed plateau and therefore reflects the actual maximum capacity level for this adsorption system. As such, the theoretical value of q_m, which is larger than the fitted value of q_m by a factor of 1.8, is basically unrealistic. This theoretical value of q_m could be a source of unexamined bias in the regression of the two-parameter Frumkin equation to estimate the parameters a and b. It appears that the theoretical calculation method for q_m proposed by Hamdaoui and Naffrechoux [10] is merely a mathematical convenience that permits the use of linear regression to evaluate the Frumkin isotherm.

3.2. Surrogate q_m based on Langmuir capacity parameter

In addition to the theoretical value of q_m, Hamdaoui and Naffrechoux [10] have used the Langmuir and Freundlich capacity parameters as surrogates to calculate θ. They recommended a Langmuir q_m value of 303.03 mg g^{-1}, obtained by fitting a linear version of the Langmuir isotherm to the 2-CP data. This Langmuir capacity parameter appears to be a reasonable surrogate, as it is similar to the experimental plateau level and the fitted value of q_m (330.4 mg g^{-1}). Fig. 1A shows the fit of the Langmuir isotherm to the 2-CP data by ordinary nonlinear regression ($q_m = 303.9$ mg g^{-1}; $b = 0.08$ L mg^{-1}). One can see that the Langmuir fit is comparable to the Frumkin fit. The Langmuir fit statistics ($R^2 = 0.990$; RRMSE $= 6.73$ mg g^{-1}) are only slightly inferior to those of the Frumkin fit (ODR; $R^2 = 0.993$; RRMSE $= 6.25$ mg g^{-1}).

Clearly, the three-parameter Frumkin isotherm is not vastly superior to the two-parameter Langmuir isotherm in representing the 2-CP data. According to the Akaike Information Criterion or AIC test, which penalizes models with a high number of fitting parameters, the 2-CP data set favors the Langmuir isotherm because the marginal improvement in fit afforded by the Frumkin isotherm is not sufficient to justify the use of three fitting parameters. To some extent, the Langmuir and Frumkin isotherms are expected to provide similar data fitting performance, since the former isotherm is a special case of the latter isotherm. As noted above, when $a = 0$ the Frumkin isotherm reduces to the Langmuir isotherm. If for some reason one must use linear regression to fit the Frumkin isotherm to experimental data, one should use the Langmuir capacity parameter as a surrogate for the Frumkin capacity parameter to calculate θ. Surprisingly, the Langmuir capacity parameter has not been used much as a surrogate, with most studies favoring the Dubinin–Radushkevich capacity parameter. We will come back to the D–R capacity parameter at a later stage.

3.3. Surrogate q_m based on Freundlich capacity parameter

Hamdaoui and Naffrechoux [10] have used the Freundlich capacity parameter as a surrogate for the Frumkin capacity parameter to calculate θ. First, they used a linear form of the Freundlich isotherm ($q = KC^{1/n}$) to correlate the 2-CP data, obtaining $K = 57.795$ mg g^{-1} L$^{1/n}$ mg$^{-1/n}$ and $n = 2.793$. Next, they calculated the Freundlich capacity parameter q_m from Eq. (13), where C_0 is the initial concentration. Eq. (13) has also been used by Ferrandon et al. [11].

$$q_m = KC_0^{1/n} \tag{13}$$

According to Hamdaoui and Naffrechoux [10], C_0 should correspond to a fixed initial concentration used in batch isotherm measurement experiments in which the adsorbent mass is varied. The fixed initial concentration used in the 2-CP isotherm measurement experiments was 100 mg L^{-1}. With known values of K, n, and C_0, Eq. (13) spits out a q_m value of 300.6 mg g^{-1}. Since this Freundlich capacity parameter is comparable to the fitted value of q_m (330.4 mg g^{-1}), its use to calculate θ seems justified. However, the concept of maximum saturation capacity is incompatible with the Freundlich isotherm because its mathematical form predicts a continuous increase in q with increasing c. More importantly, Eq. (13) is flawed because the initial concentration can assume any value. For example, if the isotherm measurement experiments had been conducted using a C_0 value of 300 mg L^{-1} instead of 100 mg L^{-1}, we would still end up with the same experimental isotherm defined by the same K and n. In this case, we would obtain a q_m value of 445.4 mg g^{-1} from Eq. (13), which contradicts the fitted value of q_m. It is clear that the agreement between the Freundlich capacity parameter and the fitted value of q_m for the 2-CP data set is fortuitous.

