Mirror, mirror on the wall, which is the fairest of them all? Comparing the Hill, Sips, Koble–Corrigan, and Liu adsorption isotherms

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ABSTRACT

Experimental equilibrium data for the adsorption of water contaminants on solid surfaces are generally correlated using suitable isotherm expressions. In most cases, adsorption isotherms are used empirically with the primary aim of finding the best fitting ones. The literature of adsorptive water decontamination is replete with such isotherm comparisons, usually evaluated on the basis of some statistical metrics such as R^2 and RMSE. For example, several studies have compared and ranked the isotherm equations of Hill, Sips, Koble–Corrigan, and Liu. These comparative evaluations imply that the four isotherms possess different data fitting abilities, and consequently it is possible to identify the most accurate one. The present study argues that this commonly held notion is incorrect. It demonstrates that the four isotherms provide the same results when fitted to three previously published data sets. This finding suggests that the four isotherms are mathematically equivalent despite apparent differences in their formulations. Indeed, a mathematical analysis unequivocally shows that the Hill, Sips, Koble–Corrigan, and Liu isotherms can be represented by a single generic equation with three arbitrary fitting parameters. As such, the four isotherms must provide exactly the same fit to a given set of isotherm data.

1. INTRODUCTION

The adsorption of water contaminants on solid surfaces is currently not amenable to a precise theoretical treatment. Consequently, experimental determinations of the adsorption characteristics of a given contaminant-adsorbent system are almost always necessary. In the context of adsorption equilibrium, the measured data are generally correlated using suitable adsorption isotherm expressions. Most of the isotherm models used in this field of research have their origins in the research literature of chemistry/chemical engineering. These isotherms have been tested in a plethora of studies, usually with the objective of finding the best fitting ones. Many studies have evaluated more than 20 isotherm equations against a single data set, presenting numerous graphs of fitted curves and tables of statistical results. The growing popularity of this curve-fitting practice may have something to do with several review articles, each showcasing an impressive compilation of isotherm equations.

The objective of this study is to draw attention to the indiscriminate practice of fitting multiple isotherm equations to adsorption data. More often than not, such curve-fitting studies inevitably report fallacious results and mistaken conclusions. Specifically, this work presents a critical evaluation of the use of four apparently unrelated isotherms (Hill, Sips, Koble–Corrigan, and Liu) to fit water contaminant adsorption data. The four isotherms have long been regarded as independent models with different data fitting abilities. This perception is pervasive within the domain of adsorptive water remediation. Indeed, many articles have compared two or more of the four isotherms; some examples are listed in Table 1. The statistical results reported in these studies seem to suggest that the most effective isotherm could be identified. Because we only want to discuss in a general way the fact that the comparison of the fits made with these four isotherms is not justified, we quote here only some examples published across a broad spectrum of journals. It should be noted that our aim is not to stigmatize the authors in question, whose experimental work is otherwise very interesting.

In the present study, we argue that it is inappropriate to compare and rank the Hill, Sips, Koble–Corrigan, and Liu isotherms. This is because, as will be considered in this work, the four isotherms may all involve an identical mathematical structure, despite apparent differences in their formulations. The four isotherms will provide exactly the same fit to a given set of isotherm data if they share the same mathematical structure. We present two pieces of evidence to support our assertion. First, we fit the isotherm equations to three previously published data sets, demonstrating that there is no difference in their performance. Second, we confirm their mathematical equivalence by formulating the four isotherms in terms of a generic equation with three arbitrary fitting parameters (called the “XYZ isotherm”). As starting points for this study, in Section 2 we present a historical account of the four isotherms, in particular a description of their original functional forms, followed by a description of their current mathematical forms.

Table 1. Comparative Evaluation of the Hill (H), Sips (S), Koble–Corrigan (K), and Liu (L) Isotherms Reported in the Literature of Environmental Adsorption

ref	adsorption system	H	S	K	L
Manjunatha et al.[1]	fluoride, dye/nanosorbent	✓	✓	✓	✓
Tabaraki and Heidarizadi[2]	dye/biosorbent	✓	✓	✓	✓
Podder and Majumder[3]	arsenic/biosorbent	✓	✓	✓	✓
Thomas and Spitzer[4]	warfare agents/nanotube	✓	✓	✓	✓
Al-Jubouri et al.[5]	metals/ion exchanger	✓	✓	✓	✓
Dolatabadi et al.[6]	pesticide/activated carbon	✓	✓	✓	
Tanzifi et al.[7]	dye/nanosorbent	✓	✓	✓	
Bhattacharya et al.[8]	copper/nanosorbent	✓	✓	✓	
Ghosal and Gupta[9]	fluoride/clay	✓	✓	✓	
Rostamian and Behnejad[10]	antibiotic/nanomaterial	✓	✓	✓	
Mahmoud et al.[11]	pesticide/nanomaterial	✓	✓	✓	
Mahmoud and Mahmoud[12]	COD/bimetallic composite	✓	✓	✓	
Mittal et al.[13]	dye/nanosorbent	✓		✓	✓
Jena et al.[14]	dye/nanosorbent	✓		✓	✓
Bayraç and Camızcı[15]	patulin/magnetic bead	✓			✓
Choudhary et al.[16]	dye, Cu, Ni/biochar	✓	✓		
Singh et al.[17]	arsenic/nanocomposite		✓	✓	
Vargas et al.[18]	dye/activated carbon		✓	✓	
Tang et al.[19]	antibiotic/nanosorbent		✓		✓
Wang et al.[20]	uranium/clay		✓		✓

2. ISOTHERM EQUATIONS

2.1. Original Forms.

2.1. Original Forms. The mathematical forms of the Hill, Sips, Koble–Corrigan, and Liu equations are reproduced here in their original nomenclature.

