

Beyond Freundlich and Langmuir: The Ruthven–virial equilibrium isotherm for aqueous-solid adsorption systems

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Chemical Papers <https://doi.org/10.1007/s11696-022-02576-4>

Abstract

It is the purpose of this paper to investigate the data fitting attributes of the exponential integral isotherm, which was first derived by Ruthven in 2004 to describe adsorption at gas-solid interfaces. The exponential integral isotherm, a variant of the virial isotherm, incorporates the two fitting parameters of the Langmuir isotherm and has an expandable mathematical structure. It has lain dormant for nearly 20 years. This fact may seem surprising considering the versatility of the isotherm, as will be shown in this work. A slightly modified form of the exponential integral isotherm, called the Ruthven–virial isotherm, is used in this work to interpret previously published aqueous-phase isotherm data. It is observed that the Ruthven–virial isotherm is capable of accurately tracking experimental adsorption isotherms with and without an apparent plateau. The Freundlich isotherm is good at describing data without a plateau, while the Langmuir isotherm excels at fitting data with a plateau. The Ruthven–virial isotherm combines the individual strengths of the Freundlich and Langmuir isotherms into a single

model. Furthermore, it is shown that the data fitting performance of the two-parameter Ruthven–virial isotherm is comparable to that of the three-parameter Sips isotherm. The Ruthven–virial isotherm is a hidden gem and a practical alternative to the Freundlich and Langmuir equations in the correlation of hyperbolic adsorption isotherms. We hope that the findings presented here will inspire the research community to evaluate the Ruthven–virial isotherm in the modeling of contaminant adsorption at aqueous-solid interfaces.

Keywords: Hyperbolic isotherm, Implicit isotherm, Plateau, Virial isotherm, Lambert W function

Introduction

With four parameters I can fit an elephant and with five I can
make him wiggle his trunk.

[John von Neumann cited in Dyson (2004)]

The virial adsorption isotherm has been widely used to describe gas-phase equilibrium data (Ruthven 1984). It was developed independently by Barrer and Gibbons (1963) and Kiselev (1968). A general form of the virial isotherm is given by Eq. (1), where p is the adsorbate partial pressure, q is the amount adsorbed, K is the Henry constant, and the A 's are the temperature-dependent virial coefficients.

$$Kp = q \exp(A_1 q + A_2 q^2 + A_3 q^3 + \dots) \quad (1)$$

As can be seen in Eq. (1), the virial isotherm is independent of the saturation capacity parameter. Another version of Eq. (1) incorporating the saturation capacity parameter is available in the literature (Barrer and Lee 1968). In the absence of experimental data at low pressure, the virial isotherm provides a convenient way to estimate Henry's law constants from data at higher loadings outside the linear region. A plot of $\ln(p/q)$ versus q should yield a linear asymptote and the intercept of such a plot gives the value of K .

The virial isotherm truncated after the second or third virial coefficient is capable of correlating the equilibrium data for many gas-solid adsorption systems with high accuracy. These versions of the virial isotherm have three or four fitting parameters, counting the Henry constant. Additional virial coefficients can, of course, be included in the virial isotherm, which would provide an excellent fit to any hyperbolic curve. The epigraph to our article is the great polymath von Neumann's quip of such over-the-top curve fitting. Given that the virial isotherm is blessed with an unlimited supply of free parameters, one may be tempted to claim that Eq. (1) could fit a whole herd of dancing elephants. Indeed, with enough free parameters, one could model anything (Boué 2019).

Here we aim, as a consequence, to test the ability of the virial isotherm with the least possible number of free parameters to describe water contaminant adsorption data. Given its wide application in gas-phase adsorption research, it is surprising to note that the virial isotherm has attracted hardly any attention in the field of water contaminant adsorption. Only a few studies have applied it to water contaminant isotherm data (Meghea et al. 1998; Tahir et al. 1998; Westall et al. 1999; Higgins and Luthy 2007; Li et al. 2019).

