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A generalized Langmuirian approach in adsorption kinetic modeling

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ABSTRACT

Liquid-phase adsorption kinetic models used in the literature include a limited number of equations, the most frequently used being those of the pseudo first-and pseudo-second order. The applicability of these two equations is discussed by researchers, which can be deduced from the Langmuir kinetic equation under specific experimental conditions. This conclusion is confirmed in this work for the pseudo-first-order model. The assumptions under which the equation is valid, i.e. single-site adsorption, are determined, whereas the pseudo-second-order-kinetic equation is deduced from the Langmuir dual-site adsorption model and the respective equation. A calculation procedure based on those models is proposed for the kinetic modeling of adsorption. The main characteristic is that the modeling procedure makes use of the Langmuir theory of adsorption and the corresponding equilibrium and kinetic equations. The only restriction is that the adsorption mechanism of the adsorbent–adsorbate system under consideration must follow the Langmuir theoretical model.

Keywords: Adsorption modeling; Kinetic equations; Langmuir model

1. Introduction

Liquid phase-adsorption continues to attract the attention of the research community in view of the large number of applications that are involved with major emphasis on pollutants' removal from water and waste water [1]. A variety of adsorbents, including activated carbon, inorganic oxides, zeolites and others, are tested for the adsorption of nearly all possible contaminants of organic and inorganic nature either in ionic or in molecular form [2].

The experimental procedure is versatile consisting of contacting adsorbent with adsorbate solution and testing the effect of variables such as: time, concentration, pH, temperature, and adsorbent load [3].

For the design of a commercial adsorption apparatus, equilibrium and kinetic data of the process are required. So the experimental results are simulated with a number of theoretical equations that allow for the calculation of the respective equilibrium and kinetic constants [4].

In the present paper, the existing models are briefly presented and commented upon, and an alternative methodology is proposed for simulating kinetic experimental results, based on the fundamental Langmuir model for adsorption [5].

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2. Equilibrium models

There is a considerable number of equilibrium model equations used in the literature to simulate adsorption equilibrium isotherms although the Langmuir Eq. (1) [5] and Freundlich, Eq. (2) [6] are the most frequently applied:

$$\bar{C}_{\mathrm{A}} = \frac{K + C_{\mathrm{A}}}{1 + KC_{\mathrm{A}}} \tag{1}$$

$$\bar{C}_{\mathrm{A}} = KC_{\mathrm{A}}^{1/n} \tag{2}$$

with $\bar{C}_{\mathrm{A}}$ = adsorbed amount of adsorbent A; C_{A} = equilibrium concentration; K = equilibrium constant; n = constant.

3. Kinetic models

In modeling adsorption kinetics, the number of models adopted in literature is relatively small. The most popular are the pseudo-first-order (Eq. (3) [7]) and the pseudo-second order (Eq. (4) [8])equations. The Elovich (Eq. (5) [9]) and Ritsi (Eq. (6) [10]) equations are used too, although less frequently. These models are discussed in literature with focus on their theoretical background and applicability [11–13]. Since the discussion is still open, this paper contributes to the derivation of these two models.

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = k_1(C_{\mathrm{Ae}} - C_{\mathrm{At}}) \tag{3}$$

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = k_2(C_{\mathrm{Ae}} - C_{\mathrm{At}})^2 \tag{4}$$

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = \alpha e^{-a\bar{C}_{\mathrm{At}}} \tag{5}$$

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} = k(1 - \Theta)^n, \tag{6}$$

where C_{Ae} = concentration at equilibrium; C_{At} = concentration at time t; Θ = surface coverage; k_1, k_2, α, k = kinetic constants.

4. Pseudo-first-order equation

The equation was allegedly introduced by Lagergren in 1898, but to our knowledge the way that the equation was deduced in the original article is not presented in literature although an interpretation based on the first order kinetics of adsorbate on adsorbent active sites is presented [14]. Instead there are some attempts to show how the equation can be deduced from existing kinetic models and more specifically on the Langmuir model equation of adsorption:

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = kC_{\mathrm{A}}\bar{C}_{\mathrm{V}} - k'\bar{C}_{\mathrm{A}} \tag{7}$$

written for the adsorption of a component A and for the adsorption mechanism:

$$A + X \leftrightarrow AX,$$

with X = adsorption active site.

