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The Sips isotherm equation: Often used and sometimes misused

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ABSTRACT

The Sips isotherm equation, proposed in 1948, is popularly used to describe the adsorption of a diverse array of water contaminants by engineered and natural adsorbents. However, that apparent popularity conceals problematic application issues. Our critique of its use in water contaminant adsorption research is threefold. First, we show that a linear version of the Sips equation promoted by several reviews is bogus. We also highlight application problems associated with two other linear versions. Second, we show that it is inappropriate to compare the Sips and Langmuir–Freundlich equations in data correlation. Because the two equations are mathematically equivalent, they must provide exactly the same fit to a given set of isotherm data. Third, we argue that there is little to be gained by applying the Sips equation to type I isotherms, which are hyperbolic curves. Such isotherm shapes can be adequately interpreted by simple two-parameter isotherm models such as the Langmuir and Freundlich equations. The modeling power of the Sips equation can be more profitably exploited by applying it to type V isotherms, which are sigmoid curves.

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Introduction

The adsorption isotherm proposed by Sips was shown to be a case of gas adsorption on heterogeneous solids governed by the local Langmuir isotherm and a certain energy distribution.[1] The Sips equation reduces to the Freundlich equation at low pressure and, like the Langmuir equation, possesses a finite saturation limit when the pressure is sufficiently high. For this reason, it is sometimes referred to as the Langmuir–Freundlich isotherm in the adsorption literature.[2]

The Sips equation has often been found to fit liquid phase adsorption data quite well, in which case the gas pressure term is replaced by the concentration of the adsorbable solute in the liquid phase. The Sips equation is popularly used as an isotherm model in the field of water contaminant adsorption.[3] With three fitting parameters, it is highly effective for data correlation, covering wide ranges of concentrations. However, the Sips equation lacks the ability to describe the effects of important solution phase variables such as pH and ionic strength. A modified form of the Sips equation has been proposed to describe pH-dependent adsorption isotherms.[4]

Another criticism of the Sips equation is that it lacks mechanistic relevance. Efforts have been made to give some semblance of a theoretical basis to the Sips equation. One of the earliest attempts is the work of Koble and Corrigan,[5] who derived the Sips equation by assuming a dissociative chemical reaction mechanism for gas adsorption to solid surfaces. The Sips equation can also be derived using Langmuir's kinetic argument for gas adsorption.[6,7]

In the field of water contaminant adsorption, the Sips equation is mostly used as an empirical expression to correlate hyperbolic (type I) adsorption isotherms. Despite its popularity, this contribution shows that there are clear problems in applying the Sips equation to water contaminant adsorption data. Three application issues are expounded here: (1) the dubious practice of using linear versions of the Sips equation to fit adsorption data; (2) the questionable practice of comparing the Sips and Langmuir–Freundlich equations; and (3) the trivial practice of fitting the Sips equation to type I isotherm data. Few studies have rigorously addressed these application issues.

The Sips equation

In a 1948 paper, Sips showed how the adsorption energy distribution of the active sites existing on a catalyst surface could be derived when the adsorption isotherm was

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specified.[1] Using the Freundlich equation, Sips derived an analytical expression for the distribution function of adsorption energy or active sites for a gas/catalyst system.

Because the Freundlich model assumes that the amount of gas adsorbed increases indefinitely with pressure, the distribution function would also predict an infinite number of active sites. To overcome this deficiency, Sips modified the Freundlich equation to the form given by Eq. 1, where θ is the fractional surface coverage, p is the gas pressure, and b and n are constants for a given gas/catalyst system. If the exponent n is set constant at unity, Eq. 1 reduces to the celebrated Langmuir isotherm equation.

$$\theta = \frac{bp^n}{1 + bp^n} \tag{1}$$

When p is very large, θ in the preceding equation is practically equal to unity. Taking advantage of this property of Eq. 1, Sips derived another distribution function that could predict a finite number of active sites on the catalyst surface. To make the derivation method work, Sips emphasized that n must be between 0 and 1. Equation 1 reduces to the Freundlich equation for small p but exhibits an adsorption maximum for large p.

In the current literature, Eq. 1 is known as the Sips or Langmuir–Freundlich equation. We mention in passing that the title of the 1948 paper by Sips, given as "On the structure of a catalyst surface," is occasionally misquoted. Erroneous titles like "Combined form of Langmuir and Freundlich equations"[8–10] and "Physical adsorption on non-uniform surfaces"[11] have been quoted in the literature.

