Surfactant Adsorption Isotherms: A Review
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ABSTRACT: The need to minimize surfactant adsorption on rock surfaces has been a challenge for surfactant-based, chemical-enhanced oil recovery (cEOR) techniques. Modeling of adsorption experimental data is very useful in estimating the extent of adsorption and, hence, optimizing the process. This paper presents a mini-review of surfactant adsorption isotherms, focusing on theories of adsorption and the most frequently used adsorption isotherm models. Two-step and four-region adsorption theories are well-known, with the former representing adsorption in two steps, while the latter distinguishes four regions in the adsorption isotherm. Langmuir and Freundlich are two-parameter adsorption isotherms that are widely used in cEOR studies. The Langmuir isotherm is applied to monolayer adsorption on homogeneous sites, whereas the Freundlich isotherm suites are applied to multilayer adsorption on heterogeneous sites. Some more complex adsorption isotherms are also discussed in this paper, such as Redlich−Peterson and Sips isotherms, both involve three parameters. This paper will help select and apply a suitable adsorption isotherm to experimental data.

1. INTRODUCTION

Surfactants have been widely used in the petroleum industry for various operations, such as drilling, demulsification, hydraulic fracturing, and chemical-enhanced oil recovery (cEOR).4 cEOR involves adding surfactants, polymers, alkalis, or combinations of these chemicals to water during reservoir water flooding operations. A crucial factor in the efficiency of surfactant-based flooding techniques is surfactant adsorption on rocks.2 Adsorption, which is the accumulation of molecular species on a solid surface, is considered a distinct area within the physical sciences due to the involvement of multidisciplinary work between chemistry, physics, and engineering.

The primary mechanism of surfactant adsorption on rocks is electrostatic attraction. An example is illustrated in Figure 1, where a cationic surfactant (positive charge on the headgroup) is attracted toward the negative charges on the rock surface, leading to the surfactant adsorption. In the case of anionic surfactants (negative charge on the headgroup), electrostatic attraction may take place with the positively charged clay edges present in the rock. Hydrogen bonding is the primary adsorption mechanism of nonionic surfactants (no charge on the headgroup), which are usually used as cosolvents in cEOR.

Aggregates of surfactant can be in the form of hemimicelles, admicelles, and micelles, as shown in Figure 2.3 Hemimicelles are monolayers in which surfactants’ headgroups are oriented toward the surface and are formed when the surfactant concentration exceeds critical hemimicelle concentration (HMC). Admicelles originate from adsorbed micelles developed on the surface and show a bilayered structure. Micelles are...
surfactant adsorption on rocks.2

The extent of surfactant adsorption is analyzed using an adsorption isotherm, which describes an equilibrium function between the fluid concentration and the amount of adsorbed substance at constant temperature. An adsorption isotherm reveals information related to the adsorption mechanism and the interactions between the adsorbent and the adsorbate. A series of static adsorption experiments can be conducted on the liquid–solid interface for several surfactant concentrations to construct the adsorption isotherm that can be modeled mathematically. The simplest adsorption isotherm is the Henry model, in which the adsorbed amount is proportional to the adsorbate’s bulk concentration (linear relationship). This model typically describes adsorption at lower concentrations where adsorption is described as the Henry regime. Langmuir, however, was the first to introduce a clear idea of homogeneous monolayer adsorption.4,5 There are several other adsorption isotherms reported in the literature and utilized to fit data from static adsorption tests, such as Freundlich, Redlich–Peterson, Sips, Temkin, etc. These adsorption models are discussed in a subsequent section.

The shape of the adsorption isotherm can be classified into three categories: L-shape (Langmuir), S-shape (S-type), and LS-shape (double plateau), as shown in Figure 3. The L-shape curve is a common adsorption isotherm for dilute solutions on a solid/liquid interface and can be described by the monomolecular adsorption equation presented by Langmuir. The S-shape curve displays a small slope in the beginning followed by a sharp rise, whereas the LS-shape curve shows double plateaus.