Eq. (7) can be written as:

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = k\left(C_{\mathrm{AO}} - \bar{C}_{\mathrm{A}}\frac{W}{V}\right)(\bar{C}_{\mathrm{m}} - \bar{C}_{\mathrm{A}}) - k'\bar{C}_{\mathrm{A}} \tag{8}$$

since,

$C_{\mathrm{A}} = C_{\mathrm{AO}} - \bar{C}_{\mathrm{A}}\frac{W}{V}$ and $\bar{C}_{\mathrm{V}} = \bar{C}_{\mathrm{m}} - \bar{C}_{\mathrm{A}}$,
where C_{AO} = initial concentration; $\bar{C}_{\mathrm{V}}$ = concentration of vacant sites; $\bar{C}_{\mathrm{m}}$ = monolayer capacity; W = adsorbate weight; V = solution volume; k = adsorption rate constant; k' = desorption rate constant.

In the first approach [15], it has been shown that the pseudo–first order model can be derived from the Langmuir equation if the initial concentration is high compared to the adsorbed amount, concluding also that the kinetic constant of the equation is not the intrinsic adsorption rate constant but a combination of adsorption and desorption constants. This approach was commented as being valid for very dilute (quasi pure) solutions [16] but has some theoretical basis because it follows the initial rate approach frequently used to simplify kinetic studies, especially for reversible reactions [17].

Another approach, somewhat different and more simplified than that of reference 15, based on initial rate approach, i.e. low adsorption times-low adsorbed amounts and in addition, high initial concentrations of adsorbent solution, can give the pseudo-first-order equation. Since $\bar{C}_{\mathrm{A}}$ is supposed to be small, the second term (desorption of A), of Eq. (8) can be neglected. C_{A0} is supposed to be high, so the difference $C_{\mathrm{A0}} - \bar{C}_{\mathrm{A}}\frac{W_{\mathrm{C}}}{V}$ approaches the value of C_{A0}. On the contrary, $\bar{C}_{\mathrm{m}}$ and $\bar{C}_{\mathrm{A}}$ have comparable values and remain in the equation, resulting finally:

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = kC_{\mathrm{AO}}(\bar{C}_{\mathrm{m}} - \bar{C}_{\mathrm{A}}) \tag{9}$$

The last equation has the same appearance with the pseudo-first-order, with $k_1 = kC_{\mathrm{Ao}}$.

This approach confirms the conclusion that the pseudo-first-order model can be applied in very dilute solutions and for low adsorption times i.e. its practical use is very limited and this may be the reason why it fails to model the adsorption kinetics in many cases. Instead of this equation, one can apply the Langmuir Eq. (1) with the procedure described elsewhere, [18] ensuring or confirming that the adsorption follows the theoretical assumptions and mechanism of this model [17]. One can guess that the adsorption mechanisms that most probably (can) obey the Langmuir model are physisorption monolayer coverage, chemisorption, single-site ion exchange, etc.

5. Pseudo-second-order equation

The pseudo-second-order kinetic equation of adsorption was also analyzed and commented in literature. Various ways of equation derivation were proposed based on the different models such as Langmuir [15] and others [16,19]. Here the derivation should be based on the dual-site Langmuir adsorption mechanism which, for instance, could possibly be the mechanism of copper adsorption on peat [8], and that can be written:

$$2X + \mathrm{Cu}^{2+} \leftrightarrow 2\mathrm{Cu}_{1/2}X,$$

or any other mechanism involving two active sites.