It should be mentioned that a specific form of the Sips equation can be found in a 1918 paper published by Langmuir.[12] One of the adsorption cases considered by Langmuir would lead to Eq. 2. However, Langmuir did not present Eq. 2 in his paper but simplified it to Eq. 3 for small p (equivalent to the Freundlich equation).

As mentioned earlier, in a 1927 paper, Chakravarti and Dhar[6] derived an adsorption isotherm similar to the Sips equation using Langmuir's kinetic argument for gas adsorption. Interestingly, also in 1927, Bradley proposed a Sips-like isotherm equation and applied it to gas-solid as well as liquid-solid adsorption systems.[13] In some publications, the Sips equation is known as the Bradley equation.[14–17]

$$\theta = \frac{bp^{0.5}}{1 + bp^{0.5}} \tag{2}$$

$$\theta = bp^{0.5} \tag{3}$$

Quite unexpectedly, the Sips equation attracted the attention of researchers working in the field of immunology.[18] A log-linearization form of the Sips equation, given here by Eq. 4, was adopted by immunologists to analyze data from antigen-antibody reactions measured by equilibrium dialysis. In Eq. 4, r denotes the ratio of the concentration of bound ligand to the concentration of antibody molecules, L is the concentration of free or unbound ligand, A is the number of ligand binding sites on the antibody molecule, K_i is the intrinsic affinity constant, and a is the index of heterogeneity, which can range from 0 to 1. This index is, of course, equivalent to the exponent n in Eq. 1. A plot of the left side of Eq. 4 against $\ln(L)$ should yield a straight line of slope a. Equation 4 is known as the Sips plot in the immunological literature. It can be used to estimate K_i and a by linear regression, provided that A is known.[18]

$$\ln\left(\frac{r}{A - r}\right) = a\ln(L) + a\ln(K_i) \tag{4}$$

Results and discussion

Linearized Sips equations

Equation 5 is the most common form of the Sips equation used to describe water contaminant adsorption data, where q is the adsorbed phase concentration, c is the liquid phase concentration, q_m is the maximum adsorption capacity, b is an equilibrium constant, and n is a fitting parameter.

$$q = \frac{q_m bc^n}{1 + bc^n} \tag{5}$$

The Sips equation is usually fitted to experimental isotherm data by nonlinear regression to determine its three unknown parameters (q_m, b, and n). Although the drawbacks of linearizing inherently nonlinear isotherm models are well publicized,[3,19–21] several linear forms of the Sips equation exist in the environmental adsorption literature. Equation 6 shows the linear form of the Sips equation as presented in a highly cited review.[22] However, Eq. 6 does not agree with the nonlinear Sips equation defined by Eq. 5. When stripped of the logarithmic transformation, Eq. 6 becomes Eq. 7, which resembles a Freundlich-type equation rather than the nonlinear Sips equation given by Eq. 5.

$$\ln\left(\frac{q_m b}{q}\right) = -n\ln(c) + \ln(b) \tag{6}$$

$$q = q_m c^n \tag{7}$$

The original form of the nonlinear Sips equation as presented by Foo and Hameed[22] is reproduced here as Eq. 8. If we set $q_e = q$, $C_e = c$, $K_S = q_m b$, $a_S = b$, and $\beta_S = n$ we recover from Eq. 8 the Sips equation adopted in the present study, that is, Eq. 5. The linear form of Eq. 8 as presented by Foo and Hameed[22] is given by Eq. 9. Removing the logarithmic transformation from Eq. 9 yields Eq. 10, which is again a Freundlich-type equation, and so differs from the original Sips equation given by Eq. 8. Evidently, mistakes were made by Foo and Hameed[22] in linearizing Eq. 8. Incredibly, the erroneous linearized Sips equation (Eq. 9) has been regurgitated verbatim in several recent reviews.[23–27] None of the reviews evinces any awareness that Eq. 9 is a linear version of a Freundlich-type equation.