Numerous adsorption studies have been conducted in the past, including surfactant adsorption, environmental remediation, etc. Kalam et al. recently published a comprehensive review on surfactant retention,7 which focuses mainly on strategies to minimize surfactant retention. Also reviewed are the mechanisms and measurement techniques of surfactant retention. Wang and Guo recently published a review showing the classification of adsorption isotherm models, their physical significance, application, and solving procedure,7 whereas Paria and Khilar reviewed experimental studies of surfactant adsorption,8 focusing on kinetics and equilibrium studies of several surfactants. Swenson and Stadie presented a centennial review of the adsorption theory proposed by Langmuir.9 Saadi et al. reviewed adsorption isotherm models for monolayer and multilayer processes for sorption from aqueous media.10 Ayawei et al. presented a review related to modeling and interpretation of adsorption isotherms.11 Linear and nonlinear regression analysis along with error function were also discussed in that paper. While most published articles reviewed adsorption studies, in general, in surfactant adsorption studies, researchers may need a quick guide to fit adsorption isotherm models on their experimental data set. An appropriate fit of the surfactant adsorption isotherm is important to understand its mechanism. This article presents a quick review specific to surfactant adsorption isotherms, showing basic theories of surfactant adsorption and the most frequently used surfactant adsorption models.

The review will help researchers quickly understand the surfactant adsorption models and underlying mechanisms to fit adsorption experimental data. Toward this end, the review is structured as follows: Section 2 discusses theories related to the surfactant adsorption isotherm; section 3 summarizes published surfactant adsorption isotherms, and section 4 concludes the review.

2. THEORIES OF ADSORPTION ISOTHERM

Two well-known theories that describe the mechanism behind adsorption isotherms are (1) the two-step theory and (2) the
four-region theory. Those theories are discussed in the following subsections.

2.1. The Two-Step Theory. Gu and Zhu introduced two models (one-step and two-step) for L-type, S-type, and LS-type adsorption isotherms; both models consider adsorption as a reaction between surfactant molecules and unoccupied surface sites.\(^6,12\) In the one-step model, hemimicelles are formed by the interaction between a surfactant monomer and an active site.\(^6\) The one-step model was originally developed for adsorption of nonionic surfactants on silica gel exhibiting the S-type curve. The general mathematical form of the one-step model was developed using mass-action law, as shown in eq 1:

\[
\Gamma = \frac{\Gamma_0 C^n}{1 + k C^n} \tag{1}
\]

where \(\Gamma\) is the adsorption density, \(\Gamma_0\) is the adsorption density (maximum) at high concentration, \(n\) shows the aggregation number of surfactant, and \(k\) is the equilibrium constant.

The two-step model is the amended form of the one-step model in which adsorption takes place in two steps.\(^6\) First, surfactant monomers are adsorbed on the solid surface at a concentration less than the critical aggregation concentration (CAC) through electrostatic interaction. Aggregates are not formed in the first step. Mathematically, it is shown in eq 2:

\[
\Gamma_1 = k_1 \Gamma C \tag{2}
\]

where \(\Gamma_1\) is the amount of adsorbed monomers, \(k_1\) is the equilibrium constant of the first step, \(\Gamma\) shows the number of sites, and \(C\) is the concentration of surfactant monomers.

In the second step, adsorption rises considerably due to the formation of hemimicelles through association or hydrophobic interaction. Mathematically, we can express this process in eq 3:

\[
\Gamma_{hm} = k_2 \Gamma_1 C^{n-1} \tag{3}
\]

where \(\Gamma_{hm}\) is the amount of hemimicelle, \(k_2\) is the equilibrium constant of the second step, and \(n\) is the aggregation number of the hemimicelle.

The general mathematical form of the adsorption isotherm was derived based on the mass action treatment and the two-step model.\(^6\) Eqs 2, 3, and the following two supplementary eqs 4 and 5 were used in the derivation of the general adsorption isotherm equation.

\[
\Gamma = \Gamma_1 + n \Gamma_{hm} \tag{4}
\]

and

\[
\Gamma_\infty = n (\Gamma_1 + \Gamma_{hm}) \tag{5}
\]

where \(\Gamma\) is the adsorbed surfactant quantity at concentration \(C\), and \(\Gamma_\infty\) is the limiting adsorption at high concentrations of surfactant. Both \(\Gamma\) and \(\Gamma_\infty\) can be obtained from surfactant adsorption experiments.