The Langmuir equation in this case is written (compare with Eq. (8)):

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = k\left(C_{\mathrm{AO}} - \bar{C}_{\mathrm{m}}\frac{W}{C}\right)\left(\bar{C}_{\mathrm{m}} - \bar{C}_{\mathrm{A}}\right)^2 - k'\bar{C}_{\mathrm{A}}^2 \tag{10}$$

and the corresponding equilibrium equation (isotherm) is:

$$\bar{C}_{\mathrm{A}} = \frac{(KC_{\mathrm{A}})^{1/2}\bar{C}_{\mathrm{m}}}{1 + (KC_{\mathrm{A}})^{1/2}} \tag{11}$$

Under the same assumptions made for the pseudo first order equation, (high C_{AO} – low $\bar{C}_{\mathrm{A}}$), Eq. (10) reduces to:

$$\frac{\mathrm{d}\bar{C}_{\mathrm{A}}}{\mathrm{d}t} = kC_{\mathrm{AO}}\left(\bar{C}_{\mathrm{m}} - \bar{C}_{\mathrm{A}}\right)^2 \tag{12}$$

neglecting the desorption and the $\bar{C}_{\mathrm{m}}\frac{W}{C}$ terms, which is the form of the pseudo-second-order, again with $k_2 = kC_{\mathrm{A0}}$.

The limitations in using the pseudo-first order are obviously valid also for the second order one. The alternative route is to apply Eqs. (10) and (11) using the same procedure for single-site Langmuir model [18], despite the non-simplicity of this procedure compared to the pseudo-second order one. Besides, the second-order-equation is found to model adsorption in the majority of cases. The success could be attributed either to the suitability of the model for the specific application or to the flexibility of its mathematical form to model most of the sorption systems [19]. From the present approach, it can be concluded that the pseudo-second-order equation applies mostly to the dual-site mechanism and should be used with care in cases where the mechanism is not certain. Alternatively, equation can be applied with the trial and error method to verify the adsorption mechanism.

In applying models, one should be aware of the compatibility between the adsorption mechanism of the system, equilibrium equation and kinetic equation employed, taking into account that those three are connected, i.e. the equations must be based on a mechanism that (most probably) governs adsorption. Then, the kinetic equation is derived from the mechanism and the equilibrium equation is deduced from this kinetic equation posing the rate to be equal to zero. This procedure has been described in applying the Langmuir model previously. In literature, often kinetic and equilibrium models are applied independent of each other and without a common mechanism making this methodology somewhat debatable. For instance, Langmuir or Freundlich (and other) equations are based on energetically homogeneous site distribution (single layer) and heterogeneous multilayer adsorption mechanisms respectively. In parallel, the models of pseudo-first-and pseudo-second-order kinetics are tested and often the second one is verified, but until now there is not any direct connection between the two equilibrium models and the two kinetic equations based on a common adsorption mechanism. So, one is not confident on the agreement between mechanism and the model equations used.

6. Development of the dual-site Langmuir model

This model follows the mechanism [20]:

$$A + 2X = 2A_{1/2}X$$

Eq. (10) can be rearranged in the form:

$$\frac{d\bar{C}_A}{dt} = a\bar{C}_A^3 + b\bar{C}_A^2 + c\bar{C}_A + d, \tag{13}$$

with $a = -k\frac{W}{V}$, $b = kC_{AO} - k' + 2k\bar{C}_m\frac{W}{V}$, $c = -\left(2k\bar{C}_m C_{AO} - k\frac{W}{V}\bar{C}_m^2\right)$ and $d = kC_{AO}\bar{C}_m^2$.

Following the same procedure described in reference [18]:

From the experimental equilibrium data, applying the linear form of Eq. (11):

$$\frac{C_A^{1/2}}{\bar{C}_A} = \frac{1}{\bar{C}_m(K)^{1/2}} + \frac{C_A^{1/2}}{\bar{C}_m}, \tag{14}$$

the $\bar{C}_m$ and K can be calculated from the slope and the intercept of the line, respectively.

The kinetic constants k and k' can be calculated by making use of the equations:

$$k = \frac{1}{t}\int_0^{\bar{C}_A} \frac{d\bar{C}_A}{\alpha\bar{C}_A^3 + \beta\bar{C}_A^2 + \gamma\bar{C}_A + \delta} \tag{15}$$

and $K = \frac{k}{k'}$

with $\alpha = -\frac{W}{V}$, $\beta = C_{AO} - \frac{1}{K} + 2\bar{C}_m\frac{W}{V}$, $\gamma = -(2\bar{C}_m C_{AO} - \frac{W}{V}\bar{C}_m^2)$ and $\delta = C_{AO}\bar{C}_m^2$.