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \tag{8}$$

$$\ln\left(\frac{K_S}{q_e}\right) = -\beta_S \ln(C_e) + \ln(a_S) \tag{9}$$

$$q_e = \frac{K_S}{a_S} C_e^{\beta_S} \tag{10}$$

To perform a linear plot using Eq. 9, an independent knowledge of K_S is needed, which appears in the logarithmic term on the left side of the equation. Figure 1 shows two such plots taken from the environmental adsorption literature.[28,29] However, the method used to estimate K_S was not described in the two reports.[28,29] As noted above, Eq. 9, on which the plots depicted in Fig. 1 are based, is not a linear version of the Sips equation; it is a linear form of the Freundlich equation defined by Eq. 10.

Apart from the erroneous Eq. 6 or 9, there are other linear versions of the Sips equation in common use. For example, Eq. 11 is a popular version, which is a simple algebraic rearrangement of Eq. 5. According to Eq. 11, a plot of $1/q$ against $(1/c)^n$ should yield a straight line. To perform such a plot, the value of n has to be known in advance. Figure 2 presents two such plots taken from recent reports.[30,31] The exponent n for the plot in

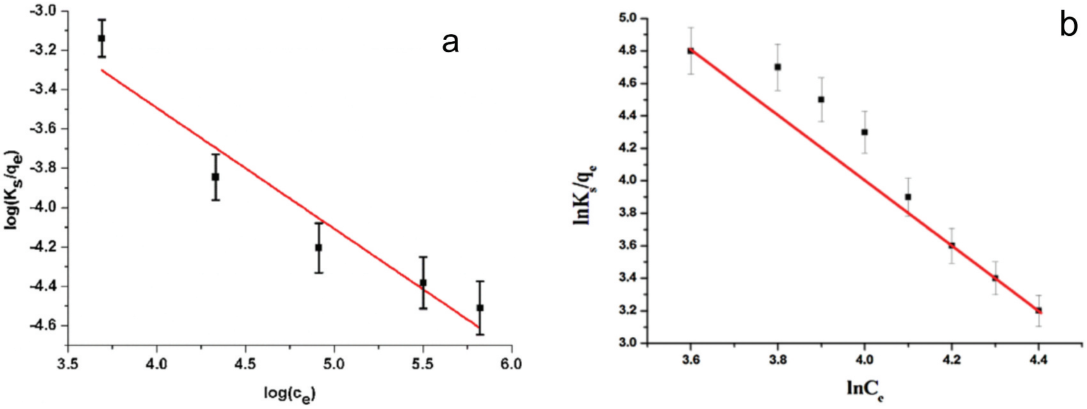

Figure 1. (a) Linear plot of Eq. 9. Figure reproduced with permission from Ref. [28]. Copyright 2016 Elsevier. (b) Linear plot of Eq. 9. Figure reproduced with permission from Ref. [29]. Copyright 2016 Elsevier.

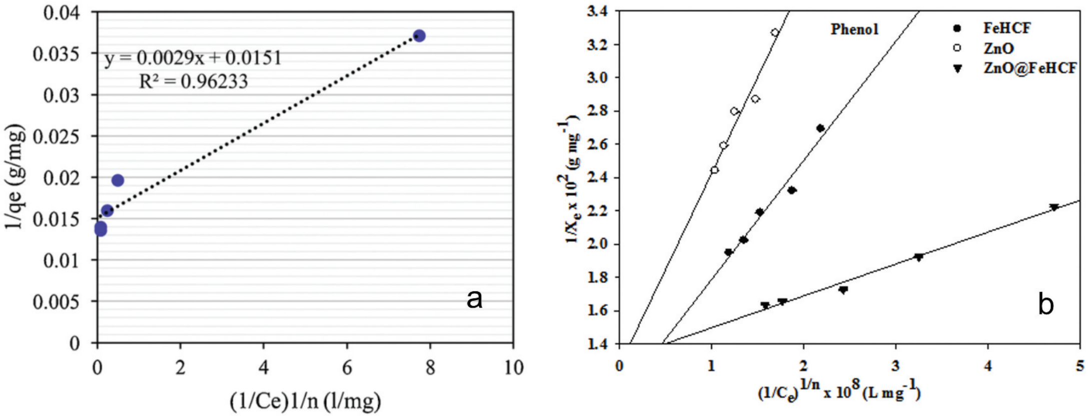

Figure 2. (a) Linear plot of Eq. 11. Figure reproduced with permission from Ref. [30]. Copyright 2019 Elsevier. (b) Linear plots of Eq. 11. Figure reproduced with permission from Ref. [31]. Copyright 2020 Elsevier.

