



Predicting equilibrium time by adsorption kinetic equations and modifying Langmuir isotherm by fractal-like approach

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ABSTRACT

In this work, the pseudo-first-order (PFO), pseudo-second-order (PSO) and Vermeulen equations were modified by introducing an adjustable parameter i.e. the fractional surface coverage θ . The Langmuir kinetic equation was modified by the fractal-like approach and the separation factor R_H was proposed to express essential characteristics of the fractal-like Langmuir isotherm. The kinetic and isotherm data obtained from nitrate adsorption on the PAN/AC composite were used to evaluate the validity of these models. Results indicated that the modified PSO equation could accurately predict the equilibrium time at different initial nitrate concentrations ($R^2 > 0.998$) and that the fractal-like Langmuir isotherm could better describe the equilibrium data at different temperatures ($R^2 > 0.994$). The magnitude of parameter b reflected the affinity of the adsorbent for the adsorbates. The innovation and significance of the present study was that the modified kinetic and isotherm models could predict the equilibrium time and describe the heterogeneous surfaces, respectively. Therefore, this work is expected to extend the application scope of the PFO, PSO and Vermeulen equations and Langmuir isotherm.

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1. Introduction

Adsorption is an attractive and promising technique for the purification of municipal and industrial wastewaters [1]. Adsorption efficiency is related to not only the equilibrium features but also the kinetics of the adsorption process for specific adsorption systems [2]. Therefore, a study of adsorption equilibrium and kinetics is essential to design industrial reactors, reduce operating cost and gain insights into adsorption processes [3].

The pseudo-first-order (PFO) [4] and pseudo-second-order (PSO) [5] equations are the most widely used kinetic models that describe the adsorption rate based on adsorption capacity. The Vermeulen equation, derived as an approximate solution of a diffusion-based Boyd equation, can predict the experimental data within the whole adsorption time [6]. Although adsorption mechanisms cannot be directly assigned by fitting the three models [7], they have received extensive attention due to their simple mathematical forms and good fitting performance. Furthermore, the three equations can also provide some important parameters such as the rate constant, equilibrium adsorption capacity and intraparticle diffusion coefficient. However, they do not directly predict the equilibrium time. Taking the importance of the equilibrium time into consideration in adsorption studies, we make

attempts to modify the PFO, PSO and Vermeulen equations to predict the equilibrium time of nitrate adsorption on the PAN/AC composite.

On the other hand, the Langmuir isotherm [8] is usually not suitable to describe the isotherm data obtained from aqueous solution due to a consequence of the fact that its underlying assumptions such as monolayer coverage of the adsorbent surface and energetic homogeneity of the adsorption sites may not be fulfilled [9]. This is particularly true for the most important adsorbent activated carbon. In adsorption studies, to enhance the affinity and selectivity of the adsorbent for solute molecules, some surface techniques such as protonation and chemical modification are adopted [10]. Thus, most of the modified adsorbents often have a heterogeneous surface with different types of adsorption sites. The Langmuir isotherm can only describe monolayer adsorption on the energetically homogeneous solid surface [11], which limits its application scope. Haerifar and Azizian demonstrate that the adsorption kinetics on energetically heterogeneous solid surfaces can be described by a fractal-like approach [12]. Herein, we make attempts to introduce the fractal-like concept into the Langmuir kinetic equation and thus propose the fractional surface coverage dependence of the adsorption rate constant.

The innovation of this work is that the modified PFO, PSO and Vermeulen equations can be directly used to predict the equilibrium time and that the fractal-like Langmuir isotherm can describe the adsorption of the adsorbates on the heterogeneous surfaces. Besides, introduction of the parameter h into the Langmuir isotherm contributes

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to improving fitting performance. The objectives of this study are: (i) to predict the equilibrium time by modifying the PFO, PSO and Vermeulen equations; and (ii) to extend the application scope of the Langmuir isotherm through introducing the fractal-like concept into the Langmuir kinetic equation. The goodness of fit for these models is evaluated by the coefficient of determination (R^2) and chi-squared analysis (χ^2).

2. Theoretical analysis

2.1. Kinetic models

In this study, kinetic models used to predict the equilibrium time include the PFO, PSO and Vermeulen equations, which are expressed as [6, 13, 14]:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (1)$$

$$q_t = q_e \left(1 - \frac{1}{1 + q_e k_2 t} \right) \quad (2)$$

$$q_t = q_e \sqrt{1 - \exp\left(-\frac{D\pi^2}{r^2} t\right)} \quad (3)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amounts of solute adsorbed per unit mass of the adsorbent at time t and at equilibrium, respectively; k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the PFO and PSO rate constants; D ($\text{cm}^2 \text{min}^{-1}$) is the intraparticle diffusion coefficient; r (cm) is the radius of the spherical adsorbent particles; and t (min) is the adsorption time.