Eq. (15) results from the integration of Eq. (13), and is applied in a set of kinetic experimental results.

Calculated values of k and k' can then be used to predict the time required for adsorption from any initial concentration C_{A0} to a concentration C_A, corresponding to an adsorbed amount $\bar{C}_A$ without recurring to expertiments. This can be accomplished by rearranging, integrating and solving for t in Eq. (13):

$$t = \int_0^t dt = \int_0^{\bar{C}_A} \frac{d\bar{C}_A}{a\bar{C}_A^3 + b\bar{C}_A^2 + c\bar{C}_A + d} \tag{16}$$

Applying the last step repeatedly, the kinetic behavior (variation of adsorbed amount, $\bar{C}_A$ with time at any C_{A0}) of the adsorption of any adsorbing system based on the adsorption isotherm and a single kinetic experiment can be predicted.

7. Examples of application of the dual-site model

An extensive literature review has been conducted and a large number of bivalent ions adsorption experimental results have been found. Many of them have been used to verify the model validity. For this purpose, adsorption equilibrium data (isotherms) were modeled by either single-site (SSL) model or dual-site Langmuir (DSL) model. Validation results of the models can be categorized in those that are better fitted by the dual-site model and the single-site model. Therefore, it can be distinguished if adsorption mechanism involves one or two active sites. Two representative examples, taken from literature, are presented here.

In Fig. 1 the experimental results of bivalent copper ion adsorption on chitosan beads blended with poly vinyl alcohol, (PVA), taken from Wan Ngah [21] are shown and fitted with both models. Apparently the two models give similar results as it can be concluded from the values of the correlation coefficients, R^2 (Table 1).

Nonetheless, it can be easily observed that the dual-site model simulates the experimental values better, as shown in Fig. 1. A comparison between models constants, Table 1, shows that the DSL one predicts higher equilibrium adsorption capacity than SSL since it exhibits a less steep increase of adsorption capacity with concentration.

A second set of experimental data have been taken from Zhou [22], for the adsorption of Cu^{+2} ions by chitosan microspheres, chemically modified with Thiourea, (TMCS). In this case, it is obvious that DSL model fails to simulate adsorption in contrast to the SSL model that successfully simulates the process as demonstrated by the R^2 values, Table 2, and by the simulation curves in Fig. 2.

The DSL model predicts (unrealistically) high adsorption capacity which confirms that the model is not valid and allowing to conclude that the dual site adsorption mechanism is to be excluded.

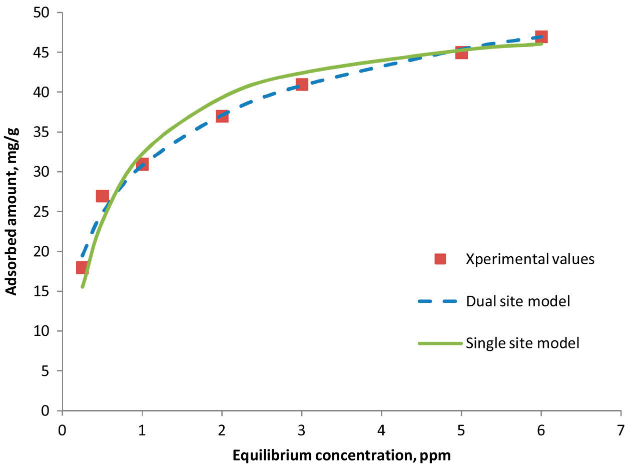

Fig. 1. Equilibrium adsorption of Cu(II) in Chitosan/PVA beads [21].