Fig. 2(a) is given as 1 in the work of Basaleh et al.[30] Note that the exponent n used in this work is equivalent to $(1/n)$ in Fig. 2. This means that, in this case, the data points were fitted to the Langmuir equation rather than the Sips equation. In the case of Fig. 2(b), no information on the exponent n can be found in the work of Rachna et al.[31] It is unclear how the three linear plots in Fig. 2(b) were constructed without specifying a value for n.

$$\frac{1}{q} = \left(\frac{1}{q_m b}\right)\left(\frac{1}{c}\right)^n + \frac{1}{q_m} \tag{11}$$

Equation 12 is another linear version of the Sips equation. It is obvious that Eq. 12 is based on the Sips plot used in the immunological literature (Eq. 4). Many researchers have applied Eq. 12 to the equilibrium data of water contaminants. Figure 3 shows two examples of data correlations using Eq. 12, reproduced from the works of Lim et al.[32] and Romzi et al.[33] According to Eq. 12, q_m is needed to calculate the left side of the equation. The values of q_m for the two linear plots in Fig. 3(a) are given as 146.1 and 216.3 mg g^{-1}, while the value of q_m for the linear plot in Fig. 3(b) is given as 328.2 mg g^{-1}.[32,33] Unfortunately, both articles did not disclose how these q_m values were estimated. Equation 12 was also used by Lu et al.[34] to fit aqueous isotherm data without expounding on how q_m was estimated. In gas adsorption research, it was used to fit the measured isotherms of nitrogen, methane, ethane, and propane.[35]

$$\ln\left(\frac{q}{q_m - q}\right) = n\ln(c) + \ln(b) \tag{12}$$

Since the nonlinear Sips equation given by Eq. 5 has three unknown parameters (q_m, b, and n), all its linear forms should also have three unknown parameters. Given that at most two unknown parameters can be determined from a linear plot, one of the three Sips parameters must be known before a linear regression can be performed on any linearized Sips equation. So, without knowing the exponent n, Eq. 11 cannot be plotted. Likewise, a value must be assigned to q_m in order to plot Eq. 12. As noted above, it is not at all clear how n and q_m were estimated in studies using Eq. 11 or 12 to fit the isotherm data. The n and q_m parameters were probably rough guesstimates obtained by trial and error, that is, various values were tested to find the optimum ones that maximized the R^2 scores. Some articles have reported the relative performances of linear and nonlinear forms of the Sips equation in data fitting, but no information was provided on the methods used to plot the linearized Sips equations.[34,36,37]

Comparing the Sips and Langmuir–Freundlich equations

Several articles have compared the data fitting ability of Eq. 13 to that of the Sips equation given by Eq. 5. Equation 13 is called the Langmuir–Freundlich equation, where q_{LF}, b_{LF}, and n_{LF} are fitting parameters. The work of Hamdaoui and Naffrechoux[38] serves as an early example of such isotherm comparisons. Hamdaoui and Naffrechoux[38] claimed that the Langmuir–Freundlich equation outperformed the Sips equation in the correlation of the measured isotherms of phenol and chlorophenols.

$$q = \frac{q_{LF}(b_{LF}c)^{n_{LF}}}{1 + (b_{LF}c)^{n_{LF}}} \tag{13}$$

Several subsequent studies replicated the modeling approach of Hamdaoui and Naffrechoux[38] by comparing the Langmuir–Freundlich and Sips equations in data fitting.[39–43] It seems that these researchers were unaware of the fact that Eq. 13 is mathematically equivalent to Eq. 5. If we set $q_{LF} = q_m$, $b_{LF}^{n_{LF}} = b$, and $n_{LF} = n$, Eq. 13 reduces to Eq. 5. If one determines the three parameters in the Langmuir–Freundlich equation by fitting Eq. 13 to a given data set, one can obtain the three parameters