As has been amply demonstrated by the Freundlich or Langmuir isotherm, an isotherm model with two free parameters is capable of correlating a hyperbolic isotherm to a significant degree of precision. Accordingly, the simplest possible virial isotherm is one with two free parameters, as shown in Eq. (2). This version of the virial isotherm is truncated at the first virial coefficient to give two free parameters, K and A_1 . As explained earlier, a linear version of Eq. (2) is commonly used to extract the Henry constant K from experimental data. Unfortunately, the virial coefficient A_1 has no physical significance. We mention in passing that Eq. (2) is analogous to the Elovich isotherm commonly used to describe aqueous-solid adsorption systems (Debord et al. 2022).

$$Kp = q \exp(A_1 q) \quad (2)$$

An intriguing alternative to the virial isotherm is a variant developed by Ruthven (2004), known as the exponential integral isotherm, which is free of the empirical virial coefficients A 's. Importantly, it has two physically meaningful parameters: the Langmuir equilibrium constant and the saturation capacity parameter. However, the exponential integral isotherm, which was derived nearly 20 years ago (Ruthven 2004), does not seem to have been evaluated in gas- or aqueous-phase adsorption research.

The primary objective of the present study is to investigate the data fitting attributes of a slightly modified version of the exponential integral isotherm, called the Ruthven–virial isotherm. It is shown that the Ruthven–virial isotherm is highly competitive against both the Langmuir and Freundlich isotherms in correlating the experimental isotherms for tetracycline (Ma et al. 2022) and nickel (Sikora et al. 2021) adsorption on solid media. Furthermore, it is observed that the data fitting performance of the two-parameter Ruthven–virial isotherm is comparable to that of the three-parameter Sips isotherm.

Isotherm equations and data fitting

Conventional isotherms

In this work, we will compare the Ruthven–virial isotherm to the isotherm equations of Langmuir (1916) [Eq. (3)], Freundlich (1907) [Eq. (4)], and Sips (1948) [Eq. (5)]. In these three equations, q is the adsorbed-phase concentration, c is the aqueous-phase concentration, b_L and q_m are, respectively, the Langmuir equilibrium constant and the monolayer saturation capacity, b_F and n_F are Freundlich fitting constants, and a_S , b_S , and n_S are Sips fitting constants.

$$q = \frac{q_m b_L c}{1 + b_L c} \quad (3)$$

$$q = b_F c^{n_F} \quad (4)$$

$$q = \frac{a_s b_s c^{n_s}}{1 + b_s c^{n_s}} \quad (5)$$

The Ruthven–virial isotherm

Most experimental isotherms for water contaminant adsorption on solid media are of type I form. Various isotherm models with multiple free parameters, such as the five-parameter equation of Fritz and Schlunder (1974), have been used to fit these relatively simple type I isotherms. With enough arbitrary parameters, a model can go through just about any set of data points. The Ruthven–virial isotherm investigated in the present study has only two free parameters, as discussed below.

A variant of the virial isotherm developed by Ruthven (2004) is given by Eq. (6). A brief description of the development of Eq. (6) can be found in the Appendix. Eq. (6), known as the exponential integral isotherm in the original study, contains the two free parameters of the Langmuir isotherm, b_L and q_m . It is obvious that Eq. (6) is similar in form to the virial isotherm given by Eq. (1) but is free of the empirical virial coefficients A 's.

$$b_L p = \frac{q}{q_m} \exp \left[\frac{q}{q_m} + \frac{1}{4} \left(\frac{q}{q_m} \right)^2 + \frac{1}{18} \left(\frac{q}{q_m} \right)^3 + \dots \right] \quad (6)$$

To apply Eq. (6) to aqueous-phase adsorption data, the sorbate pressure p is replaced by the aqueous-phase concentration c , as shown in Eq. (7). It should be noted that Eq. (7) is a modified version of Eq. (6) in that the numerical constants in the exponential have been dropped. This modification amplifies the effect of the first few q/q_m terms, reducing the need for higher-order q/q_m terms. Eq. (7) is referred to as the Ruthven–virial isotherm.

$$b_L c = \frac{q}{q_m} \exp \left[\frac{q}{q_m} + \left(\frac{q}{q_m} \right)^2 + \left(\frac{q}{q_m} \right)^3 + \dots \right] \quad (7)$$