2.1.1. Hill Equation. More than 100 years ago, Archibald Vivian Hill, a 1922 Nobel Prize laureate in physiology or medicine, presented an empirical equation to describe the interaction of hemoglobin aggregates with oxygen.[21] Equation 1 is the original form of Hill’s equation, where y is the percentage saturation of hemoglobin with oxygen, x is the partial pressure of oxygen, K is the equilibrium constant of the reaction, and n is the average number of hemoglobin molecules aggregated together.

$$y = 100\frac{Kx^n}{1 + Kx^n} \tag{1}$$

In the current literature, the exponent n is known as the Hill coefficient, while a log-linearization version of eq 1 is called the Hill plot, which is commonly used in the pharmacological literature to describe sigmoid or S-shaped curves ($n > 1$). We mention in passing that the equation of A. V. Hill is sometimes misattributed to T. L. Hill, who proposed different isotherm models.[22,23]

2.1.2. Sips Equation. In a paper published in 1948, Robert Sips developed a rigorous mathematical method to derive the adsorption energy distribution of the active sites existing on a catalyst surface when the adsorption isotherm was specified.[24] Using the Freundlich isotherm, Sips successfully deduced a unique distribution function for the adsorption energy/active site. However, because of the limitation of the Freundlich isotherm (adsorption increases indefinitely with gas pressure), the distribution function would predict an infinite number of active sites. To solve this problem, Sips replaced the Freundlich isotherm with eq 2, where θ is the fractional surface coverage, p is the gas pressure, and A and c are constants for a given gas/catalyst system.

$$\theta = \frac{Ap^c}{1 + Ap^c} \tag{2}$$

Unlike the Freundlich isotherm, eq 2 approaches a saturation limit at large p. Consequently, the new distribution function derived by Sips could predict a finite number of active sites. It should be mentioned here that in a follow-up study[25] in response to criticism of his 1948 paper, Sips modified eq 2 to the form given by eq 3, where a is a constant. A specific form of eq 3 ($c = 0.5$) can be found in a 1928 paper published by Zeise.[26]

$$\theta = \left(\frac{p}{a+p} \right)^{c} \tag{3}$$

To derive a valid distribution function for all physical cases, Sips stressed that the values of c must be between 0 and 1. However, this statement does not in any way imply that eq 2 will fail if c is greater than unity. Many studies have used the Sips equation to fit sigmoid type V isotherms which require c to be greater than unity, as expounded by Inglezakis et al.[27] and Buttersack.[28] Sips imposed the restrictive condition on the exponent to avoid mathematical difficulties in his derivation work. Debord et al.[29,30] have extended the mathematical approach of Sips to cover cases where the exponent is greater than unity.

It should be pointed out here that, obviously, some authors have not read the original paper by Sips,[24] or even seen it, because they quote a title which is erroneous. Indeed, the article is entitled “On the structure of a catalyst surface” and not “Combined form of Langmuir and Freundlich equations” as one often sees![8–10,31–36] Additionally, the Sips equation is sometimes referred to as “the Langmuir–Freundlich equation”. This could be due to the fact that in the abstract of his second article[25] Sips writes about the equation he established and which now bears his name: “this simplest isotherm is a generalization of both the Freundlich and the Langmuir isotherms”.

2.1.3. Koble–Corrigan equation. Four years after the publication of the Sips equation (eq 2), Robert Koble and Thomas Corrigan published a paper in which they commented that the Sips equation was put forward without any derivation.[37] By assuming a dissociative chemical reaction mechanism, they derived a Sips-like isotherm equation with physically significant parameters. Their equation, in its original nomenclature, is given here by eq 4, where C_A is the adsorbed phase concentration, p_A is the gas pressure, L' is the total concentration of active sites, K' is an equilibrium constant, and n is an integer or a fraction as is implied by the dissociative adsorption assumption.

$$C_A = \frac{L'K'p_A^{\ n}}{1 + K'p_A^{\ n}} \tag{4}$$

2.1.4. Liu Equation. To describe the biosorption of metal ions by microbial aggregates, Yu Liu and colleagues proposed a biosorption model using a thermodynamic approach.[38] Their model is reproduced here as eq 5, where Q_e is the adsorbed phase concentration, Q_{th}^e is the biosorption capacity, C_e is the fluid phase concentration, ΔG^0 is the effective free energy change, R is the gas constant, T is the temperature, and α and β are positive constants.

$$Q_e = \frac{Q_{th}^e C_e^{\alpha/\beta}}{\left[\exp\left(\Delta G^0 / RT\right)\right]^{1/\beta} + C_e^{\alpha/\beta}} \tag{5}$$

A probabilistic interpretation of the preceding equation can be suggested as follows. According to Sips,[24] the global isotherm is the weighted mean of the many local isotherms. As described in a previous study (see eq 33 in Debord et al.[29]), the local isotherm can be written in the form $b/(b + x)$, where b is the binding constant (distributed), x is a function of C_e, K_d (the apparent dissociation constant, $K_d = \exp(\Delta G^0/RT)$), and some other parameters. The global isotherm can then be written as eq 6, where γ is the exponent of the Sips distribution (inversely related to the dispersion of the b values). By comparison with eq 5 we get $\gamma = 1/\beta$ and $x = C_e^{-\alpha}$, so the local isotherm becomes $b/(b + C_e^{-\alpha})$.

$$\frac{Q_e}{Q_{th}^e} = \frac{1}{1 + \left(K_d x\right)^{\gamma}} \tag{6}$$

Hence, for eq 5 the local isotherm is of the Sips type while for the other equations it is of the Langmuir type. So, there are two exponents: one from the Sips distribution ($1/\beta$) and one from the local isotherm (α). Unfortunately, they cannot be determined separately by nonlinear regression. Note that a similar situation occurs in the NICA model of two-component adsorption, but here the two exponents can be estimated separately.[39]

For data correlation, Liu et al.[38] reformulated eq 5 in the form of eq 7, where $K_{ads} = \left[\exp\left(\Delta G^0/RT\right)\right]^{1/\beta}$ and $n = \alpha/\beta$. Liu et al.[38] used eq 7 to fit their experimental data, but eq 5 was never used in their modeling work.

