Fitting a little-known isotherm equation to S-shaped adsorption equilibrium data

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Abstract

A research topic of current interest concerns the measurement and modeling of adsorption equilibrium isotherms of water contaminants. The bulk of measured equilibrium isotherms exhibit the convex-upward or favorable curve shape, which can be described by the two-parameter Langmuir and Freundlich isotherms. An increasing number of recent studies have however reported S-shaped or sigmoidal equilibrium isotherms. Modeling such equilibrium data requires the use of isotherm equations with a highly flexible functional form. This work introduces a little-known isotherm useful for tracking the trajectory of S-shaped equilibrium data. This relatively simple three-parameter isotherm, first proposed by Krishnamurti in 1951, has theoretical merit because it is based on a co-operative adsorption mechanism. It is shown that previously published S-shaped equilibrium data of water contaminants can be represented by the Krishnamurti isotherm. Specific examples discussed are (1) ammonium ion adsorption by the clay mineral sepiolite, (2) uptake of the antibiotic ciprofloxacin by a magnetic nanosorbent, and (3) fluoride ion removal by a layered double hydroxide adsorbent. Further, it is found that a modified form of the Krishnamurti isotherm is superior to its original counterpart in tracing sigmoidal equilibrium data. The original and modified Krishnamurti isotherms can be practically very useful to describe S-shaped equilibrium data and for adsorptive process modeling.

Keywords: adsorption modeling; equilibrium data; S-shaped; sigmoid; type V isotherm

1. Introduction

Adsorption is an efficient technology for trace contaminant removal from large volumes of aqueous wastes. Mathematical simulations of various adsorption processes of practical interest (fixed bed, expanded bed, fluidized bed, moving bed, and simulated moving bed) require precise knowledge of adsorption equilibria and kinetics. Although the equilibrium characteristics of organic contaminant adsorption may be estimated using predictive correlations based on specific compound and adsorbent properties [1,2], such predictive methods are limited to certain classes of organic contaminants and adsorbents. In general, equilibrium isotherms of various water contaminants are invariably obtained from laboratory experiments.

It is well known that experimental equilibrium isotherms are capable of exhibiting different curve shapes. Adsorbent heterogeneity appears to play a significant role in establishing the adsorption isotherm shapes [3,4]. Although the major classes of isotherm shapes according to the Brunauer-Deming-Deming-Teller (BDDT) classification have been observed in aqueous adsorption systems [5], the vast majority of measured equilibrium data of water contaminants have been found to exhibit
the convex-upward or favorable isotherm shape. This particular isotherm shape can be easily represented by the two-parameter Langmuir and Freundlich isotherms. To fit equilibrium data of this kind, it is rarely necessary to use more intricate isotherms, particularly those involving three or more adjustable parameters.

In recent years, an increasing number of studies have however reported S-shaped or sigmoidal equilibrium data. Such isotherms are concave to the horizontal x-axis at low liquid-phase concentrations and convex at higher liquid-phase concentrations (type V isotherm shape according to the BDDT classification). Some recent examples include the works of Soares et al. [6], Jiang et al. [7], Mitrogiannis et al. [8], and Gago et al. [9]. Soares et al. [6] reported the uptake of the antibiotic ciprofloxacin by a silica-based magnetic nanosorbent. The equilibrium data set displaying a sigmoidal profile was reasonably well fitted by the Dubinin-Radushkevich isotherm. In the work of Jiang et al. [7], equilibrium experiments produced S-shaped isotherms for the adsorption of 2,4,6-trichlorophenol on high-silica zeolites. Mathematical simulations were used to explore the mechanism responsible for the sigmoidal adsorption trend, but no attempts were made to fit macroscopic isotherms to the S-shaped data. Mitrogiannis et al. [8] found that the uptake of phosphate by a zeolite adsorbent was characterized by an S-shaped adsorption profile, which was well tracked by the Zhu-Gu isotherm. Gago et al. [9] used the Sips isotherm to represent the sigmoidal curve exhibited by the adsorption of methylene blue on a cellulose-based adsorbent. It is of note that some of the isotherms used to describe aqueous sigmoidal equilibrium data are semi-empirical in nature. Their principal utility is to offer a practical way to track the sigmoidal shape of experimental isotherms, without implying the inherent validity of their mechanistic assumptions. By contrast, rigorous theoretical models are available for a priori prediction of gas-phase sigmoidal equilibrium isotherms [10].