Data fitting

The isotherm models evaluated in this study were fitted to literature data [tetracycline adsorption data (Ma et al. 2022); nickel adsorption data (Sikora et al. 2021)] using a nonlinear least-squares fitting algorithm to minimize the sum of squared residuals (SSR) defined by Eq. (8), where $q_{i,obs}$ is the i th observed value of q , $q_{i,fit}$ is the i th value of q calculated from a particular isotherm model, and z is the number of data points. Because the Ruthven–virial isotherm is implicit in q , a numerical scheme was incorporated into the least-squares fitting algorithm to calculate $q_{i,fit}$ at each iteration of the fitting process. All nonlinear least-squares fittings were carried out using Mathematica. The coefficient of determination (R^2) is used as a statistical metric for isotherm comparison. The Akaike Information Criterion (AIC) test (Akaike 1974) is used to compare isotherm models with different numbers of fitting parameters.

$$SSR = \sum_{i=1}^z (q_{i,obs} - q_{i,fit})^2 \quad (8)$$

Results and discussion

This work explores the ability of the Ruthven–virial isotherm with two free parameters to describe hyperbolic isotherms selected from the literature of water contaminant adsorption. Two data sets are used to evaluate and compare the data fitting attributes of the Ruthven–virial, Freundlich, Langmuir, and Sips isotherms. The first data set exhibits a hyperbolic curve without an apparent plateau. The Freundlich isotherm excels at fitting data of this type. The second data set displays a hyperbolic curve with an apparent plateau. The Langmuir isotherm is well known for its ability to fit such data trends. The versatile Sips isotherm can fit hyperbolic curves with and without a plateau.

Isotherm data with no apparent plateau

This data set, taken from the work of Ma et al. (2022), describes the uptake of the antibiotic tetracycline by a biochar adsorbent. As can be seen in Fig. 1, the measured isotherm shows an

increasing trend of q without an apparent plateau at large values of c . The Ruthven–virial isotherm was fitted to the tetracycline adsorption data by varying the number of q/q_s terms in the argument of the exponential, as shown in Eqs. (9)–(12). The resulting parameter estimates and R^2 statistics are given in Table 1. Note that Eq. (9) is analogous to the Elovich isotherm (Debord et al. 2022).

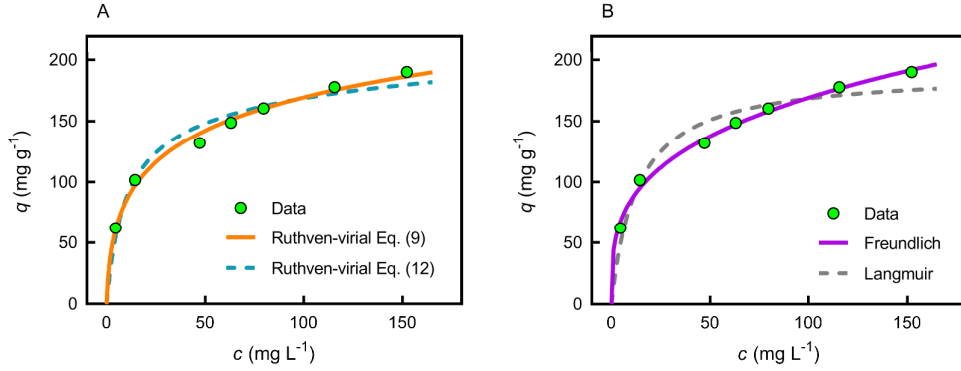


Fig. 1 Comparison of isotherm fits and tetracycline adsorption data (Ma et al. 2022)

$$b_L c = \frac{q}{q_m} \exp\left(\frac{q}{q_m}\right) \quad (9)$$

$$b_L c = \frac{q}{q_m} \exp\left[\frac{q}{q_m} + \left(\frac{q}{q_m}\right)^2\right] \quad (10)$$

$$b_L c = \frac{q}{q_m} \exp\left[\frac{q}{q_m} + \left(\frac{q}{q_m}\right)^2 + \left(\frac{q}{q_m}\right)^3\right] \quad (11)$$

$$b_L c = \frac{q}{q_m} \exp\left[\frac{q}{q_m} + \left(\frac{q}{q_m}\right)^2 + \left(\frac{q}{q_m}\right)^3 + \left(\frac{q}{q_m}\right)^4\right] \quad (12)$$