$$Q_e = \frac{Q_{th}^{e} C_e^{\,n}}{K_{ads} + C_e^{\,n}} \tag{7}$$

2.2. Current Forms. Equations 8–11 are the most common Hill, Sips, Koble–Corrigan, and Liu equations used in the current literature. The mathematical forms of eqs 8–11 have been consistently adopted by numerous investigators. In these equations, q is the adsorbed phase concentration, c is the fluid phase concentration (also used to denote the exponent in eqs 2 and 3), and the remaining symbols represent adjustable parameters.

$$\text{Hill: } q = \frac{q_m c^{n_H}}{K_H + c^{n_H}} \tag{8}$$

$$\text{Sips: } q = \frac{q_m b_S c^{n_S}}{1 + b_S c^{n_S}} \tag{9}$$

$$\text{Koble–Corrigan: } q = \frac{Q c^{n_K}}{1 + b_K c^{n_K}} \tag{10}$$

$$\text{Liu: } q = \frac{q_m \left(b_L c\right)^{n_L}}{1 + \left(b_L c\right)^{n_L}} \tag{11}$$

It is interesting to compare the original and modern forms of each of the four equations. The parameter K in the original Hill equation has been replaced by the parameter K_H in the modern version. The original and current forms of the Sips equation are essentially the same. The product $L'K'$ in the original Koble–Corrigan equation has been replaced by the parameter Q in the modern version. The Liu equation is an interesting case: its original version (eq 7) is similar to the modern Hill equation (eq 8), while its current version (eq 11) is similar to the modern Sips equation (eq 9) (the two equations have different b terms). In fact, the

Sips/Langmuir–Freundlich equation label is used to denote either eq 9 or 11 in the adsorption literature. The assignment of the Liu equation label to eq 11 is a relatively recent development.

3. RESULTS AND DISCUSSION

3.1. Empirical Data Fitting. Most of the isotherm models used to describe water contaminant adsorption have their origins in the gas adsorption literature, with the Langmuir isotherm being a classic example. The more than century-old Langmuir isotherm is an eminently elegant but highly idealized adsorption model.[40] It was originally derived to describe chemisorption of a pure gas on a nonporous, homogeneous surface. Most real-world adsorbents are however highly porous and energetically heterogeneous. Irving Langmuir, fully aware of the limitations of his namesake isotherm, said in his 1918 paper[41] that: "It must be remembered that the phenomena of adsorption by porous bodies are inherently very complex and that we should not expect them to be represented by a simple formula." In gas phase adsorption, the Langmuir isotherm empirically describes experimentally measured gas adsorption isotherms for many adsorption systems of practical interest.[42] It has been extensively used as the backbone for developing more sophisticated isotherm models that account for adsorbent heterogeneity, lateral interaction between adsorbed molecules, and multilayer adsorption.[40,42]

Likewise, the Langmuir isotherm is merely a convenient empirical expression used to trace the hyperbolic curves exhibited by liquid phase adsorption data. It cannot describe the impact of solution chemistry (e.g., pH and ionic strength) on the binding of inorganic aqueous solutes to solid surfaces, which is amenable to treatment by more phenomenologically relevant models (e.g., surface complexation models). The binding of organic aqueous contaminants to solid surfaces is often complicated by other phenomena such as oxidation reactions which lead to irreversible adsorption. For example, some phenolic compounds are known to adsorb on activated carbon surfaces irreversibly. Through a systematic sequence of experiments, Grant and King[43] showed that phenolic compounds can undergo oxidative coupling reactions on activated carbon surfaces and that these reactions produce polymeric products that are irreversibly adsorbed. Such oxidation reactions have been further confirmed by Cooney and Xi.[44] The Langmuir model can be used to fit the adsorption isotherms of phenolic compounds on activated carbons. Obviously, a good fit does not imply that the Langmuir model, which assumes reversible adsorption, has mechanistic relevance.

Like the Langmuir model, the four isotherms evaluated in this work lack proper theoretical relevance when applied to aqueous adsorption systems. In the context of the Hill equation (eq 1),[21] it was not devised to describe adsorption because there was no solid phase in the hemoglobin/oxygen system investigated by Hill. Consequently, there was no interphase mass transfer—a standard feature of adsorption processes. Also, nowhere in Hill's 1910 paper does the word "adsorption" appear. More importantly, Hill treated the two fitting parameters in eq 1, K and n, as purely empirical—useful for tracking sigmoid curve shapes. In the more recent literature of biological sciences, the exponent n is interpreted as an index of cooperative binding of ligands (usually small molecules) to macromolecules. It is unclear whether such a physical meaning, especially the notion of negative cooperative binding denoted by $n < 1$, can be extended to describe the binding of a diverse array of pollutants to solid adsorbents, many of which are natural materials with poorly characterized or even unknown surface properties. However, the probabilistic interpretation of the Hill equation can be extended to enzyme reactions, if we admit that the binding constant (or rate constant) is distributed among the many conformers of the enzyme.[45]

The Sips equation given by eq 2 has long been treated as an empirical isotherm in the adsorption literature. In his 1948 paper, Sips indicated that he knew of no case where eq 2 had represented any actual experimental data.[24] Nevertheless, the Sips equation is a practical isotherm model in gas adsorption research. It is extensively used to describe type I gas adsorption isotherms on energetically heterogeneous adsorbents. Its exponent is a temperature-dependent parameter used to account for different degrees of adsorbent heterogeneity for different adsorbates by the same adsorbent.[46]

Because Sips presented his equation without any derivation, Koble and Corrigan took it upon themselves to derive the Sips equation by assuming that gas adsorption on solids could be described by a dissociative chemical reaction mechanism.[37] They used a linear version of eq 4 to fit gas adsorption data, obtaining nonintegral values of n. According to the dissociative reaction mechanism, n should be an integer, or a fraction composed of small integers. The nonintegral values of n exposed the simplistic nature of the theoretical treatment of Koble and Corrigan. Therefore, eq 4 does not have a sound theoretical basis.