Putting eqs 2 and 3 into eq 4, we get

\[
\Gamma = k_1 \Gamma C + n k_2 \Gamma_1 C^{n-1} \tag{6}
\]

\[
\Gamma = k_1 \Gamma C + n k_2 (k_1 \Gamma C) C^{n-1} \tag{7}
\]

Putting eqs 2 and 3 into eq 5, we get

\[
\Gamma_\infty = n \Gamma_1 + n k_1 \Gamma C + n k_2 \Gamma_2 C^n \tag{8}
\]

Dividing eq 7 by eq 8, we get

\[
\frac{\Gamma}{\Gamma_\infty} = \frac{k_1 \Gamma C + n k_2 (k_1 \Gamma C) C^{n-1}}{n \Gamma_1 + n k_1 \Gamma C + n k_2 \Gamma_2 C^n} \tag{9}
\]

\[
\frac{\Gamma}{\Gamma_\infty} = \frac{\Gamma_0 C^n (1 + k_2 C^{n-1})}{n (1 + k C + k_2 C^n)} \tag{10}
\]

\[
\frac{\Gamma}{\Gamma_\infty} = \frac{\Gamma_0 k_1 C^{n-1} + k_2 C^{n-1}}{1 + k_2 C (1 + k C^n)} \tag{11}
\]

Equation 11 is the general adsorption isotherm equation and can be converted into L-shape, S-shape, and LS-shape curves by substituting \(k_1, k_2, n\) with suitable values. When \(k_2 \to 0\) and \(n \to 1\), it reduces to Langmuir’s L-shape model (eq 12).

\[
\Gamma = \frac{\Gamma_0 k_1 C}{1 + k_2 C} \tag{12}
\]

If \(n > 1\), eq 11 has two possibilities: (a) when \(k_1 C^{n-1} \ll \frac{1}{n}\), it reduces to eq 13, the L-shape equation in which \(\Gamma_\infty/n\) is the monomolecular adsorption instead of \(\Gamma_\infty\); (b) when \(k_1 C^{n-1} \gg \frac{1}{n}\) or \(k_2 C \ll 1\) and \(k C \ll k_2 C^n\), eq 11 reduces to eq 14, representing the S-shape curve.

\[
\Gamma = \frac{(\Gamma_0/n) k_1 C}{1 + k_2 C} \tag{13}
\]

\[
\Gamma = \frac{\Gamma_0 C^n}{1 + k C^n} \tag{14}
\]

where \(k = k_1 k_2\).

If the concentration is high \((k_2 C \gg 1)\), eq 11 will convert to eq 15, showing the LS-shape curve.

\[
\Gamma = \frac{\Gamma_0 (\frac{1}{n} + k_2 C^{n-1})}{1 + k_2 C^{n-1}} \tag{15}
\]

When the surfactant concentration keeps increasing, eq 11 reduces to eq 16, indicating that hemimicelles occupy all adsorption sites.

\[
\Gamma = \Gamma_\infty \tag{16}
\]

2.2. The Four-Region Theory. The Somasundaran–Fuerstenau isotherm is the most common form of the adsorption isotherm developed for adsorption of ionic surfactant on sites containing opposite charges.\(^{13}\) In situ fluorescence, Raman, and electron spin resonance (ESR) studies have supported this theory.\(^{14}\) When plotted on a log–log scale, the adsorption isotherm is distributed into four distinct regions, as shown in Figure 4. The chemistry behind each region is described below.

Region I usually obeys Henry’s law and is applicable to low adsorption densities. The electrostatic force of attraction between the charged surface and surfactant ions is responsible for adsorption in this region. Surfactants are adsorbed as monomers and do not react with each other. The slope is unity, keeping ionic strength conditions constant.

Region II features a sharp increase in adsorption density. Because of the lateral interactions between hydrocarbon chains, the formation of aggregates starts in this region in the form of hemimicelles, admicelles, etc. Therefore, the driving forces in this region are electrostatic attraction and lateral associations,
resulting in a dramatic rise in the slope of the isotherm. The transition between regions I and II are linked with HMC.

Region III shows a decline in the isotherm’s slope as adsorption transitions from region II to region III. In this region, electrostatic forces are not operative because of the neutralization of the solid surface by adsorption of surfactant ions. Therefore, the driving force in this region is lateral attraction only, resulting in the reduced slope of the adsorption isotherm.