It is important to note that k_1 , $q_e k_2$ and $D\pi^2/r^2$ have identical dimensions (i.e. reciprocal time, min^{-1}). According to the above three equations, the relationships between the fractional surface coverage ($\theta = q_t/q_e$) at time τ_e and the parameters k_1 , $q_e k_2$ and $D\pi^2/r^2$ are defined as:

$$k_1 = -\frac{1}{\tau_e} \cdot \ln(1-\theta) \quad (4)$$

$$q_e k_2 = \frac{1}{\tau_e} \cdot \frac{\theta}{(1-\theta)} \quad (5)$$

$$\frac{D\pi^2}{r^2} = -\frac{1}{\tau_e} \cdot \ln(1-\theta^2) \quad (6)$$

Substitution of Eq. (4) to Eq. (1), Eq. (5) to Eq. (2) and Eq. (6) to Eq. (3) leads to

$$q_t = q_e \left(1 - \exp\left(\left[\frac{1}{\tau_e} \ln(1-\theta)\right] t\right) \right) \quad (7)$$

$$q_t = q_e \left(1 - \frac{1}{1 + \left[\frac{\theta}{(1-\theta)\tau_e}\right] t} \right) \quad (8)$$

$$q_t = q_e \sqrt{1 - \exp\left(\left[\frac{1}{\tau_e} \ln(1-\theta^2)\right] t\right)} \quad (9)$$

One can readily see that the terms k_1 , $q_e k_2$ and $D\pi^2/r^2$ are converted to the equilibrium time (τ_e) under specific θ value and the mathematical structure of the above equations has not changed through this transformation. It should be emphasized that θ is an adjustable constant according to the actual requirements. Thus, selecting the appropriate θ value as the state of equilibrium will contribute to reducing the operating cost and optimizing the design of adsorption systems.

2.2. Modification of Langmuir isotherm

The Langmuir kinetic equation, which is commonly used to describe monolayer adsorption on the energetically homogeneous solid surfaces, can be given as [15]:

$$\frac{d\theta}{dt} = k_a C(1-\theta) - k_d \theta \quad (10)$$

where θ is the fractional surface coverage that is a dimensionless constant; k_a ($\text{L mg}^{-1} \text{min}^{-1}$) and k_d (min^{-1}) are the adsorption and desorption rate constants, respectively; and C (mg L^{-1}) is the concentration of solute at time t .

The nonlinear form of the Langmuir isotherm at equilibrium is expressed as [16]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (11)$$

where q_{\max} (mg g^{-1}) is the maximum adsorption capacity; K_L (L mg^{-1}) is the Langmuir constant ($K_L = k_a/k_d$); C_e (mg L^{-1}) is the concentration of solute at equilibrium.

In order to facilitate the following analyses, another form of Eq. (11) is written as:

$$C_e = \frac{q_e}{K_L(q_{\max} - q_e)} \quad (12)$$

Inspired by the fractal-like concept [3, 12], we argue that solute molecules can be freely adsorbed on the bare solid surface (homogeneous or heterogeneous) in the initial phase of adsorption. As time goes on, solute molecules adsorbed on the solid surface may affect adsorption paths of the incoming solute molecules and thus adsorption of the incoming solute molecules on the solid surface is suffered from the fractional surface coverage. Consequently, the adsorption rate constant is a function of the fractional surface coverage. In this study, we introduce the fractal-like concept or the fractional surface coverage dependence of the adsorption rate constant to the Langmuir kinetic equation, which is expressed as:

$$k_a = k_{a,0} \theta^{-h} \quad (0 \leq h \leq 1) \quad (13)$$

where $k_{a,0}$ ($\text{L mg}^{-1} \text{min}^{-1}$) is the fractal-like adsorption rate constant, h is a constant parameter.

When adsorption process reaches equilibrium, substitution of Eq. (13) into Eq. (10) leads to

$$C_e = \frac{q_e^{(h+1)}}{b q_{\max}^h (q_{\max} - q_e)} \quad (14)$$

where b (L mg^{-1}) is the fractal-like isotherm constant ($b = k_{a,0}/k_d$). It is worthy to note that introducing the fractal-like concept into the Langmuir kinetic equation extends the application scope of the Langmuir isotherm. The fractal-like Langmuir isotherm can describe solute adsorption on the heterogeneous surfaces according to the above analysis.

In addition, Eq. (14) includes the description of the equilibrium between the feed concentration C_0 and the saturation level q_0 , which may occur in the fixed-bed adsorption column. Dimensionless concentrations, $Y = (q_e/q_0)$ and $X = (C_e/C_0)$, are introduced to Eq. (14), resulting in

$$\left(\frac{q_e}{q_0}\right)^{(h+1)} = \frac{C_e \left(1 + b C_0 \left(\frac{q_0}{q_{\max}}\right)^{-h}\right)}{C_0 \left(1 + b C_e \left(\frac{q_e}{q_{\max}}\right)^{-h}\right)} \quad (15)$$

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