The Liu isotherm given by eq 5 seems to have a rigorous conceptual basis, since it was derived from thermodynamic considerations.[38] As noted earlier, it is not possible to fit eq 5 to experimental data to determine all its unknown parameters. Consequently, some of the parameters are lumped together in order to obtain the usable isotherm eq 7. Because the physical significance of the lumped parameters is unclear, the Liu isotherm is at best only partly theoretically sound. Furthermore, conformity to a particular isotherm does not necessarily mean that the theoretical basis of the isotherm is valid. In summary, we are of the view that the parameters of the Hill, Sips, Koble–Corrigan, and Liu equations lack rigorous physical significance and can thus be treated as empirical descriptors of adsorption data trends, although they can have a statistical significance with respect to energy distributions (this point will be taken up more fully in Section 3.6). Therefore, restraint is appropriate in attempts to draw mechanistic conclusions from agreement between any of the four isotherms and experimental observations. In the following sections, the macroscopic isotherms are evaluated against three previously published data sets from the angle of empirical data fitting.

3.2. Case 1: Comparison of Four Isotherms. This example is based on an experimental and modeling study reported by Podder and Majumder.[3] Arsenic(III) and arsenic(V) were removed from synthetic solutions by living bacterial cells immobilized on a solid support. The arsenic uptake process was attributed to biosorption and bioaccumulation. Figure 1 shows the fits of 19 isotherm equations, including the Hill, Sips, Koble–Corrigan, and Liu equations, to a data set of arsenic(V) adsorption. Note that the Liu equation is called the Langmuir–Freundlich equation in the work of Podder and Majumder.[3] Another 11 isotherm equations were also fitted to the arsenic(V) data (not shown in Figure 1). Therefore, the original authors[3] tested a total of 30 isotherms against a single data set. As can be seen in Figure 1, the equilibrium data exhibit a typical type I or favorable isotherm shape, manifesting a monotonic approach to an adsorption maximum. Figure 1 shows that such an isotherm shape can be well described by the 19 isotherms selected.[3] Figure 1 can be criticized in that it has no good purpose since it is impossible to deduce any useful information from the 19 homogeneous plots.

Although the fitted curves of the Hill, Sips, Koble–Corrigan, and Liu equations depicted in Figure 1 cannot be distinguished, their statistical metrics provide unambiguous information. The reported R^2 and RMSE values for the four isotherm fits are as follows: $R^2 = 0.9994$ (Hill, Sips, Liu), $R^2 = 0.9959$ (Koble–Corrigan), RMSE = 13.47 mg g^{-1} (Hill, Sips, Liu), RMSE = 34.57 mg g^{-1} (Koble–Corrigan). It is evident that the fit statistics for the Hill, Sips, and Liu equations are identical, while those for the Koble–Corrigan equation are clearly inferior. To verify the reported fit statistics, in this work, the four isotherms were fitted to the arsenic(V) data using the nonlinear regression procedure of GraphPad Prism 9.1.2. The resulting statistics for the four isotherm fits are identical (R^2 of 0.9994 and RMSE of 13.51 mg g^{-1}), contradicting the results of Podder and Majumder.[3] More will be said about these different findings in Section 3.5. The four fitted curves shown in Figure 2 speak for themselves—they are practically identical.

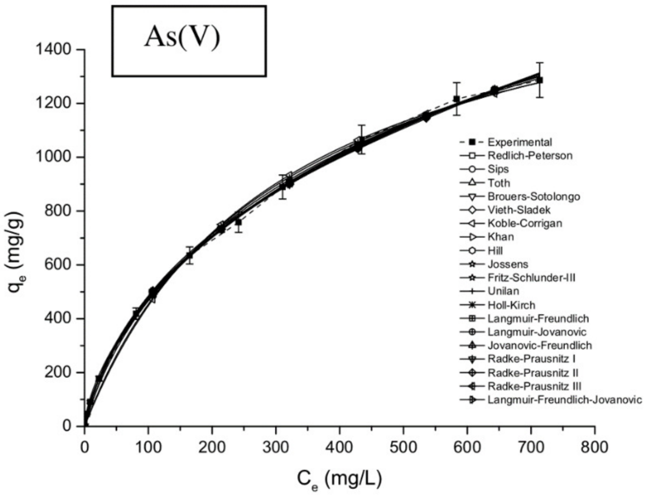

Figure 1. Comparison of isotherm fits and arsenic(V) adsorption data. Reproduced with permission (Podder and Majumder[3]). Copyright 2016, Elsevier.

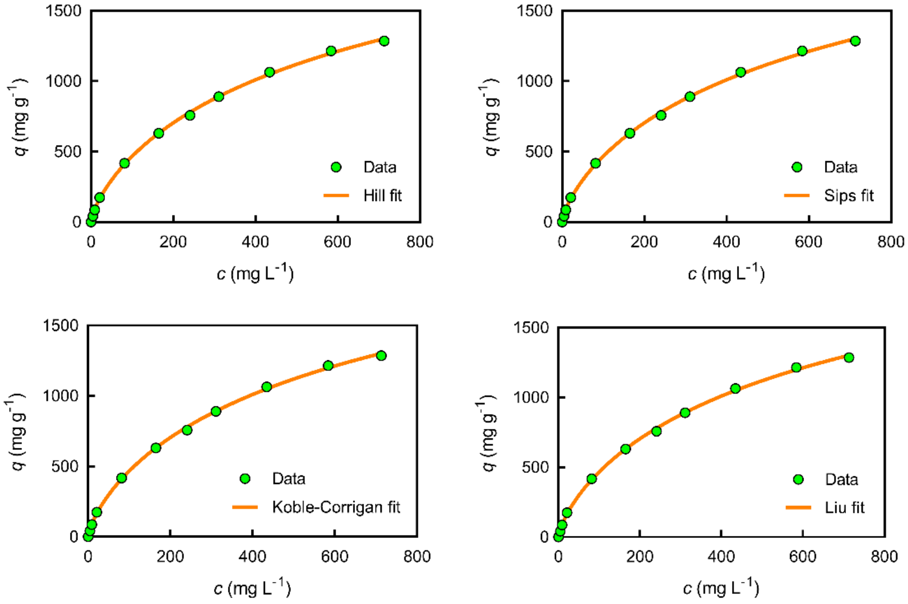

Figure 2. Comparison of isotherm fits and arsenic(V) adsorption data reported by Podder and Majumder.[3]