As an aside, we call attention to two misconceptions relating to the Frumkin isotherm. The first is related to the work of Hamdaoui and Naffrechoux [10]. Due to the unsatisfactory fits of some isotherm data, Hamdaoui and Naffrechoux [10] commented that the Frumkin isotherm was only good for $\theta < 0.6$ when the Langmuir and Freundlich capacity parameters were used as surrogates for the linearized Frumkin isotherm. This comment, which was only relevant to their method of evaluating the Frumkin isotherm using surrogate capacity parameters of other isotherms, has been misrepresented as a general rule. Some authors have made the incorrect claim that the Frumkin isotherm is only valid for $\theta < 0.6$ [49,50]. The second misconception concerns the use of the Frumkin isotherm and the Fowler–Guggenheim isotherm to fit the same isotherm data [51–57]. As noted above, the Frumkin isotherm is mathematically analogous to the Fowler–Guggenheim isotherm. Therefore, identical results should be obtained when the two isotherms are applied to the same data set. The two isotherms have even been listed separately in a review article [58], creating the impression that they are independent models.

3.4. Surrogate q_m based on Dubinin–Radushkevich capacity parameter

The D–R capacity parameter is widely used as a surrogate for the Frumkin capacity parameter to calculate θ [13–21]. Like the Langmuir and Freundlich isotherms, the two-parameter D–R isotherm can be easily linearized, allowing its capacity parameter to be estimated by linear regression. Here, we examine two cases involving the use of the D–R and Frumkin isotherms in data correlation. Sarıcı-Özdemir and Önal [16] have applied several isotherm models, including the Frumkin and D–R isotherms, to their ascorbic acid isotherm data. The capacity parameter of the linearized D–R isotherm was found to be 7.67×10^{-3} mol g^{-1}, which translates to a capacity of 1350.8 mg g^{-1}. This D–R capacity parameter was used as a surrogate for the Frumkin capacity parameter to calculate θ. The linearized Frumkin isotherm was then fit to the ascorbic acid data. Fig. 2 shows the three-parameter Frumkin fit of the same data, returning a q_m estimate of 455.2 mg g^{-1}. Given that the D–R capacity parameter is greater than the fitted value of q_m by approximately a factor of three, the common practice of using the D–R capacity parameter as a surrogate for the Frumkin capacity parameter is questionable.

In the second example, Makrigianni et al. [27] have applied several isotherm models including the Frumkin and D–R isotherms to their phenol and methylene blue adsorption data. For the phenol data, the D–R fit produced a value of 23.19 mg g^{-1} for the capacity parameter. The linearized Frumkin isotherm was fit to the phenol data, but Makrigianni et al. [27] did not disclose how θ was calculated. Here, the three-parameter Frumkin isotherm was fit to the phenol data (Fig. 3), returning a q_m estimate of 69.3 mg g^{-1}, which differs rather significantly from the D–R capacity parameter (23.19 mg g^{-1}). It is evident that the D–R capacity parameter bears little resemblance to the value of q_m extracted from the isotherm data. The finding of this example is consistent with that of the first example discussed above, that is, the D–R capacity parameter is a very poor surrogate for the Frumkin capacity parameter.