Mathematical simulations of adsorption processes such as fixed bed and simulated moving bed adsorbers have shown that S-shaped isotherms exerted a significant impact on the process dynamics [11-13]. Since isotherm models serve as critical input parameters to process models, there is a need to develop reliable isotherm models capable of representing different types of sigmoidal equilibrium data. To correlate S-shaped equilibrium data to a significant degree of precision, isotherm equations with an appropriate functional form are needed. Although a number of macroscopic isotherms capable of fitting sigmoidal equilibrium data are available [14,15], there is a shortage of simple mechanistic isotherm models. This communication attempts to address this gap by exploring the ability of a simple isotherm proposed by Krishnamurti [16] to fit S-shaped equilibrium data. The Krishnamurti isotherm, which is based on a co-operative adsorption mechanism, seems to have attracted no attention thus far. According to Google Scholar, the work of Krishnamurti [16], published in 1951, has not been cited in the open literature. In this work, three sets of previously published S-shaped equilibrium data of water contaminants are used to test the little-known Krishnamurti isotherm. Further, this paper reports the modeling results obtained with a modified form of the Krishnamurti isotherm.
2. Theory

The main assumption of the adsorption model proposed by Krishnamurti [16] is that the uptake of an adsorbate by an adsorbent follows a co-operative adsorption mechanism where previously adsorbed molecules facilitate the adsorption of more molecules in neighboring positions. Under such conditions, the rate of increase in the number of adsorbed molecules \( n \) with increase in the concentration of the molecules in the solution \( c \) will depend upon the number of molecules already adsorbed and also upon the concentration of the molecules still available for adsorption in the solution. Mathematically this adsorption model can be expressed as

\[
\frac{dn}{dc} = kn(N - n)
\]

where \( n \) = the number of adsorbed molecules; \( c \) = the solution phase concentration; \( k \) = a constant; and \( N \) = the total number of molecules originally present in the solution.

Integrating the preceding equation gives

\[
n = \frac{N}{1 + k_1 \exp(-k_2 c)}
\]

where \( k_1 \) and \( k_2 \) are constants.

Dividing both sides of this last equation by the mass of adsorbent yields

\[
q = \frac{N_0}{1 + k_1 \exp(-k_2 c)}
\]

where \( q \) = the adsorbed phase concentration and \( N_0 \) = the total number of molecules per unit mass of adsorbent. The three parameters to be fitted are \( N_0 \), \( k_1 \), and \( k_2 \). An isotherm equation similar to Eq. (3) has been proposed by Meghea et al. [17], who were probably unaware of Krishnamurti’s isotherm.

3. Nonlinear least-squares regression

Nonlinear least-squares regression was applied to the models tested in this work to estimate their free parameters. Model fit was assessed using average relative error (ARE) and residual root mean square error (RRMSE). The dimensionless ARE is a relative measure of overall fit, whereas the RRMSE [18], which has the same units as \( q \), is an absolute measure of overall fit. The two statistical metrics are given by Eqs. (4) and (5).

\[
\text{ARE} = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{q_i - \hat{q}_i}{q_i} \right|
\]

(4)

\[
\text{RRMSE} = \sqrt{\frac{\sum_{i=1}^{m} (q_i - \hat{q}_i)^2}{m - p}}
\]

(5)
where $q_i = \text{experimental values}; \hat{q}_i = \text{model values}; m = \text{the number of data points}; p = \text{the number of regression parameters};$ and $(m - p) = \text{the number of degrees of freedom of the regression. A lower ARE or RRMSE value indicates a better fit.}

4. Results and discussion

To our knowledge, a paper by the originator of the isotherm defined by Eq. (3) appears to be the only work where the Krishnamurti isotherm was used to fit S-shaped equilibrium data [19]. As such, there is a need to conduct a comprehensive testing of Eq. (3). In this work, three sets of previously published equilibrium data of water contaminants are used to test the Krishnamurti isotherm: (1) ammonium ion adsorption by sepiolite [20], (2) ciprofloxacin removal by a magnetic nanosorbent [6], and (3) fluoride ion adsorption by a layered double hydroxide adsorbent [21].