3.3. Case 2: Comparison of Three Isotherms. This case, taken from the work of Rostamian and Behnejad,[10] describes the adsorption of the antibiotic sulfamethoxazole by two carbon nanomaterials: a graphene nanosheet and a graphene oxide sheet. Seven isotherms (Langmuir, Freundlich, Toth, Redlich–Peterson, Hill, Sips, and Koble–Corrigan) were used to fit the sulfamethoxazole adsorption data measured at different temperatures. Only three of the four isotherms of interest (Hill, Sips, and Koble–Corrigan) were fitted to the sulfamethoxazole adsorption data in the original study.[10] A data set for sulfamethoxazole adsorption on graphene oxide sheet is reproduced in Figure 3, which shows the fits of the Sips, Redlich–Peterson, and Koble–Corrigan equations. Unfortunately, the Hill isotherm fit was not included in Figure 3. Nevertheless, one can see that the Koble–Corrigan equation manifests good agreement with the isotherm data, outperforming the Sips equation. It is worth pointing out that the shape of the experimental isotherm is sigmoid type V, which is somewhat uncommon for aqueous adsorption systems.

According to the R^2 scores given in the original paper[10] for the three isotherm fits, the descending order of the fit accuracy is the following: Koble–Corrigan (0.9962) > Sips (0.9726) > Hill (0.9155). An analogous order can also be observed in the reported RMSE values (mg L^{-1}): Koble–Corrigan (6.34) < Sips (32.56) < Hill (156.76). These statistical results, as reported by Rostamian and Behnejad,[10] indicate that the Koble–Corrigan equation was the best performing model, while the Hill equation was the least accurate. The statistical results of our nonlinear fits of the same isotherm data are, however, different from those of the original study. The R^2 and RMSE scores for the three isotherm fits are identical (R^2 of 0.9972 and RMSE of 2.24 mg g^{-1}). An inspection of Figure 4 will show that the sulfamethoxazole adsorption data are very well represented by the three isotherms. The three fitted curves are clearly sigmoid in shape and equivalent to each other. All three isotherms are capable of generating sigmoid curves when the corresponding exponent (n_H, n_S, n_K) is greater than unity. The Sips isotherm fit depicted in Figure 4 is superior to the Sips isotherm fit of the original study shown in Figure 3. It is our belief that the data fitting results reported by Rostamian and Behnejad[10] are flawed (we elaborate more on that in Section 3.5).

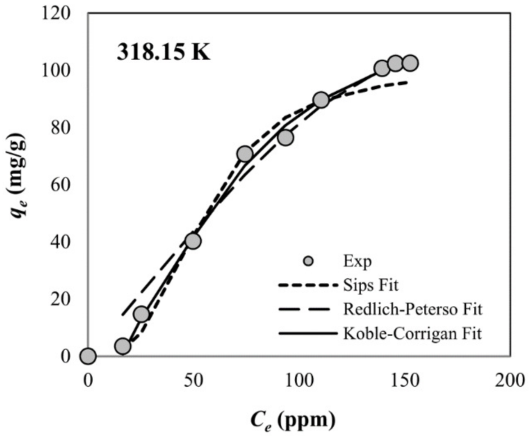

Figure 3. Comparison of isotherm fits and sulfamethoxazole adsorption data. Reproduced with permission (Rostamian and Behnejad[10]). Copyright 2016, Elsevier.

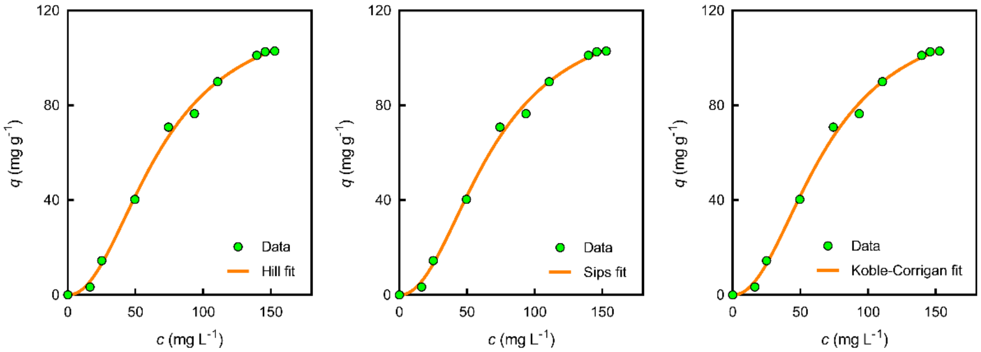

Figure 4. Comparison of isotherm fits and sulfamethoxazole adsorption data reported by Rostamian and Behnejad.[10]

3.4. Case 3: Comparison of Two Isotherms. The adsorption of three dyes by an activated carbon adsorbent has been studied by Vargas et al.[18] Ten isotherms (Langmuir, Freundlich, Temkin, Toth, Dubinin–Radushkevich, Brouers–Sotolongo, Radke–Prausnitz, Vieth–Sladek, Sips, and Koble–Corrigan) were fitted to the measured adsorption data. Of the 10 isotherms, the Sips and Koble–Corrigan fits are relevant for the present study. The original data fitting results[18] for one of the dyes, Acid Red 18, are shown in Figure 5. Hereafter the Sips fit is renamed the Liu fit because the mathematical form adopted by Vargas et al.[18] for their Sips equation corresponds to eq 11, which is our Liu equation. As can be seen in Figure 5, the measured isotherm for the red dye is type I with a highly favorable shape. In process modeling, such a highly favorable isotherm is often approximated by a rectangular model, which can simplify the mathematical treatment of mechanistic process models. Indeed, the Koble–Corrigan and Dubinin–Radushkevich fits depicted in Figure 5 are rectangular in shape. According to Vargas et al.,[18] the Koble–Corrigan isotherm fit with an R^2 value of 0.9778 outperformed the Liu isotherm fit with an R^2 score of 0.9217. The large difference in the reported R^2 values seems to be supported by the fitted curves calculated from the equations of Koble–Corrigan and Liu (designated by Sips in Figure 5), which look rather different, as can be seen in Figure 5. Our data fitting results dispute the findings of Vargas et al.[18] The fits of the Koble–Corrigan and Liu equations to the dye adsorption data are identical, as shown in Figure 6. Consequently, the two fits share the same R^2 value, which is 0.982. It is conceivable that the different R^2 scores reported by Vargas et al.[18] are erroneous (we discuss more on that in Section 3.5). Note that the two fits depicted in Figure 6 are essentially rectangular in shape.