Table 1
Models constants for Wan Ngah [21] experimental data

Model	Equilibrium capacity (mg/g)	Equilibrium const.	R^2
Single site Langmuir	49.97	1.8994	0.997
Dual site Langmuir	70.44	0.6441	0.994

Table 2
Models constants for Zhou [22] experimental results

Model	Equilibrium capacity (mg/g)	Equilibrium const.	R^2
Single site Langmuir	67.27	0.02345	0.997
Dual site Langmuir	331.04	0.00022	0.275

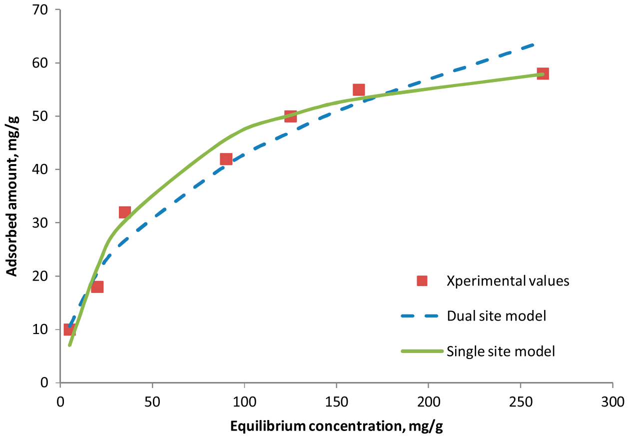

Fig. 2. Adsorption isotherm of Cu^{2+} by TMCS [22].

The second step in model validation is to check the suitability of the kinetic equation in simulating the experimental results. In a complete adsorption study, except equilibrium data, kinetic experimental data are required in order to fully describe the process. Then, both equilibrium and kinetic models can be employed in the design and operation of the full-scale equipment. Since the DSL model was successfully applied in modeling copper adsorption equilibrium in chitosan/PVA, the DSL kinetic model was tested for the same system experimental kinetic results. As can be seen in Fig. 3, the model fits quite well the experimental results although deviates somewhat for long adsorption times. In Table 3 the kinetic constants of DSL model are reported and can be used in Eq. (16). Therefore, Eqs. (11) and (16) and their respective constants (Tables 1 and 3) represent a complete qualitative and quantitative description (model) of the adsorption process. Equipment designers can then make use of the model to design and operate adsorption equipment.

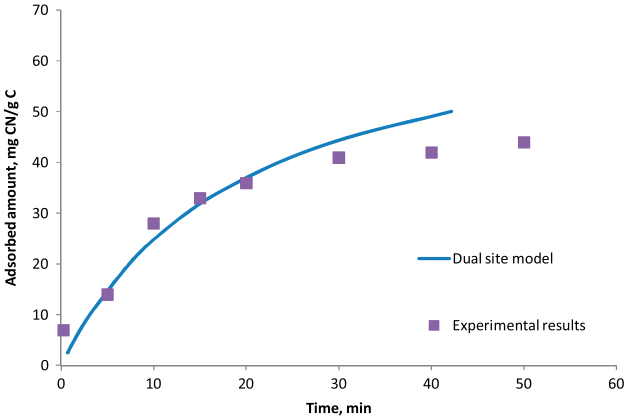

Fig. 3. Modeling of copper adsorption kinetics in Chitosan/PVA beads.

Table 3
Dual site Langmuir model kinetic constants (Wan Ngah [21] experimental data)

Adsorption constant, k, ($g^2_{adsorbent}/mg^2_{adsorbate}\cdot h$)	4.74×10^{-5}
Desorption constant, k' ($l/h\cdot mg_{adsorbate}$)	7.36×10^{-5}

7. Conclusions

In modeling adsorption, adopted models for simulating equilibrium and kinetic experimental results have to obey the same adsorption mechanism; instead, models are often applied independently. Pseudo-first- and pseudo-second-order kinetic models although successful in modeling data, seem to be applicable under specific experimental conditions and to be particular cases of the Langmuir model. The above mentioned drawbacks can be overcome by applying the Langmuir model for adsorption that allows for testing diverse mechanisms such as single site, dual site and others. A procedure is proposed based on a limited number of experiments and on the Langmuir theory that models adsorption in a rational and consistent mode. Equations that are determined by applying models can be used in modeling and designing large-scale equipment. So, theoretical models of adsorption tested experimentally are important in industrial practice. Engineers can calculate adsorption columns' size reliably or rate the performance of existing columns.

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