4.1. Ammonium ion adsorption by sepiolite

Balci [20] reported several sets of equilibrium data on the uptake of ammonium ion by sepiolite, a naturally occurring clay mineral. Most data sets exhibited S-shaped curves, one of which is shown in Fig. 1A. Balci [20] found that the S-shaped data sets were well represented by the Toth and Langmuir-Freundlich (Sips) isotherms. The mathematical forms of these two isotherms are quite similar—both are power law functions. The Krishnamurti isotherm, Eq. (3), was fitted to the Fig. 1A data by nonlinear regression, as shown in Fig. 1A. It can be seen that the isotherm fit is
closely aligned with the entire experimental profile. The ARE and RRMSE values for the isotherm fit are respectively 1.48 and 0.05 mmol/g. For comparison, the Sips isotherm was also fitted to the Fig. 1A data, yielding inferior ARE and RRMSE scores of 2.78 and 0.07 mmol/g respectively. It is apparent that the Krishnamurti isotherm is highly effective in correlating this data set and is superior to the Sips isotherm. Fig. 1B shows a plot of residuals (the differences between observed and calculated q values) for the Krishnamurti isotherm fit. The absence of residual systematic behavior in Fig. 1B indicates that the Krishnamurti isotherm is appropriate for this data set.

4.2. Ciprofloxacin adsorption by nanosorbent

![Graphs](image-url)

Fig. 2. (A) Krishnamurti isotherm fit (solid line, \( N_0 = 819.7 \) mg/g; \( k_1 = 0.03 \) L/mg; \( k_2 = 651.7 \)) compared to observed ciprofloxacin equilibrium data; (B) residual plot.

Soares et al. [6] synthesized three different types of magnetic nanoparticles which were used to remove the antibiotic ciprofloxacin from aqueous solutions. Of interest to the present study are the equilibrium characteristics of the three adsorption systems. Two of the three adsorption systems were found to exhibit favorable convex-upward curve shapes, which were well fitted by the Langmuir isotherm. The remaining one exhibited a sigmoidal curve, as shown in Fig. 2A. The S-shaped curve was attributed to the presence of cooperative binding in the adsorption system. The authors fitted the Langmuir, Freundlich, and Dubinin-Radushkevich isotherms to the Fig. 2A data. As expected, the data were poorly described by the Langmuir and
Freundlich isotherms. By contrast, the Dubinin-Radushkevich isotherm fit was satisfactory. Here, an adequate fit with the Krishnamurti isotherm has also been obtained, as may be seen in Fig. 2A. The ARE and RRMSE values for the isotherm fit are 2.75 and 50.46 mmol/g respectively. The Krishnamurti isotherm seems to work very well for this data set. Fig. 2B plots residuals as a function of the liquid-phase concentration. The absence of a systematic trend in the behavior of the residual values suggests that there is no reason to reject the Krishnamurti isotherm as unacceptable.

4.3. Fluoride ion adsorption by layered double hydroxide

This third example, reported by Lv et al. [21], deals with the adsorptive removal of fluoride from aqueous solutions. Like the study of Soares et al. [6] discussed above, Lv et al. [21] synthesized their own adsorbent. The resulting adsorbent, layered double hydroxide, was used to purify aqueous solutions containing fluoride. The adsorption system produced an S-shaped equilibrium curve, which was fitted with the Langmuir, Freundlich, and Sips isotherms. According to Lv et al. [21], the Sips isotherm produced a very high quality of fit whereas the Langmuir and Freundlich isotherms yielded very poor fits. Fig. 3A shows this set of S-shaped equilibrium data together with the Krishnamurti isotherm fit (solid line). The figure includes another model fit (dashed line), and it will be discussed later. Although the Krishnamurti isotherm fit seems somewhat decent (ARE = 14.60 and RRMSE = 17.38 mg/g), one can see from Fig. 3A that the solid curve did not pass through the majority of the data points. In the low liquid-phase concentration region, there is noticeable deviation between the calculated curve and experimental data. The residual plot shown in Fig. 3B reveals a randomly distributed set of residuals, suggesting that the functional form of the Krishnamurti isotherm is suitable for this data set. Unfortunately, the Krishnamurti isotherm is not flexible enough to trace the trajectory of the data points to a significant degree of accuracy.

Further, when \( c = 0 \) the Krishnamurti isotherm becomes

\[
q = \frac{N_0}{1 + \kappa_0 c} \tag{6}
\]

The preceding equation predicts a non-zero \( q \) value at \( c = 0 \). The Krishnamurti isotherm therefore has the undesirable property of not being constrained to go through the origin. This data set reveals the deficiencies of the Krishnamurti isotherm as
a modeling tool for S-shaped equilibrium data. The next section discusses how the Krishnamurti isotherm may be modified in order to improve its data fitting ability.