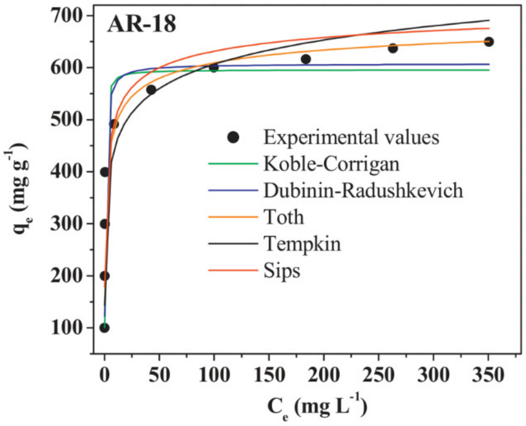

Figure 5. Comparison of isotherm fits and dye (Acid Red 18) adsorption data. Reproduced with permission (Vargas et al.[18]). Copyright 2012, Elsevier.

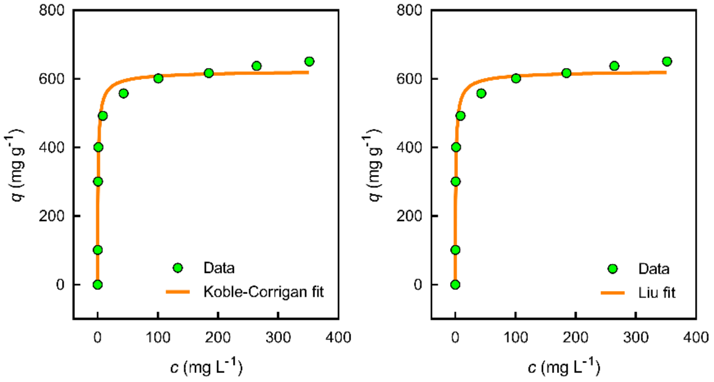

Figure 6. Comparison of isotherm fits and dye (Acid Red 18) adsorption data reported by Vargas et al.[18]

3.5. Mathematical Equivalence. Our data fitting results for cases 1–3 indicate that there is no difference in the performance of the Hill, Sips, Koble–Corrigan, and Liu equations. Fitting two or more of the four isotherms to a given data set will lead to the same goodness-of-fit statistics (R^2 or RMSE). Evidently, what in the literature has sometimes appeared as different fitting results from the four isotherms turns out, on re-evaluation, to have been due to errors in earlier work. Therefore, our results challenge the original findings of cases 1–3, that is, the four isotherms possess different data fitting abilities and it is possible to identify the most effective isotherm. It seems that this important finding of the present study is underreported or even ignored because it is incompatible with the widely accepted notion that the four isotherms are independent models. Case 1 is a pertinent example—the original study[3] reported the same statistical results for the Hill, Sips, and Liu isotherm fits (Section 3.2) but there was no discussion of this key finding. In fairness to the authors of the original study, we must hasten to say that it would probably be near impossible for them to pick out this fact (identical fit statistics) from several tables listing statistical results and parameter estimates for 30 isotherm fits.

We speculate that the original results for cases 1–3 are erroneous because the nonlinear regression methods used to fit the isotherm data are flawed. In case 1, nonlinear regression was conducted using the OriginPro 8.5.1 software. The original study of case 2 provides no information on the nonlinear regression method employed. In case 3, data fitting was performed using the nonlinear regression procedure of the Origin 6.0 software. Given that Origin software is widely used to fit data to nonlinear models, its misapplication in cases 1 and 3 is puzzling.

It is plausible that some of the suboptimal isotherm fits reported in previous studies could have been due to the use of inappropriate initial values of the isotherm parameters in the nonlinear regression procedure. Poorly selected starting values can lead a nonlinear regression software to never converge on a solution or more insidiously converge to a local minimum. Commercial regression software usually implements local optimizers which accept only decreases of the objective function. If the function has multiple minima, the algorithm may easily get stuck in one of the local ones instead of locating the desired global minimum. Indeed, when the GRG nonlinear algorithm of Excel Solver was used to determine three unknown parameters of a generalized Langmuir–Freundlich equation (equivalent to the Liu equation), the starting values had to be varied several times to find the best possible fit.[47] The problem of converging to an unwanted local minimum is intrinsic to nonlinear regression and is more likely to occur when the fitting algorithm has to determine multiple parameters. As noted above, this problem can be overcome by performing the regression analysis several times using different starting values for the isotherm parameters.[47] Heuristic global optimization methods, which do not require the user to supply sensible starting values, provide another way to alleviate the problem of local minima. Notable examples of such heuristic methods include genetic algorithm (e.g., Excel Solver's evolutionary algorithm), differential evolution, particle swarm optimization, ant colony optimization, and simulated annealing.

We contend that the only possible explanation for our data fitting results is that the Hill, Sips, Koble–Corrigan, and Liu equations are mathematically equivalent. To verify our claim, we propose a generic expression with three arbitrary fitting parameters (X, Y, Z), given here by eq 12, to represent the four isotherms. We shall call eq 12 the "XYZ isotherm", which is shamelessly modeled after the "ABC isotherm" of Zelinka et al.[48]

$$q = \frac{X}{1 + Yc^{-Z}} \tag{12}$$

After some algebraic manipulation, the unknown parameters of the four isotherms defined by eqs 8–11 are expressed in terms of the three arbitrary fitting parameters of eq 12. These parameter relations are summarized in Table 2. From these relations, one can calculate the undetermined parameters of eqs 8–11 if X, Y, and Z are known. The three arbitrary parameters can, of course, be estimated by fitting eq 12 to experimental data.