Region IV is the plateau region of adsorption. When the surfactant concentration is equal to or above the CMC, micelles are formed and the adsorption density does not vary further. The activity of the surfactant monomer becomes constant, and the main driving force behind adsorption is the lateral hydrophobic interaction between hydrocarbon chains. Region IV usually starts above the CMC.

3. ADSORPTION ISOTHERMS

The well-known adsorption isotherms along with some latest developments are discussed in this section.

3.1. Henry’s Isotherm. It is a one-parameter model and the most basic adsorption isotherm. It proposes a linear relationship between the adsorbed amount and the adsorbate’s bulk concentration, as presented by eq 17.

\[ q_e = \frac{q_o K_e C_e}{1 + K_e C_e} \]  
(17)

where \( q_e \) is the adsorbed amount at equilibrium in mg/g, \( K_e \) is Henry’s adsorption constant in L/mg, and \( C_e \) is the adsorbate’s equilibrium concentration in mg/L.

A plot of \( q_e \) versus \( C_e \) produces a straight line, with a slope equal to \( K_e \).

Henry’s model can be used when the coverage ratio of the adsorption sites is minimal. It approximates the data trend only at low solute concentrations. Hence, it shows monolayer adsorption at initially low adsorbate concentrations. An example of Henry’s model can be seen in region 1 of Figure 4. This simplest model is invalid at the high concentrations of surfactant.

3.2. Langmuir Isotherm. The Langmuir isotherm was initially developed for gas–solid interaction but is also used for various adsorbents.\(^1\) It is an empirical model based on kinetic principles; that is, the surface rates of adsorption and desorption are equal with zero accumulation at equilibrium conditions.\(^5\) Based on the following assumptions, (a) monolayer adsorption, (b) homogeneous sites, (c) constant adsorption energy, and (d) no lateral interaction between the adsorbed molecules, the Langmuir isotherm can be written as

\[ q_e = \frac{q_o K_e C_e}{1 + K_e C_e} \]  
(18)

where \( q_o \) is the maximum amount of adsorbed surfactant in mg/g and \( K_e \) is the Langmuir constant in L/mg. The linearized version of eq 19 is

\[ \frac{C_e}{q_e} = \frac{1}{K_e q_o} + \frac{C_e}{q_o} \]  
(19)

A plot between \( C_e/q_e \) versus \( C_e \) will generate a straight line with a slope of \( 1/q_o \) and an intercept equals to \( 1/K_e q_o \)\(^8\).

The monolayer assumption requires identical adsorption sites, and only one molecule can be adsorbed at each site. There is no more adsorption in a site once a surfactant molecule has occupied it. This model converts to Henry’s model at very low concentrations (\( K_e C_e \ll 1 \)). The L-shape curve in Figure 3 shows the Langmuir isotherm model having a single plateau.

An important parameter related to the Langmuir model is the separation factor or equilibrium parameter, denoted as \( R_L \), which is used to check if surfactant adsorption is favorable or unfavorable.\(^18\) Mathematically, it can be shown as

\[ R_L = \frac{1}{1 + K_e C_o} \]  
(20)

where \( K_e \) and \( C_o \) are the Langmuir constant and highest initial concentration of surfactant, respectively.

In general, \( R_L < 1 \) indicates that adsorption is favorable; \( R_L \approx 0 \) indicates that adsorption is irreversible; \( R_L = 1 \) indicates that the adsorption isotherm is linear, and \( R_L > 1 \) corresponds to unfavorable adsorption.

3.3. Freundlich Isotherm. Unlike the Langmuir isotherm, this empirical model can be used for multilayer adsorption on heterogeneous sites. It assumes that the adsorption heat distribution and affinities toward the heterogeneous surface are nonuniform.\(^19\) The mathematical model can be shown as

\[ q_e = b C_e^{1/n} \]  
(21)

where \( b \) is the adsorption capacity in L/mg and \( 1/n \) is the adsorption intensity or surface heterogeneity. When \( 0 < 1/n < 1 \), adsorption is considered favorable. Unfavorable adsorption occurs when \( 1/n > 1 \) and is irreversible at \( 1/n = 1 \).

The linearized form can be written as

\[ \ln q_e = \ln b + \frac{1}{n} \ln C_e \]  
(22)

A plot of \( \ln q_e \) versus \( \ln C_e \) produces a straight line with a slope = \( 1/n \) and intercept = \( \ln b \).