Table 1 Parameter estimates obtained by isotherm fits of tetracycline adsorption data (Ma et al. 2022)

Isotherm	Equation	b_L (L mg ⁻¹)	q_m (mg g ⁻¹)	b_F (L ^{n_F} mg ^(1-n_F) g ⁻¹)	n_F	R^2
Ruthven–virial	(9)	0.812	52.57			0.991
	(10)	0.156	142.99			0.981
	(11)	0.097	189.46			0.972
	(12)	0.079	212.96			0.964
Langmuir	(3)	0.076	190.70			0.933
Freundlich	(4)			42.89	0.298	0.992

The R^2 metric decreases with an increasing number of q/q_m terms. The most effective Ruthven–virial isotherm is the one given by Eq. (9), while the worst performing one is Eq. (12), as can be seen in Table 1. These two contrasting fits are shown in Fig. 1A. For comparison, Fig. 1B depicts the fits of the Freundlich and Langmuir isotherms. As expected, the Langmuir fit is the least accurate, returning the smallest R^2 score of 0.933. The Langmuir isotherm is incapable of handling isotherm data without an apparent plateau because it is designed to describe saturable adsorption. The Freundlich fit, by contrast, manifests good agreement with the tetracycline adsorption data. This result is not surprising since the Freundlich isotherm predicts that adsorption increases indefinitely with increasing c . As can be seen in Table 1, the difference between the R^2 scores for the Freundlich and Ruthven–virial [Eq. (9)] fits is trivial.

The important finding derived from the tetracycline adsorption data is that the Ruthven–virial isotherm defined by Eq. (9) has the ability to track isotherm data without a plateau. It therefore behaves like the Freundlich isotherm. Similar to the b_F and n_F parameters in the Freundlich isotherm, the two parameters in Eq. (9), b_L and q_m , have no physical significance. Note that the concentration ratio q/q_m for all data points is greater than unity, which is nonsensical. In this case, q_m loses its meaning and is used as an empirical parameter to correlate the tetracycline isotherm data.

Isotherm data with an apparent plateau

In this second example, the selected data set describes the adsorption of nickel ions by a magnetic ion exchanger (Sikora et al. 2021). The adsorption isotherm, depicted in Fig. 2, displays a hyperbolic curve shape with an apparent plateau. As can be seen in Fig. 2, the experimental isotherm is almost rectangular, with the last two data points defining a saturation region characterized by a maximum q value of approximately 110 mg g^{-1} . The four versions of the Ruthven–virial isotherm defined by Eqs. (9)–(12) were fitted to the nickel adsorption isotherm, and the resulting parameter estimates and R^2 statistics are presented in Table 2.

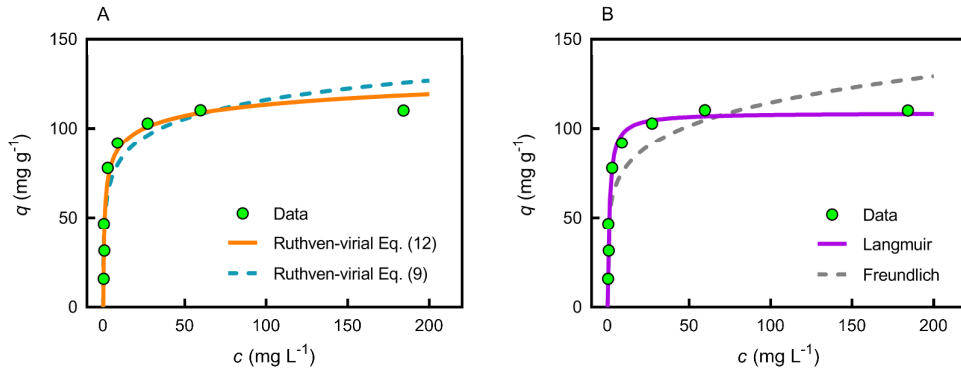


Fig. 2 Comparison of isotherm fits and nickel adsorption data (Sikora et al. 2021)

Table 2 Parameter estimates obtained by isotherm fits of nickel adsorption data (Sikora et al. 2021)