Table 2. Parameter Relations for the Hill, Sips, Koble–Corrigan, Liu, and XYZ Equations

isotherm	parameter relation
Hill	$X = q_m$; $Y = K_H$; $Z = n_H$
Sips	$X = q_m$; $Y = 1/b_S$; $Z = n_S$
Koble–Corrigan	$X = Q/b_K$; $Y = 1/b_K$; $Z = n_K$
Liu	$X = q_m$; $Y = b_L^{-n_L}$; $Z = n_L$

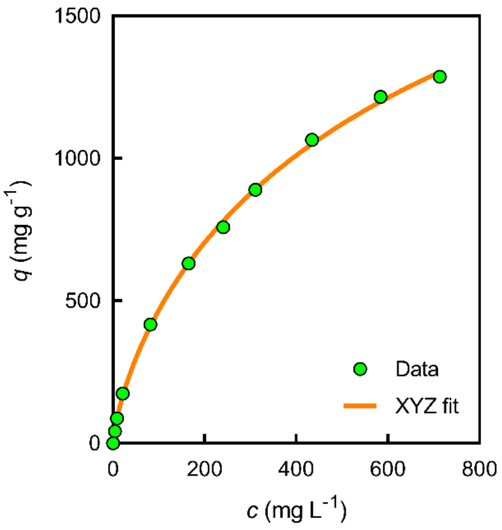

Figure 7. Comparison of XYZ equation fit and arsenic(V) adsorption data reported by Podder and Majumder.[3]

The XYZ equation given by eq 12 can be used to fit isotherm data in lieu of any of the four isotherms. To expand on this point, eq 12 was fitted to the arsenic(V) adsorption data depicted in Figure 1 by nonlinear regression. Figure 7 shows the fit of the XYZ equation (R^2 of 0.994 and RMSE of 13.51 mg g^{-1}). The resulting parameter estimates are $X = 2795$ mg g^{-1}, $Y = 156.3$ (mg $L^{-1})^Z$, and $Z = 0.748$. Next, plugging the fitted values of X, Y, and Z into the relations in Table 2 yields all the parameters of the four isotherms, and they are listed in column 2 of Table 3. We recall that in case 1 the four isotherms were fitted to the arsenic(V) adsorption data by nonlinear regression (fitted curves are presented in Figure 2). The resulting parameter estimates for the four isotherm fits are listed in column 3 of Table 3. It is immediately evident that the fitted isotherm parameters are identical to the corresponding isotherm parameters obtained from the XYZ equation. Also, the R^2 and RMSE scores for the four isotherm fits are identical to the R^2 and RMSE values for the XYZ equation fit (R^2 of 0.9994 and RMSE of 15.31 mg g^{-1} for all fits). So, a single fit of the XYZ equation is equivalent to four separate fits of the Hill, Sips, Koble–Corrigan, and Liu equations. This analysis proves that the four isotherms are mathematically equivalent to the XYZ equation and hence to each other. Because of this mathematical equivalence, the Hill, Sips, Koble–Corrigan, and Liu equations will give the same results when applied to a given set of isotherm data. It is therefore a fallacy to compare and rank the four isotherm equations.

Table 3. Comparison of Calculated and Fitted Values of Isotherm Parameters[a]

isotherm parameter	calculated value (XYZ equation)	fitted value (isotherm equation)
Hill		
q_m	2795	2795
K_H	156.3	156.3
n_H	0.748	0.748
Sips		
q_m	2795	2795
b_S	0.006	0.006
n_S	0.748	0.748
Koble–Corrigan		
Q	17.88	17.89
b_K	0.006	0.006
n_K	0.748	0.748
Liu		
q_m	2795	2795
b_L	0.001	0.001
n_L	0.748	0.748

[a] q_m: mg g^{-1}; K_H: mg L^{-1}; b_S: $\left(\text{L mg}^{-1}\right)^{n_S}$; Q: $\left(\text{mg g}^{-1}\right)\left(\text{L mg}^{-1}\right)^{n_K}$; b_K: $\left(\text{L mg}^{-1}\right)^{n_K}$; b_L: L mg^{-1}

Although the Hill equation and the Sips equation have been developed independently of each other, their mathematical equivalence has long been known to researchers working in the area of biological sciences. For instance, the 1975 paper of Rodbard and Feldman[49] points out that a linear version of the Hill equation used in enzymology is analogous to a linear version of the Sips equation used in immunology. This mathematical equivalence has also been discussed by researchers working in the field of adsorption,[39] and it does not require further exposition here.

It is unclear when the Koble–Corrigan equation label was first used in the literature of adsorptive water remediation. The emergence of this equation label is probably due to a misreading of the paper by Koble and Corrigan.[37] As discussed earlier, the intention of Koble and Corrigan was to provide a conceptual basis for the derivation of the Sips equation (associative adsorption mechanism). They quoted the Sips equation in their paper. The equation derived by them, eq 4, cannot be anything but the Sips equation. Most importantly, nowhere in their paper did Koble and Corrigan claim to have developed a new isotherm.

Likewise, the appearance of the Liu equation label is likely due to a misinterpretation of the work of Liu et al.[38] As stated above, the general model of biosorption (eq 5) proposed by Liu et al. was never used to fit isotherm data. Equation 7, a simplified version of eq 5, was instead used in all their modeling work. They specifically pointed out that eq 7 is equivalent to the Hill or Sips equation. It is straightforward to convert the current Liu equation, eq 11, to the original eq 7 used by Liu et al. It is therefore somewhat perplexing that eq 11 is referred to as the Liu equation in the current literature, implying that it is an independent isotherm distinct from the Hill or Sips equation. Equation 11 is usually called the Sips/Langmuir–Freundlich equation in the mainstream adsorption literature.