The linearized form is easy and straightforward. On the other hand, the linearization process generates propagating errors, which results in erroneous predictions of parameters. Therefore,
the use of nonlinear regression to solve the nonlinear Freundlich model is recommended for the calculation of the model parameters.7

The Freundlich isotherm describes multilayer adsorption and assumes exponential decay in the energy distribution of adsorbed sites. However, it is not valid for a large range of adsorption data.20

3.4. Temkin Isotherm. The Temkin model, which presumes a multilayer adsorption process, considers interactions between the adsorbent and the adsorbate,21 but it ignores very small and very large concentration values.19 The nonlinearized form of the Temkin isotherm is expressed by

\[ q_e = \frac{RT}{b} \ln(K_mC_e) \]  

(23)

where \( R \) is the universal gas constant in J/(mol K), \( T \) is the temperature in K, \( b \) is the Temkin constant related to sorption heat in J/mol, and \( K_m \) is the Temkin isotherm constant in L/g.

The linearized form can be written as

\[ q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln K_m \]  

(24)

Plotting \( q_e \) versus \( \ln C_e \) will produce a straight line with slope \( = \frac{RT}{b} \) and intercept \( = \frac{RT}{b} \ln K_m \).

As the surface coverage increases, the Temkin model assumes that the heat of adsorption of all molecules in the layer reduces linearly instead of logarithmically.

3.5. Elovich Isotherm. The Elovich adsorption isotherm is based on kinetic principles and considers multilayer adsorption. It postulates that adsorption sites increase exponentially with the adsorption. Mathematically, it is expressed as

\[ \frac{q_e}{q_o} = KeCe e^{-\frac{q_e}{Ko}} \]  

(25)

where \( K_e \) is the Elovich constant.

The linearized form can be written as

\[ \ln \frac{q_e}{C_e} = \ln K_oq_o - \frac{q_e}{q_o} \]  

(26)

A plot of \( \ln \frac{q_e}{C_e} \) versus \( q_e \) yields a straight line with slope \( = -1/q_o \) and intercept \( = \ln K_oq_o \).

3.6. Redlich–Peterson Isotherm. This three-parameter adsorption isotherm possesses the characteristics of both the Langmuir and the Freundlich isotherms and so does not exhibit ideal monolayer adsorption behavior.23 Being a hybrid version, the Redlich–Peterson isotherm can be used in both homogeneous and heterogeneous systems. The mathematical form of the model is given by eq 27.

\[ q_e = \frac{K_CE_e}{1 + \alpha C_e^\beta} \]  

(27)

where \( K \) is the Redlich–Peterson isotherm constant in L/g, \( \alpha \) is a constant in L/mg, and \( \beta \) is an exponent that ranges between 0 and 1. At low concentrations (\( \beta \sim 1 \)), the model approaches the Langmuir isotherm, and at high concentrations (\( \beta \sim 0 \)), it approaches the Freundlich isotherm.

The linear form of the Redlich–Peterson isotherm is expressed as

\[ \ln \frac{C_e}{q_e} = \beta \ln C_e - \ln K_r \]  

(28)

A plot of \( \ln \frac{C_e}{q_e} \) versus \( C_e \) will provide \( \beta \) and \( K_r \) from the slope and intercept, respectively.