Isotherm	Equation	b_L (L mg^{-1})	q_m (mg g^{-1})	b_F ($\text{L}^{n_F} \text{mg}^{(1-n_F)} \text{g}^{-1}$)	n_F	R^2
Ruthven–virial	(9)	46.773	17.65			0.879
	(10)	3.325	62.84			0.919
	(11)	1.612	90.63			0.939
	(12)	1.188	106.23			0.949
Langmuir	(3)	0.911	108.73			0.960
Freundlich	(4)			51.57	0.173	0.802

According to the R^2 scores, Eq. (9) is the least accurate isotherm, while Eq. (12) is the most effective one. Fig. 2A plots the fits of Eqs. (9) and (12), which are the worst and best performers, respectively. The fits of the Freundlich and Langmuir isotherms to the same isotherm data are shown in Fig. 2B. With an R^2 score of 0.802, the Freundlich isotherm is the least accurate one in this group of six competing isotherm equations as it is not designed to describe saturable adsorption. As expected, the Langmuir isotherm is good at fitting the saturable adsorption data of nickel. With an R^2 value of 0.960, the fit of the Langmuir isotherm is marginally superior to that of the Ruthven–virial isotherm represented by Eq. (12) ($R^2 = 0.949$). The two parameter estimates obtained by the fit of Eq. (12) are similar to those produced by the Langmuir isotherm fit, and the former can thus be regarded as having the same physical significance as the latter. In summary, the Ruthven–virial isotherm with four q/q_m terms in the exponential is a practical alternative to the Langmuir isotherm.

Ruthven–virial versus Sips

The data fitting analyses presented above clearly demonstrate that the Ruthven–virial isotherm with a flexible mathematical structure can handle isotherm data with and without a plateau. It is therefore highly competitive against both the Freundlich and Langmuir isotherms. It is of interest to compare the Ruthven–virial isotherm to the Sips isotherm (Sips 1948), which is well known for its ability to correlate diverse forms of hyperbolic isotherm data. The Sips isotherm is given by Eq. (5). The fits of the three-parameter Sips isotherm to the isotherm data of tetracycline and nickel are presented in Fig. 3. The resulting parameter estimates and R^2 scores are given in Table 3. The Sips isotherm is indeed highly effective in correlating the two experimental isotherms with and without an apparent plateau. It must be noticed, however, that while the Sips isotherm predicts a plateau, this is not the case for any of the Ruthven–virial isotherm versions, for which $q/q_m \rightarrow \infty$ when $c \rightarrow \infty$.

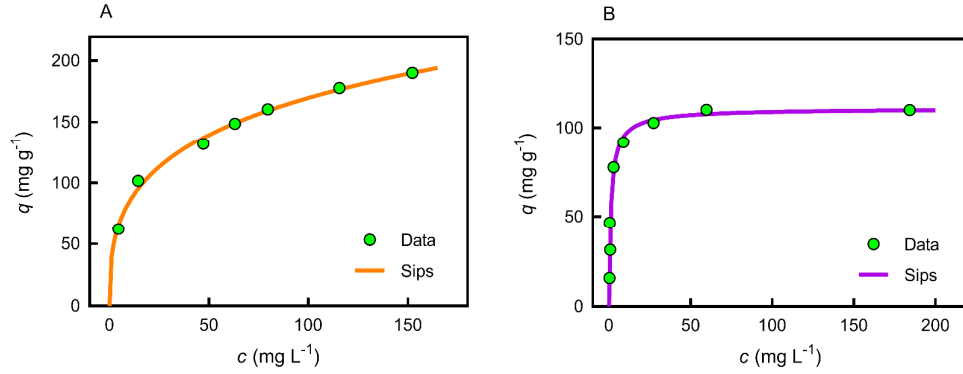


Fig. 3 Sips isotherm fits of tetracycline (A) and nickel (B) adsorption data

Table 3 Parameter estimates obtained by Sips isotherm fits of tetracycline and nickel adsorption data

Contaminant	a_s (mg g^{-1})	b_s ($\text{L}^{n_s} \text{mg}^{(1-n_s)} \text{g}^{-1}$)	n_s	R^2
Tetracycline	631.85	0.065	0.376	0.993
Nickel	111.16	0.846	0.885	0.962