The two examples show that the D–R capacity parameter should not be used as a surrogate for the Frumkin capacity parameter. Instead, one

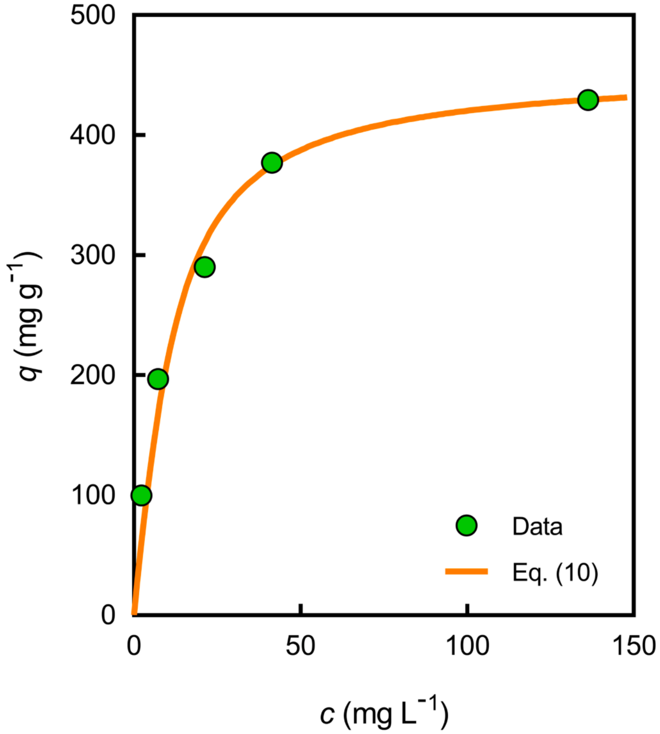

Fig. 2. Three-parameter Frumkin fit [Eq. (10)] compared to observed ascorbic acid data reported by Sarıcı-Özdemir and Önal [16].

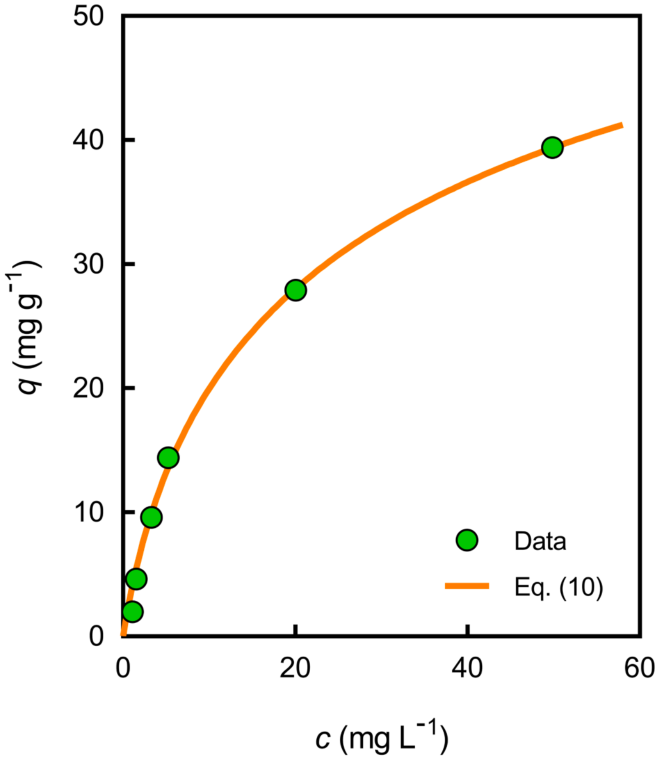

Fig. 3. Three-parameter Frumkin fit [Eq. (10)] compared to observed phenol isotherm data reported by Makrigianni et al. [27].

should treat the latter as a fitting parameter to ensure reliable modeling results. Very few studies have applied the three-parameter Frumkin isotherm in data correlation [37,59,60]. Pennanen et al. [37] have used an iterative method to handle the implicit Frumkin isotherm. In the work of Durimel et al. [59], the objective function given by Eq. (7) was used in nonlinear regression analyses, with the implicit Frumkin isotherm presumably solved by a Newton algorithm. In the study by Fideles et al. [60], nonlinear regression was performed using MATLAB, but it is not clear which numerical routine was used to manipulate the implicit Frumkin isotherm.