3.7. Sips Isotherm. Sips suggested an equation that combines the Freundlich and Langmuir isotherms after

### Table 1. Summary of Adsorption Isotherms

| S no. | Adsorption isotherm | Number of parameters | Ordinate | Abscissa | slope | Intercept | Summary | Ref. |
|-------|---------------------|----------------------|----------|----------|-------|-----------|---------|------|
| 1     | Henry               | 1                    | \( q_e \) | \( C_e \) | \( K_{HE} \) |          |          |        |      |
| 2     | Langmuir           | 2                    | \( C_e/q_e \) | \( C_e \) | \( 1/q_e \) | \( \frac{1}{K_m} \) |          | Langmuir, 1916 |
| 3     | Freundlich         | 2                    | \( \ln q_e \) | \( \ln C_e \) | \( 1/n \) | \( \ln b \) | suitable for heterogeneous surfaces | Foo and Hameed, 2010 |
| 4     | Temkin             | 2                    | \( q_e \) | \( \ln C_e \) | \( \frac{RT}{b} \) | \( \frac{RT}{b} \ln K_m \) | with increase in surface coverage, the heat of adsorption of all molecules in the layer decreases linearly instead of logarithmically |Foo and Hameed, 2010 |
| 5     | Elovich            | 2                    | \( \ln \frac{q_e}{C_e} \) | \( q_e \) | \( -1/q_o \) | \( \ln K_oq_o \) | based on kinetic principles and considers multilayer adsorption | Elovich and Larinov, 1962 |
| 6     | Redlich–Peterson   | 3                    | \( \ln \frac{C_e}{q_e} \) | \( \ln C_e \) | \( \beta \) | \( K_r \) | is a hybrid model, i.e., can be applied to homogeneous and heterogeneous systems | Saadi et al., 2015, Al-Ghouti and Da’ana, 2010 |
| 7     | Sips               | 3                    | \( \beta \ln C_e \) | \( \ln \frac{1}{q_o} \) | \( k_i \) | \( \ln \alpha_i \) | overcomes limitations associated with the increased concentrations of the adsorbate in Freundlich model | Belhaj et al., 2021 |

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recognizing the issue of a continual rise in the adsorbed quantity with an increase in concentration in the Freundlich equation. This results in an equation that shows a finite limit at high concentration.\(^{20}\) The Sips model is the most appropriate, three-parametric isotherm used for monolayer adsorption of surfactant. It can be used for heterogeneous systems and is valid for localized adsorption without adsorbate–adsorbate interactions.\(^{20}\) The mathematical form is

\[
q_s = \frac{k_s C^\beta_s}{1 + \alpha_s C_e^\beta}
\]

(\(29\))

where \(\beta_s\) is a model exponent and \(\alpha_s\) and \(k_s\) are model constants in L/mg and L/g, respectively. The linearized version of the isotherm is given by

\[
\beta_s \ln C_e = -\ln \left(\frac{k_s}{q_s}\right) + \ln \alpha_s
\]

(\(30\))

A plot between \(\beta_s \ln C_e\) versus \(\frac{1}{q_s}\) will yield \(k_s\) and \(\alpha_s\) from the slope and intercept, respectively, which allows determination of \(k_s\) and \(\alpha_s\).\(^{19}\)

The Sips model does not follow Henry’s law at low concentrations of adsorbate because it approaches the Freundlich isotherm. On the other hand, it shows the monolayer adsorption behavior of the Langmuir model at a high concentration. The parameters of the model are controlled by temperature, pH, and change in concentration.

Some most applied surfactant adsorption isotherms have been discussed in this section. With a single parameter, the most basic isotherm is Henry’s model, applicable at low surfactant concentrations only. Monolayer adsorption on homogeneous sites and multilayer adsorption on heterogeneous sites can be modeled using Langmuir and Freundlich adsorption, respectively. Both adsorption isotherms involve two parameters. The Temkin adsorption isotherm is also a two-parametric model, which presumes multilayer adsorption. The Elovich model is based on kinetic principles and assumes that adsorption sites increase exponentially with adsorption, representing multilayer adsorption. With three parameters, Redlich–Peterson and Sips adsorption isotherms are the hybrid form of the Langmuir and Freundlich models. Both models can be applied for homogeneous or heterogeneous adsorption processes. In general, all of the adsorption models should be applied and tested on the surfactant adsorption data set to find the best fit model and the corresponding adsorption mechanism. Nonlinear regression should be applied to estimate parameters of the adsorption isotherms more accurately. A summary of the adsorption isotherm models discussed in this section is presented in Table 1.

### 4. CONCLUSIONS

Curve fitting of the experimental adsorption data with the appropriate adsorption isotherm model is essential to understand the adsorption mechanism in a system and predict its behavior. Henry’s isotherm is a linear model, contains one parameter, and is only applicable at low concentrations. Langmuir and Freundlich’s isotherms are the most commonly used two-parameter models. The Langmuir isotherm is applicable for monolayer adsorption on a homogeneous site, whereas Freundlich is valid for multilayer adsorption on heterogeneous sites. Redlich–Peterson and Sips models are more complex, contain three parameters, and were developed using Langmuir and the Freundlich isotherms. Therefore, appropriate models can be selected considering the system’s level of complexity.

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**Notes**

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