Table 4 compares the relative performance of the Sips and Ruthven–virial isotherms in correlating the tetracycline and nickel isotherm data. According to the R^2 scores, the Sips isotherm is slightly superior to the Ruthven–virial isotherm in both cases. However, its superiority is due to the use of three fitting parameters. As pointed out by von Neumann, as the number of free parameters in a model increases, so does the flexibility of the model to fit any set of quantitative data. From a statistical viewpoint, information-theoretic metrics such as the Akaike Information Criterion (AIC) (Akaike 1974) are more appropriate than the simple R^2 metric for discriminating models with different numbers of free parameters. According to the AIC test, the model with the largest Akaike weight is the best performing one in a group of competing models. The method for calculating the Akaike weight can be found in the book by Motulsky and Christopoulos (2004). The Akaike weights for the Sips and Ruthven–virial fits

of the two data sets are presented in Table 4. In each case, the AIC test overwhelmingly favors the Ruthven–virial isotherm over the Sips isotherm. The slight increase in fit quality obtained by the Sips isotherm is insufficient to justify the use of three fitting parameters. The AIC test supports von Neumann’s philosophy that the best model is one that gives a good fit with a minimal number of free parameters.

Table 4 Values of statistical metrics for Sips and Ruthven–virial isotherm fits

Contaminant	Isotherm	R^2	Akaike weight (%)
Tetracycline	Sips	0.993	0.3
	Ruthven–virial, Eq. (9)	0.991	99.7
Nickel	Sips	0.962	1.7
	Ruthven–virial, Eq. (12)	0.949	98.3

Inversion of the Ruthven–virial isotherm

The Ruthven–virial isotherm is implicit in q , which precludes the use of standard least-squares algorithms to minimize the difference between $q_{i,obs}$ and $q_{i,fit}$ [Eq. (8)]. The Ruthven–virial isotherm given by Eq. (9) can be inverted by means of the Lambert W function (Kesisoglou et al. 2021; Brião and Chu 2022; Debord et al. 2022) to obtain an expression explicit in q , as shown in Eq. (13), where $W(y)$ denotes the Lambert W function with argument $y = b_{LC}$. The Lambert W function is not available in Excel, but analytical approximations can be used to calculate the $W(y)$ term in Eq. (13). For example, a fairly simple approximation is given by Eq. (14), which approximates $W(y)$ with a maximum relative error of less than 2% and can be used for $y > 0$ (Winitzki 2003). The loading-explicit Eq. (13) allows the use of standard nonlinear regression algorithms in data correlation to minimize the objective function represented by Eq. (8).

$$q = q_m W(y) \quad (13)$$

$$W(y) \approx \ln(1+y) \left\{ 1 - \frac{\ln[1 + \ln(1+y)]}{2 + \ln(1+y)} \right\} \quad (14)$$

However, not all implicit isotherm models are amenable to treatment by the Lambert W function. Here, we will use a more general method to invert the other versions of the Ruthven–virial isotherm. Using Eq. (12) as our example, we describe the steps of the general inversion method. First, we calculate the numerical values of the product $b_L c$ from the right-hand side of Eq. (12) by assigning a series of values to q/q_m over the range of 0–1. Second, we plot the calculated data points in the form of q/q_m versus $b_L c$, which displays a hyperbolic curve shape that asymptotes toward unity, as can be seen in Fig. 4. In the final step, we select an appropriate equation to fit the calculated data points in Fig. 4. As an example, we use the Sips-like function given by Eq. (15), where n_1 through n_4 are fitting parameters. The fit of Eq. (15) to the calculated data is excellent (Fig. 4), returning a perfect R^2 score of 1.0. The resulting parameter estimates are given in Eq. (16). Eq. (15), with four free parameters, amply illustrates von Neumann’s quip that a model with enough free parameters can fit any curve.