3.5. Type V isotherm data

The majority of previous studies in this area have focused on using the Frumkin isotherm to describe experimental isotherms of type I, such as those shown in Figs. 1–3. Although effective, using the Frumkin isotherm with three fitting parameters to correlate type I data seems like overkill. Indeed, type I isotherm data can be effectively handled by two-parameter isotherms such as the Langmuir and Freundlich equations. In addition to type I isotherm data, the Frumkin isotherm can be used to correlate sigmoid or type V isotherm data [61]. Such isotherms have been observed in a number of aqueous adsorption systems [62]. Satisfactory results have been obtained when the Frumkin isotherm was used to correlate type V isotherm data of water contaminants [63–66]. Koubaissy et al. [63,64] and Beltrán-Heredia and Sánchez-Martín [65] have applied the three-parameter Frumkin isotherm to their type V isotherm data, but Benosmane et al. [66] have used the linearized Frumkin isotherm to fit their type V data. To ensure good fits, linear regression analyses were restricted to a partial range of the data points ($\theta < 0.6$). Here, the three-parameter Frumkin isotherm was fit to the isotherm data of two anti-inflammatory drugs [paracetamol (PCT) and niflumic acid (NFA)] reported by Benosmane et al. [66]. All data points were used in the ODR fitting procedure. As can be seen in Fig. 4, the three-parameter Frumkin fits manifest excellent conformity with the two sigmoid data trends, returning unique parameter estimates as well as impressive statistical metrics (Table 2).

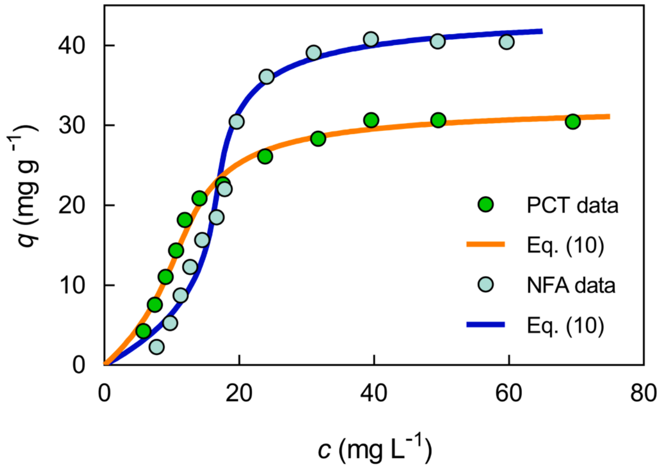

Fig. 4. Three-parameter Frumkin fits [Eq. (10)] compared to observed paracetamol (PCT) and niflumic acid (NFA) isotherm data reported by Benosmane et al. [66].

4. Conclusions

The key results of this work are the following:

- The theoretical saturation capacity calculated for the 2-CP/carbon adsorption system was found to differ significantly from the Frumkin capacity parameter extracted from the 2-CP isotherm data. Consequently, the former should not be used as a surrogate for the latter.
- Similarly, the Dubinin-Radushkevich capacity parameter was found to be a poor surrogate for the Frumkin capacity parameter. This popular surrogate is inappropriate, and its use should be discouraged.
- The Freundlich capacity parameter should not be used as a surrogate for the Frumkin capacity parameter, because it is based on a faulty equation.
- Since the Langmuir isotherm is a special case of the Frumkin isotherm, the Langmuir capacity parameter is generally a good surrogate for the Frumkin capacity parameter. However, it is totally unnecessary to make the Frumkin isotherm dependent on the Langmuir isotherm given that the Frumkin capacity parameter can be extracted from experimental data.
- The concept of surrogate capacity parameter is merely a mathematical convenience because its main function is to convert the three-parameter Frumkin isotherm to the two-parameter Frumkin isotherm so that linear regression can be used for parameter estimation. The Frumkin isotherm can stand on its own and does not need any help from other isotherm models. Its three undetermined parameters can be estimated directly from experimental data.