Fig. 3. (A) Krishnamurti isotherm fit (solid line, see Section 4.4 for parameter estimates) and modified Krishnamurti isotherm fit (dashed line, see Section 4.4 for parameter estimates) compared to observed fluoride equilibrium data; (B) residual plot of the Krishnamurti isotherm fit; (C) residual plot of the modified Krishnamurti isotherm fit.

4.4. Modified Krishnamurti isotherm

To reduce its lack-of-fit error, the Krishnamurti isotherm defined by Eq. (3) is modified via a logarithmic transformation of the variable c. This method of logarithmic transformation was previously successfully used to enhance the ability of a mathematical function to fit fixed bed breakthrough curves [22]. Here we show that the Krishnamurti isotherm can be transformed in the same spirit as the fixed bed model. Because c is a dimensioned quantity, it must first be made dimensionless before the logarithmic transformation can be applied to the Krishnamurti isotherm. The specific steps involved are described below.

Step 1: Assign the variable c an appropriate set of units, e.g., mg/L.
Step 2: Define a new variable $c^*$, which is numerically equal to 1 mg/L.

Step 3: Multiply the $(-k_1c)$ term in Eq. (3) by $c^* / c^*$.

$$q = \frac{N_0}{1 + k_2 \exp \left(-k_1c\left(\frac{c^*}{c^*}\right)\right)}$$

(7)

Note that Eq. (7) is numerically identical to Eq. (3).

Step 4: Rearrange Eq. (7).

$$q = \frac{N_0}{1 + k_2 \exp \left(-k_1c^*\right) \ln \left(\frac{c}{c^*}\right)}$$

(8)

Step 5: We can now take the logarithm of $(c/c^*)$, which is a dimensionless quantity.

$$q = \frac{N_0}{1 + k_2 \exp \left(-k_1c^*\right) \ln \left(\frac{c}{c^*}\right)}$$

(9)

Step 6: Eq. (9) can be simplified and expressed as

$$q = \frac{N_0}{1 + k_2 \left(\frac{c}{c^*}\right)^{-1/k_1}}$$

(10)

Step 7: Since $c^* = 1$ mg/L, for convenience, it may be omitted from Eq. (10).

$$q = \frac{N_0}{1 + k_2 c^{-k_1}}$$

(11)

One should bear in mind that $c$ and $k_1$ in Eq. (11) represent pure numbers numerically equal to the actual $c$ (mg/L) and the actual $k_1$ (L/mg), respectively.

To assess the data fitting ability of Eq. (11), it was fitted to the Fig. 3A data by nonlinear regression. The resulting fit, shown in Fig. 3A (dashed line), reveals that the modified isotherm is very effective, tracing closely most of the data points. As may be seen in Fig. 3C, the residuals clearly exhibit random behavior, validating the appropriateness of the modified isotherm's functional form. Comparison of the statistical measures for the two fits in Fig. 3A indicates that the modified isotherm fit (ARE = 2.24 and RRMSE = 4.25 mg/g) is vastly superior to the original isotherm fit (ARE = 14.60 and RRMSE = 17.38 mg/g). However, the modified isotherm is
obviously undefined at \( c = 0 \) because of the logarithmic transformation of \( c \). Nevertheless, it can track \( q \) values that correspond to very small \( c \) values, as may be seen in Fig. 3A.

The performance of an isotherm model is often assessed according to the sole criterion of overall fit. One may adopt a broader approach by evaluating the statistical significance of fitted parameters. A 95% confidence interval is commonly used to assess uncertainty in parameter estimates. For the modified and original Krishnamurti isotherm fits shown in Fig. 3A, the asymptotic confidence interval of each parameter estimate was computed using the GraphPad Prism software. For the modified isotherm fit, the fitted parameter values and their 95% confidence intervals (indicated by values in parenthesis) are as follows: \( N_0 = 319.4 \) (304.9 to 335.5) mg/g, \( k_1 = 2.46 \) (2.21 to 2.75) L/mg, and \( k_2 = 549.4 \) (315.1 to 1047). For the original isotherm fit, the fitted parameter values and their 95% confidence intervals are as follows: \( N_0 = 297.5 \) (251.2 to 345) mg/g, \( k_1 = 0.26 \) (0.18 to 0.49) L/mg, and \( k_3 = 30.2 \) (13.1 to 234). For both isotherm fits, the confidence intervals of \( N_0 \) and \( k_1 \) are rather narrow, indicating that both parameters can be estimated precisely. By contrast, the confidence intervals of \( k_2 \) are larger than the estimated values, suggesting that the fitted \( k_2 \) values are not statistically significant. Given that the width of a confidence interval is influenced by the number of degrees of freedom in the estimation process, a feasible way to reduce the width is to use more data points. Fig. 3A shows that only eight data points were collected for the fluoride adsorption system, with a cluster of five appearing in the low concentration range. It seems that more data points might be able to reduce the standard error (and thus the confidence interval) of \( k_2 \).