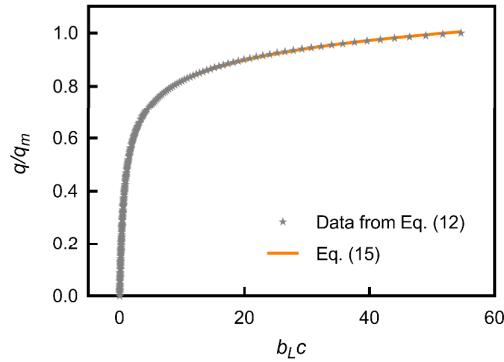


Fig. 4 Fit of Eq. (15) to synthetic data generated from Eq. (12)

$$\frac{q}{q_m} = \frac{n_1 (b_L c)^{n_2}}{1 + n_3 (b_L c)^{n_4}} \quad (15)$$

$$q = \frac{q_m (1.278) (b_L c)^{1.07}}{1 + (1.829) (b_L c)^{0.976}} \quad (16)$$

Hence, Eq. (16) is a surrogate model for Eq. (12). Given that Eq. (16) is explicit in q , it can be fitted to isotherm data using a standard nonlinear regression method to determine the two unknown parameters q_m and b_L . For example, Eq. (16) was fitted to the nickel adsorption data plotted in Fig. 2 using the GRG nonlinear algorithm of Excel Solver. The resulting parameter estimates are $q_m = 104.51 \text{ mg g}^{-1}$ and $b_L = 1.21 \text{ L mg}^{-1}$, which are very similar to those obtained by the fit of the loading-implicit Eq. (12), given in Table 2.

Conclusions

The Ruthven–virial isotherm investigated in this work is a viable alternative to the more than century-old Freundlich and Langmuir isotherms, which have dominated the landscape of adsorption modeling for a very long time. The Ruthven–virial isotherm, a variant of the virial isotherm, is highly effective in data correlation because it has a flexible mathematical structure. The unknown virial coefficients have been replaced by the adsorbed-phase concentration ratio q/q_m . As a result, the Ruthven–virial isotherm has only two free parameters, the Langmuir equilibrium constant b_L and the saturation capacity parameter q_m . Its data fitting attributes are dependent on the number of q/q_m terms in the argument of the exponential. With a single q/q_m term, the Ruthven–virial isotherm is capable of tracking hyperbolic isotherm data without an apparent plateau. Its two parameters, in this case, have no physical significance. It thus behaves like the Freundlich isotherm. With three or four q/q_m terms, the Ruthven–virial isotherm excels at correlating isotherm data with an apparent plateau. Its two parameter estimates are comparable to those of the Langmuir isotherm. It therefore resembles the Langmuir isotherm in correlating data of this kind. As such, the Ruthven–virial isotherm may be an adequate choice for use in process design or adsorbent development.

The Sips isotherm also has the ability to fit isotherm data with and without a plateau. However, it uses three fitting parameters. A drawback of the Ruthven–virial isotherm is that it

is implicit in q , and this precludes the use of conventional least-squares algorithms in data correlation. It is demonstrated that the loading-implicit Ruthven–virial isotherm is invertible to an explicit form. Further research is under way to examine whether the Ruthven–virial isotherm consistently manifests good agreement with other hyperbolic isotherms characterized by intricate curve shapes.

Appendix: Derivation of Ruthven’s exponential integral isotherm

We start with Eq. (3) in Table 1 of Ruthven (2004), reproduced here as Eq. (A1), where b is the Langmuir equilibrium constant and $Ei(x)$ is the exponential integral with $x = q/q_m$, which is defined by Eq. (A2).

$$\ln(bp) = Ei(x) \quad (A1)$$

$$Ei(x) = \int_{-\infty}^x \frac{\exp(t)}{t} dt \quad (A2)$$

The series expansion of the exponential integral is given by Eq. (A3), where γ is the Euler–Mascheroni constant (0.5772156649...).

$$\ln(bp) = \gamma + \ln(x) + x + \frac{x^2}{4} + \frac{x^3}{18} + \dots \quad (A3)$$

So, we obtain Eq. (A4) from Eq. (A3). In Eq. (6) the b_L value is in fact $b/\exp(\gamma) \approx b/1.781$.

$$bp = \exp(\gamma) x \exp\left(x + \frac{x^2}{4} + \frac{x^3}{18} + \dots\right) \quad (A4)$$

Acknowledgement

The authors would like to dedicate this paper to the late Professor Douglas Morris Ruthven (1938–2021) whose exponential integral isotherm (Ruthven 2004) provided the inspiration for this work.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Data availability All the datasets supporting the findings of this study are available within the article.

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