Table 2
Parameter estimates and statistical metrics for Frumkin fits of the Fig. 4 data. Bracketed values represent standard errors for parameter estimates.

Frumkin parameter and statistical metric	Adsorbate	
	Paracetamol (PCT)	Niflumic acid (NFA)
a	−2.59 (0.20)	−3.51 (0.14)
b (L mg^{-1})	0.02 (0.002)	0.01 (0.0007)
q_m (mg g^{-1})	32.62 (0.57)	44.01 (0.72)
R^2	0.9999	0.9992
RRMSE (mg g^{-1})	1.03	2.31

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Declaration of competing interest

The authors declare no competing financial interests.

References

[1] V. Puccia, M.J. Avena, On the use of the Dubinin-Radushkevich equation to distinguish between physical and chemical adsorption at the solid-water interface, Colloids Interface Sci. Commun. 41 (2021) 100376.

[2] A. Frumkin, Die Kapillarkurve der höheren Fettsäuren und die Zustandsgleichung der Oberflächenschicht, Z. Phys. Chem. 116 (1925) 466–484.

[3] R.H. Fowler, E.A. Guggenheim, Statistical Thermodynamics, Cambridge University Press, Cambridge, 1939.

[4] S. Suwanayuen, R.P. Danner, A gas adsorption isotherm equation based on vacancy solution theory, AIChE J. 26 (1980) 68–76.

[5] R. Afonso, L. Gales, A. Mendes, Kinetic derivation of common isotherm equations for surface and micropore adsorption, Adsorption 22 (2016) 963–971.

[6] J.M. Arroyave, M. Avena, Determining rate coefficients for ion adsorption at the solid/water interface: better from desorption rate than from adsorption rate, Phys. Chem. Chem. Phys. 22 (2020) 11695.

[7] G. Barbero, L.R. Evangelista, I. Lelidis, Effective adsorption energy and generalization of the Frumkin-Fowler-Guggenheim isotherm, J. Mol. Liq. 327 (2021) 114795.

[8] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.

[9] L. Koopal, W. Tan, M. Avena, Equilibrium mono- and multicomponent adsorption models: from homogeneous ideal to heterogeneous non-ideal binding, Adv. Colloid Interface Sci. 280 (2020) 102138.

[10] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater. 147 (2007) 381–394.

[11] O. Ferrandon, H. Bouabane, M. Mazet, Contribution à l'étude de la validité de différents modèles, utilisés lors de l'adsorption de solutés sur charbon actif, Rev. Sci. Eau 8 (1995) 183–200.

[12] W. Li, J. Yan, Z. Yan, Y. Song, W. Jiao, G. Qi, Y. Liu, Adsorption of phenol by activated carbon in rotating packed bed: experiment and modeling, Appl. Therm. Eng. 142 (2018) 760–766.

[13] A. Kilislioglu, The effect of various cations and pH on the adsorption of U(VI) on Amberlite IR-118H resin, Appl. Radiat. Isot. 58 (2003) 713–717.

[14] C.A. Başar, Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, J. Hazard. Mater. 135 (2006) 232–241.

[15] E. Malkoc, Y. Nuhoglu, Determination of kinetic and equilibrium parameters of the batch adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*, Chem. Eng. Process. 46 (2007) 1020–1029.

[16] Ç. Sarıcı-Özdemir, Y. Önal, Statistical analysis of equilibrium and kinetic data for ascorbic acid removal from aqueous solution by activated carbon, Desalin. Water Treat. 51 (2013) 4658–4665.

[17] N.A. Oladoja, Y. Liu, J.E. Drewes, B. Helmreich, Preparation and characterization of a reactive filter for groundwater defluoridation, Chem. Eng. J. 283 (2016) 1154–1167.

[18] N.A. Oladoja, M.L. Seifert, J.E. Drewes, B. Helmreich, Influence of organic load on the defluoridation efficiency of nano-magnesium oxide in groundwater, Sep. Purif. Technol. 174 (2017) 116–125.