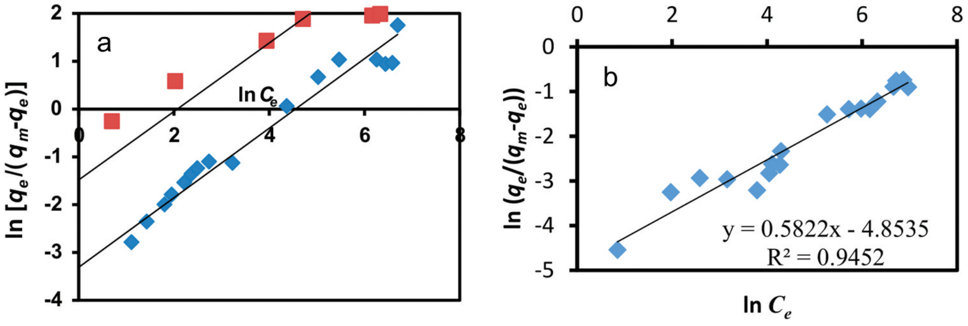

Figure 3. (a) Linear plots of Eq. 12. Figure reproduced with permission from Ref. [32]. Copyright 2016 Taylor & Francis. (b) Linear plot of Eq. 12. Figure reproduced with permission from Ref. [33]. Copyright 2022 Taylor & Francis.

in the Sips equation without having to fit Eq. 5 to the same data set. This means that the Langmuir–Freundlich equation is interconvertible with the Sips equation. No meaningful insights can be obtained by fitting the Langmuir–Freundlich and Sips equations separately to the same set of isotherm data and comparing their performances. In principle, one should obtain the same quality of fit when the two equations are fitted to a given set of isotherm data.

It should be mentioned that Eq. 13 is also called the Liu equation in the environmental adsorption literature. The Liu equation is, of course, analogous to the Sips equation. These two equations have been shown to provide exactly the same fit to a given set of isotherm data.[44] Therefore, it is a fallacy to compare the data fitting abilities of the Liu/Langmuir–Freundlich equation (Eq. 13) and the Sips equation (Eq. 5). In fact, the Hill and Koble–Corrigan equations are also analogous to the Sips equation, as pointed out by Chu et al.[44] Many researchers have compared the data fitting abilities of the Sips, Liu (or Langmuir–Freundlich, Eq. 13), Hill, and Koble–Corrigan equations, seemingly unaware of the fact that they are mathematically equivalent to each other. Several such meaningless studies have been published in *Separation Science and Technology*.[42,45–47]

Correlation of types I and V isotherm data

The Sips equation is commonly used to describe type I isotherm data. However, the modeling of type I adsorption isotherms is a crowded field. Simple isotherm equations with two fitting parameters, e.g., the Langmuir and Freundlich models, are capable of fitting such hyperbolic curves. With three adjustable parameters, the Sips equation will generally provide a better fit to a type I isotherm compared to the two-parameter Langmuir and Freundlich models, but more often than not, the former offers only a modest degree of improvement in the goodness of fit.

Statistical tests that consider both the number of fitting parameters and quality of fit, e.g., the Akaike weight,[48] tend to punish models with multiple fitting parameters. To illustrate this point, Fig. 4 shows the fits of the Sips, Langmuir, and Freundlich equations to a set of cadmium isotherm data taken from the work of Hashem et al.[49] As can be seen in Fig. 4, the measured cadmium isotherm manifests a type I curve shape without an apparent plateau. The R^2 scores for the Langmuir and Freundlich fits are 0.9992 and 0.9916, respectively, which are inferior to that of the Sips fit ($R^2 = 0.9997$). Note that the difference in performance between the Sips equation and the Langmuir equation is only reflected in the fourth decimal place of R^2.

The Akaike weights indicate that the performance of the three equations is in the following order: Langmuir (72.9%) > Sips (27.1%) > Freundlich (0%). With the largest Akaike weight, the Langmuir equation is the best model for tracking the cadmium isotherm. Although more accurate than the Langmuir equation, the Sips equation is rejected by the Akaike test because its superior fit quality is insufficient to offset the penalty of having one extra parameter. From a statistical perspective, it is inappropriate to compare isotherm models with different numbers of fitting parameters according to simple metrics such as R^2.