For comparison, the Sips isotherm was fitted to the Fig. 3A data, yielding \( \text{ARE} = 2.24 \) and \( \text{RRMSE} = 4.25 \) mg/g. These statistical scores are identical to those of the modified Krishnamurti isotherm fit (\( \text{ARE} = 2.24 \) and \( \text{RRMSE} = 4.25 \) mg/g). This agreement is not surprising because the modified Krishnamurti isotherm is mathematically analogous to the Sips isotherm. To demonstrate this mathematical equivalence, Eq. (11) may be rewritten as

\[
\frac{q}{N_0} = \frac{(1/k_3) c^h}{1 + (1/k_3) c^h}
\]

(12)
It is evident that the preceding equation is the well-known Sips isotherm. When \( k_1 < 1 \), the modified Krishnamurti isotherm can be used to fit convex-upward curves, just like the Langmuir and Freundlich isotherms. When \( k_1 > 1 \) it can fit S-shaped or sigmoidal curves. It is interesting to note that Sips [23] devised his eponymous isotherm to overcome a major deficiency of the Freundlich isotherm, that is, the Freundlich isotherm does not approach an adsorption maximum at high concentrations. In addition, Sips [23] points out that the maximum value that the exponent \( k_1 \) in Eq. (12) can assume is unity. It is well known that the Sips isotherm reduces to the Langmuir isotherm when \( k_1 \) is set to unity. Since the case of \( k_1 > 1 \) was not considered by Sips, one can conclude that the Sips isotherm lacks theoretical merit when it is applied to S-shaped equilibrium data.

The superiority of the modified Krishnamurti isotherm versus its original counterpart is largely due to the fact that the former has a floating inflection point while the latter has a fixed one. The original isotherm is mathematically analogous to the well-known logistic equation of population growth as well as the Bohart-Adams, Thomas, and Yoon-Nelson models of fixed bed adsorption [23]. The inflection point of a sigmoidal curve predicted by the logistic equation is invariant, and is located at the curve's mid-point. Accordingly, the inflection point of an S-shaped curve predicted by the original isotherm is always located at \( q/N_0 = 0.5 \). This means that the original isotherm produces sigmoidal curves that are always symmetric, that is, the convex and concave curves on either side of the inflection point have the same curvature. The data fitting ability of the original isotherm is thus somewhat limited since it is confined to fitting highly symmetric S-shaped curves. By contrast, the inflection point of the modified isotherm varies with the parameter \( k_1 \), and is given by the following expression:

\[
\frac{q}{N_0} = \frac{k_1 - 1}{2k_1} \quad \text{for} \quad k_1 > 1
\]  

(13)

With a floating inflection point, the modified isotherm can fit both symmetric and asymmetric S-shaped curves to a significant degree of precision. Like the Sips isotherm, the modified Krishnamurti isotherm has no theoretical merit and should thus be treated as a convenient empirical representation of S-shaped equilibrium data.
5. Conclusions

This study tested the ability of the Krishnamurti isotherm to fit S-shaped equilibrium data of water contaminants. The Krishnamurti isotherm was found to track closely the sigmoidal data trends of ammonium ion adsorption by sepiolite and ciprofloxacin adsorption by a nanosorbent. Thus, its practical value is evident. However, the isotherm was found less accurate in representing the S-shaped equilibrium data of fluoride adsorption by a layered double hydroxide adsorbent. In this particular case, a modified form of the Krishnamurti isotherm was found to outperform its original counterpart. Both the original and modified Krishnamurti isotherms are useful additions to the existing pool of isotherm equations capable of fitting S-shaped equilibrium data. Further testing using observed equilibrium data of other water contaminants will be required to confirm that they can indeed track different types of sigmoidal equilibrium data.

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