[19] M. Danish, T. Ahmad, S. Majeed, M. Ahmad, L. Ziyang, Z. Pin, S.M. Shakeel Iqbal, Use of banana trunk waste as activated carbon in scavenging methylene blue dye: kinetic, thermodynamic, and isotherm studies, Bioresour. Technol. Rep. 3 (2018) 127–137.

[20] T.D. Saliu, O.J. Akinyeye, I.A. Ololade, E.I. Unuabonah, N.A. Oladoja, Expounding the role of interference on the recovery of nutrient fractions from aqua matrix using calcined gastropod shell, J. Water Process Eng. 27 (2019) 152–161.

[21] M. Ponnuchamy, A. Kapoor, B. Pakkirisamy, P. Sivaraman, K. Ramasamy, Optimization, equilibrium, kinetic and thermodynamic studies on adsorptive remediation of phenol onto natural guava leaf powder, Environ. Sci. Pollut. Res. 27 (2020) 20576–20597.

[22] Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol. 61 (2008) 229–242.

[23] H.M. Abd El-Lateef, M.A. Al-Omair, A.H. Touny, M.M. Saleh, Enhanced adsorption and removal of urea from aqueous solutions using eco-friendly iron phosphate nanoparticles, J. Environ. Chem. Eng. 7 (2019) 102939.

[24] H. Demiral, İ. Demiral, F. Tümsek, B. Karabacakoğlu, Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models, Chem. Eng. J. 144 (2008) 188–196.

[25] A.O. Babatunde, Y.Q. Zhao, Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge, J. Hazard. Mater. 184 (2010) 746–752.

[26] A. Öztürk, E. Malkoc, Cationic basic yellow 2 (BY2) adsorption onto manure ash: surface properties and adsorption mechanism, Desalin. Water Treat. 54 (2015) 209–226.

[27] V. Makrigianni, A. Giannakas, Y. Deligiannakis, I. Konstantinou, Adsorption of phenol and methylene blue from aqueous solutions by pyrolytic tire char: equilibrium and kinetic studies, J. Environ. Chem. Eng. 3 (2015) 574–582.

[28] Ç. Sarici Özdemİr, Adsorptive removal of methylene blue by fruit shell: isotherm studies, Fuller. Nanotub. Car. Nanostruct. 26 (2018) 570–577.

[29] E. Rossi, Ú.M. Rojo, P. Cerrutti, M.L. Foresti, M.I. Errea, Carboxymethylated bacterial cellulose: an environmentally friendly adsorbent for lead removal from water, J. Environ. Chem. Eng. 6 (2018) 6844–6852.

[30] A.A. Narvekar, J.B. Fernandes, S.G. Tilve, Adsorption behavior of methylene blue on glycerol based carbon materials, J. Environ. Chem. Eng. 6 (2018) 1714–1725.

[31] P. Prediger, T. Cheminski, T. de Figueiredo Neves, W.B. Nunes, L. Sabino, C.S. F. Picone, R.L. Oliveira, C.R.D. Correia, Graphene oxide nanomaterials for the removal of non-ionic surfactant from water, J. Environ. Chem. Eng. 6 (2018) 1536–1545.

[32] R. Ramadoss, D. Subramaniam, Removal of divalent nickel from aqueous solution using blue-green marine algae: adsorption modeling and applicability of various isotherm models, Sep. Sci. Technol. 54 (2019) 943–961.

[33] S. Karakuş, N. Taşaltın, C. Taşaltın, A. Kilislioğlu, Comparative study on ultrasonic assisted adsorption of basic blue 3, basic yellow 28 and acid red 336 dyes onto hydromagnesite stromatolite: kinetic, isotherm and error analysis, Surf. Interfaces 20 (2020) 100528.

[34] O. Kireç, İ. Alacabey, K. Erol, H. Alkan, Removal of 17β-estradiol from aqueous systems with hydrophobic microspheres, J. Polym. Eng. 41 (2021) 226–234.