There is little to be gained by fitting the Sips equation to type I isotherm data, which can be effectively modeled by two-parameter isotherm equations. The utility of the Sips equation can be exploited much more profitably by fitting it to type V or sigmoid isotherm data.[50] Every type V isotherm is characterized by an inflection point at which the isotherm goes from concave upward to

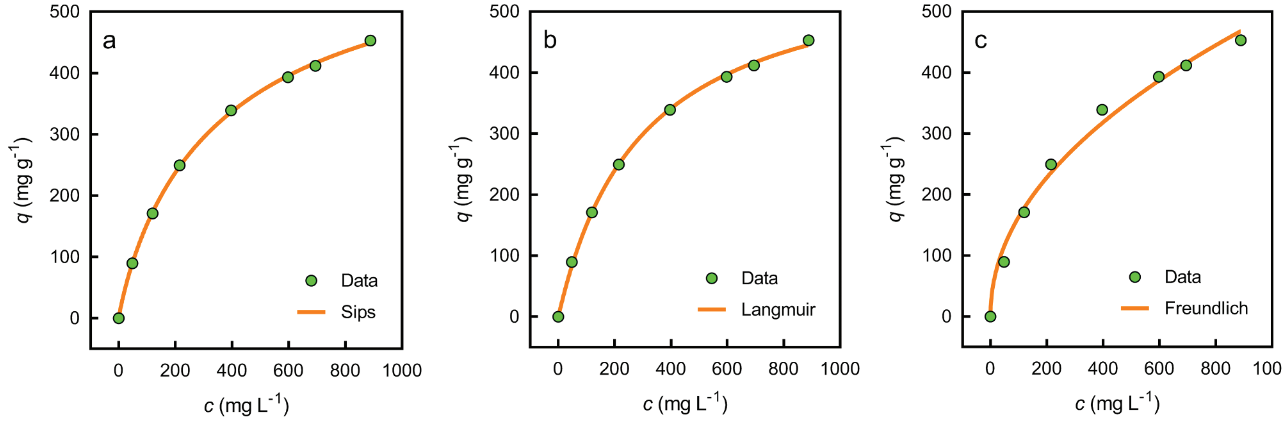

Figure 4. Comparison of isotherm fits and cadmium adsorption data.[49] (a) Sips equation fit. (b) Langmuir equation fit. (c) Freundlich equation fit.

concave downward. A type V isotherm is said to be symmetric if its inflection point is located at $q/q_m = 0.5$ and asymmetric if it is not.

Determining the location of the inflection point of a type V curve predicted by the Sips equation involves three steps. First, we derive the second derivative of Eq. 5, given here by Eq. 14. Next, we set the left side of Eq. 14 to zero and solve the resulting equation for c^n. The result is given by Eq. 15. Finally, we substitute Eq. 15 into Eq. 5, obtaining Eq. 16. According to Eq. 16, the location of the inflection point is a function of n. In other words, the Sips equation has a floating inflection point whose location falls within the range of $q/q_m = 0$ to $q/q_m = 0.5$. Consequently, the floating inflection point permits the Sips equation to fit symmetric as well as asymmetric type V isotherms.

$$\frac{d^2q}{dc^2} = -\frac{q_m bnc^{n-2}[bc^n(1+n) - n + 1]}{(1+bc^n)^3} \tag{14}$$

$$c^n = \frac{1}{b}\left(\frac{n-1}{1+n}\right) \tag{15}$$

$$\frac{q}{q_m} = \frac{n-1}{2n} \tag{16}$$

Figure 5 illustrates the ability of the Sips equation to interpret a type V isotherm, taken from the work of Muntean et al.[51] The experimental isotherm was measured for the adsorption of a direct red dye by a beech wood material. Figure 5 shows that the Sips equation tracks the entire sigmoid shape to a significant degree of precision ($R^2 = 0.9976$). The fitted value of n is 2.67, which gives the location of the inflection point at $q/q_m = 0.31$, calculated from Eq. 16. This location ($q/q_m \neq 0.5$) confirms that the isotherm shape is asymmetric.