We reiterate that the Hill, Sips, Koble–Corrigan, and Liu equations are empirical modeling tools capable of describing hyperbolic isotherm data of aqueous adsorption systems. It makes no difference which of the four equations is used in data fitting since they are mathematically equivalent. In fact, hyperbolic type I isotherm data are well described by simple isotherm models with two free parameters (Langmuir and Freundlich). From a curve-fitting perspective, using any one of the four isotherms with three free parameters to fit such simple curve shapes is essentially overkill.

3.6. Energy Distribution. As alluded to earlier, the parameters of the four isotherms can have a statistical significance with respect to energy distributions. A brief discussion of this topic is certainly appropriate. To compute the energy distribution for any one of the four isotherms, we need the mean dissociation constant K_d and the exponent γ of eq 6. By comparison with eq 12 we get $K_d = Y^{1/Z}$ and $\gamma = Z$.

From K_d we calculate the mean adsorption free energy using eq 13, where K_d is expressed in mol L^{-1} (in agreement with the standard concentration $C^0 = 1$ mol L^{-1}), R is the gas constant, and T is the absolute temperature.

$$E_0 = RT \ln K_d \tag{13}$$

To facilitate the computation, we define the nondimensional variable ε, as shown in eq 14, where E is the adsorption free energy.

$$\varepsilon = \frac{E - E_0}{RT} \tag{14}$$

According to a previous study,[29,30] the probability density function (p.d.f.) of the random variable ε is given by eq 15, where $\phi^* = \pi\ \mathrm{frac}(\gamma)$ and cosh denotes the hyperbolic cosine: $\cosh x = \left[\exp(x) + \exp(-x)\right]/2$.

$$f_\varepsilon(\varepsilon) = \frac{\gamma \sin\phi^*}{\phi^*} \frac{\exp(\gamma\varepsilon)}{1 + 2\exp(\gamma\varepsilon)\cos\phi^* + \exp(2\gamma\varepsilon)} = \frac{\gamma \sin\phi^*}{2\phi^*} \frac{1}{\cosh(\gamma\varepsilon) + \cos\phi^*} \tag{15}$$

From eq 15 we get the p.d.f. of the random variable E by equating the probabilities:

$$f_E(E)\,dE = f_\varepsilon(\varepsilon)\,d\varepsilon \tag{16}$$

Hence:

$$f_E(E) = f_\varepsilon(\varepsilon)\frac{d\varepsilon}{dE} = \frac{f_\varepsilon(\varepsilon)}{RT} \tag{17}$$

For example, with the arsenic(V) case study[3] and a molar mass of 140.43 g mol^{-1} (mean of $\mathrm{H_2AsO_4^-}$ and $\mathrm{HAsO_4^{2-}}$ that are the two As(V) species present in equivalent amounts at pH = 7.0), $K_d = K_H^{1/n_H}$ = 857.24 mg L^{-1} = 6.104 × 10^{-3} mol L^{-1}, and T = 303.15 K, we obtain E_0 = –

12.85 kJ mol^{-1} and the curve plotted in Figure 8. In the same figure we have plotted the two approximations discussed in the work of Debord et al.:[29]

- The Gaussian distribution having the same interquartile range (corresponding here to a standard deviation of 2.85 kJ mol^{-1}).
- The logistic distribution having the same exponent (here $\gamma = 0.748$). This corresponds to the "condensation approximation".

In agreement with the work of Debord et al.[29] (see their Figure 6), for this value of the exponent, Figure 8 shows that the Gaussian distribution gives the best approximation.

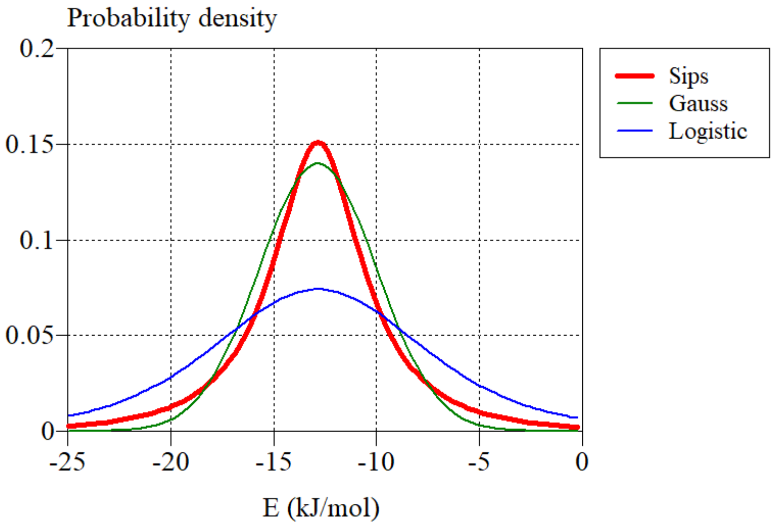

Figure 8. Plot of the energy distribution for the arsenic(V) example reported by Podder and Majumder,[3] showing the Sips distribution (red) and its approximations by a Gaussian distribution (green) or a logistic distribution (blue).

4. CONCLUSIONS

In the literature of adsorptive water decontamination, the equations of Hill, Sips, Koble–Corrigan, and Liu have long been regarded as having distinct data fitting abilities. Several review articles have repeatedly promulgated this notion by listing and discussing the four isotherms separately. This work has shown that the four isotherms are in fact mathematically equivalent and can be represented by a single generic expression, termed the XYZ equation. As such, the four isotherms and the XYZ equation will produce exactly the same fit to a given set of isotherm data. Because the XYZ equation is not, by any stretch of imagination, a new adsorption isotherm, it should not be used to fit experimental data of any kind.

Many previous studies have reported differences in the data fitting performance of the four isotherms. These differences are most likely due to the improper application of nonlinear regression in data fitting. Because meaningful results cannot be obtained by comparing the relative performance of the four isotherm equations, we recommend that only one of them be used to fit experimentally measured isotherms. We urge researchers to discard the widely held belief that the Hill, Sips, Koble–Corrigan, and Liu isotherm equations can be treated separately in data fitting. It is a fairy tale.

Notes

The authors declare no competing financial interest.

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