[35] H.M. Hamadeen, E.A. Elkhatib, M.E.I. Badawy, S.A.M. Abdelgaleil, Green low cost nanomaterial produced from *Moringa oleifera* seed waste for enhanced removal of chlorpyrifos from wastewater: mechanism and sorption studies, J. Environ. Chem. Eng. 9 (2021) 105376.

[36] G. Kemmer, S. Keller, Nonlinear least-squares data fitting in Excel spreadsheets, Nat. Protoc. 5 (2010) 267–281.

[37] T. Pennanen, V. Srivastava, M. Sillanpää, T. Sainio, Compost: potent biosorbent for the removal of heavy metals from industrial and landfill stormwater, J. Clean. Prod. 273 (2020) 122736.

[38] M.C. Annesini, F. Gironi, M. Ruzzi, C. Tomei, Adsorption of organic compounds onto activated carbon, Water Res. 21 (1987) 567–571.

[39] G.A. Sorial, M.T. Suidan, R.D. Vidic, S.W. Maloney, Competitive adsorption of phenols on GAC. I: adsorption equilibrium, J. Environ. Eng. 119 (1993) 1026–1043.

[40] Q. Lu, G.A. Sorial, Adsorption of phenolics on activated carbon—impact of pore size and molecular oxygen, Chemosphere 55 (2004) 671–679.

[41] G.O. Cassol, R. Gallon, M. Schwaab, E. Barbosa-Coutinho, J.B. Severo Júnior, J. C. Pinto, Statistical evaluation of non-linear parameter estimation procedures for adsorption equilibrium models, Adsorpt. Sci. Technol. 32 (2014) 257–273.

[42] P.T. Boggs, R.H. Byrd, R.B. Schnabel, A stable and efficient algorithm for nonlinear orthogonal distance regression, SIAM J. Sci. Stat. Comp. 8 (1987) 1052–1078.

[43] M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: comparing the options, J. Hazard. Mater. 158 (2008) 73–87.

[44] J. Poch, I. Villaescusa, Orthogonal distance regression: a good alternative to least squares for modeling sorption data, J. Chem. Eng. Data 57 (2012) 490–499.

[45] J.L. Beltrán, J.J. Pignatello, M. Teixidó, ISOT_Calc: a versatile tool for parameter estimation in sorption isotherms, Comput. Geosci. 94 (2016) 11–17.

[46] F. Yan, Y. Chu, K. Zhang, F. Zhang, N. Bhandari, G. Ruan, Z. Dai, Y. Liu, Z. Zhang, A.T. Kan, M.B. Tomson, Determination of adsorption isotherm parameters with correlated errors by measurement error models, Chem. Eng. J. 281 (2015) 921–930.

[47] P.T. Boggs, R.H. Byrd, J.E. Rogers, R.B. Schnabel, User's Reference Guide for ODRPACK Version 2.01: Software for Weighted Orthogonal Distance Regression, National Institute of Standards and Technology, Gaithersburg, 1992.

[48] H.P. Helfrich, D. Zwick, A trust region method for implicit orthogonal distance regression, Numer. Algorithms 5 (1993) 535–545.

[49] N. Ayawei, A.N. Ebelegi, D. Wankasi, Modelling and interpretation of adsorption isotherms, J. Chem. 2017 (2017) 3039817.

[50] R. Ramadoss, D. Subramaniam, Removal of divalent nickel from aqueous solution using blue-green marine algae: adsorption modeling and applicability of various isotherm models, Sep. Sci. Technol. 54 (2019) 943–961.

[51] S. Basha, S. Jaiswar, B. Jha, On the biosorption, by brown seaweed, *Lobophora variegata*, of Ni(II) from aqueous solutions: equilibrium and thermodynamic studies, Biodegradation 21 (2010) 661–680.