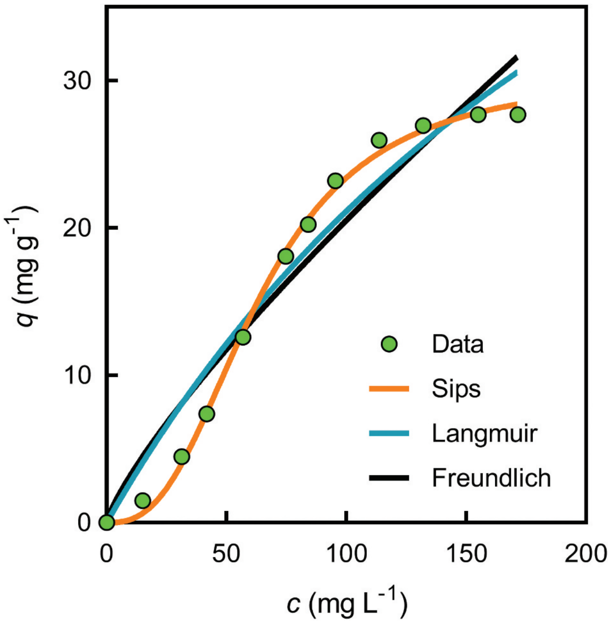

Figure 5. Comparison of isotherm fits and dye adsorption data.[51]

Also shown in Fig. 5 are the fits of the Langmuir equation ($R^2 = 0.952$) and the Freundlich equation ($R^2 = 0.9353$). The R^2 values confirm the inadequacy of these two equations. The Akaike test also favors the Sips equation. The Fig. 5 results reveal the superiority of the Sips equation in correlating the experimental type V isotherm, easily outperforming the Langmuir and Freundlich equations. This powerful data fitting ability is not exploited when the Sips equation is applied to type I isotherm data.

The sigmoid shape of an adsorption isotherm is generally regarded as indicative of a cooperative adsorption effect.[52] According to this conceptual framework, a mathematical expression analogous to the Sips equation can readily be derived from the classical mass action law. Consequently, the exponent n (>1) can be interpreted as the degree of cooperativity of the adsorption process. In this way, n takes on a physical meaning. In the fitting of type I isotherms, on the other hand, n (<1) is typically treated as an empirical parameter. Therefore, it is more meaningful to apply the Sips equation to type V isotherms than to type I isotherms. Because n is usually less than unity when the Sips equation is used to fit type I isotherm data, such values are sometimes interpreted as a sign of negative cooperativity. However, typical type I data can also be well described by the Langmuir model, which assumes noncooperative adsorption.

Conclusions

We have discussed three application issues regarding the use of the Sips equation to correlate water contaminant adsorption data. The first issue relates to the use of three linearized versions of the Sips equation to fit isotherm data. Of the three linearized Sips equations, one version is bogus; it is a linear form of a Freundlich-type equation rather than a linear version of the Sips equation. All three linear versions require one of the three unknown Sips parameters to be specified before a linear plot can be performed. The only way to do this is by trial and error, which introduces some uncertainty into the linear regression process. Hence, parameter estimates obtained in this way must be viewed with considerable caution. Given that the three fitting parameters of the Sips equation can be easily estimated by nonlinear regression, the persistent use of linear regression in this area of research is puzzling.

The second issue concerns the practice of comparing the data fitting abilities of the Sips and Langmuir–Freundlich equations. Because the two equations are mathematically equivalent, they must provide exactly the same fit to a given set of isotherm data. Reported differences in the data fitting abilities of the two equations are most likely due to the use of faulty regression methods. It should be noted that the Sips equation is also analogous to the Hill, Koble–Corrigan, and Liu equations.

The third issue concerns the practice of comparing isotherm models with different numbers of fitting parameters. Numerous studies have reported that the Sips equation with three fitting parameters easily surpassed the Langmuir and Freundlich equations with two fitting parameters in tracking type I isotherm data. Further research highlighting the superiority of the Sips equation adds no new knowledge to this body of literature. The practical utility of the Sips equation lies in its ability to interpret the sigmoid shape of type V isotherms. With a floating inflection point, the Sips equation is a powerful modeling tool for tracking such isotherms.

Disclosure statement

The authors declare that they have no known competing financial interests.

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Statement of novelty

The Sips isotherm equation is widely used to correlate water contaminant adsorption data. However, that apparent popularity conceals problematic application issues. For the first time, this paper addresses three application issues found in the literature of adsorptive water remediation. They are: (1) the dubious practice of using linear versions of the Sips equation to fit adsorption data; (2) the questionable practice of comparing the Sips and Langmuir–Freundlich equations; and (3) the trivial practice of fitting the Sips equation to hyperbolic type I isotherm data. It is hoped that the material presented in this work will lead to a better comprehension of the Sips equation.

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