[52] R.P. Mokkapati, V.N. Ratnakaram, J.S. Mokkapati, Utilization of agro-waste for removal of toxic hexavalent chromium: surface interaction and mass transfer studies, Int. J. Environ. Sci. Technol. 15 (2018) 875–886.

[53] P. Prediger, T. Cheminski, T. de Figueiredo Neves, W.B. Nunes, L. Sabino, C.S. F. Picone, R.L. Oliveira, C.R.D. Correia, Graphene oxide nanomaterials for the removal of non-ionic surfactant from water, J. Environ. Chem. Eng. 6 (2018) 1536–1545.

[54] T. Cheminski, T. de Figueiredo Neves, P.M. Silva, C.H. Guimarães, P. Prediger, Insertion of phenyl ethyleneglycol units on graphene oxide as stabilizers and its application for surfactant removal, J. Environ. Chem. Eng. 7 (2019) 102976.

[55] T. de Figueiredo Neves, P. Kushima Assano, L. Rodrigues Sabino, W. Bardelin Nunes, P. Prediger, Influence of adsorbent/adsorbate interactions on the removal of cationic surfactants from water by graphene oxide, Water Air Soil Pollut. 231 (2020) 304.

[56] A.K. Nayak, A. Pal, Utilization of lignocellulosic waste for acridine orange uptake: insights into multiparameter isotherms modeling with ANN-aimed formulation, J. Environ. Eng. 146 (2020), 04020096.
[57] M. Ponnuchamy, A. Kapoor, B. Pakkirisamy, P. Sivaraman, K. Ramasamy, Optimization, equilibrium, kinetic and thermodynamic studies on adsorptive remediation of phenol onto natural guava leaf powder, Environ. Sci. Pollut. Res. 27 (2020) 20576–20597.
[58] R. Saadi, Z. Saadi, R. Fazaeli, N.E. Fard, Monolayer and multilayer adsorption isotherm models for sorption from aqueous media, Korean J. Chem. Eng. 32 (2015) 787–799.
[59] A. Durimel, S. Altenor, R. Miranda-Quintana, P. Couespel Du Mesnil, U. Jauregui-Haza, R. Gadiou, S. Gaspard, pH dependence of chlordecone adsorption on activated carbons and role of adsorbent physico-chemical properties, Chem. Eng. J. 229 (2013) 239–249.
[60] R.A. Fideles, G.M.D. Ferreira, F.S. Teodoro, O.F.H. Adarme, L.H.M. da Silva, L. F. Gil, L.V.A. Gurgel, Trimellitated sugarcane bagasse: a versatile adsorbent for removal of cationic dyes from aqueous solution. Part I: batch adsorption in a monocomponent system, J. Colloid Interface Sci. 515 (2018) 172–188.
[61] C. Buttersack, Modeling of type IV and V sigmoidal adsorption isotherms, Phys. Chem. Chem. Phys. 21 (2019) 5614–5626.
[62] K.H. Chu, Fitting a little-known isotherm equation to S-shaped adsorption equilibrium data, Sep. Purif. Technol. 259 (2021) 118079.
[63] B. Koubaissy, G. Joly, P. Magnoux, Adsorption and competitive adsorption on zeolites of nitrophenol compounds present in wastewater, Ind. Eng. Chem. Res. 47 (2008) 9558–9565.
[64] B. Koubaissy, G. Joly, I. Batonneau-Gener, P. Magnoux, Adsorptive removal of aromatic compounds present in wastewater by using dealuminated faujasite zeolite, Ind. Eng. Chem. Res. 50 (2011) 5705–5713.
[65] J. Beltrán-Heredia, J. Sánchez-Martín, Removal of sodium lauryl sulphate by coagulation/flocculation with *Moringa oleifera* seed extract, J. Hazard. Mater. 164 (2009) 713–719.
[66] S. Benosmane, M. Bendjelloul, E.H. Elandaloussi, M. Touhami, L.-C. de Ménorval, Experimental and modeling study on adsorption of emerging contaminants onto hyper-crosslinked cellulose, Chem. Pap. 75 (2021) 4021–4034.