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Research Article

A weighted average kinetic equation and its application in estimating mass transfer coefficients in liquid phase adsorption

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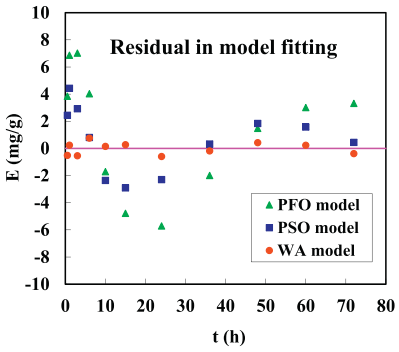
HIGHLIGHTS

- A new adsorption kinetic model is presented.
- The model parameters are related to mass transfer coefficients.
- The model fits adsorption kinetic data very well.

GRAPHICAL ABSTRACT



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ABSTRACT

The pseudo-first-order (PFO) and pseudo-second-order (PSO) models are widely used to describe liquid phase adsorption kinetics due to their simplicity and easy application. But these models do not take into account the diffusion or mass transfer effects that exist in adsorption. In this work a new weighted average (WA) kinetic model is presented. The model parameters are related to mass transfer coefficients, which allows for the estimation of the film mass transfer and surface diffusion coefficients from adsorption kinetic data. The WA model is applied to four adsorption systems and compared with the PFO and PSO models by using the Akaike Information Criterion (AIC). The results show that the WA model fits the experimental kinetic data much better than the PFO and PSO models.

1. Introduction

Kinetics in liquid phase adsorption is often modeled by the pseudo-first-order (PFO) and pseudo-second-order (PSO) equations due to their simplicity and easy application [1–6]. But these models do not take into account the diffusion or mass transfer steps which occur in adsorption. The diffusion processes generally include the film or external diffusion and the intraparticle or internal diffusion (pore diffusion or surface diffusion or a combination of both) [7–14]. The governing equations for diffusion processes are partial differential equations which in general have to be solved numerically. The mass transfer coefficients (the film mass transfer coefficient, the pore and/or the surface diffusion coefficients) are usually obtained by matching the numerical solution to experimental kinetic data [8–14], which is not a simple task and makes the mass transfer model much less popular than the adsorption kinetic models.

The objective of this work is to present a new adsorption kinetic equation which is based on weight-averaging of the PFO and PSO

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models. Relationships between the new model parameters and the mass transfer coefficients are obtained which allow for the estimation of the film mass transfer and surface diffusion coefficients.

2. Theory

2.1. Adsorption kinetic models

The pseudo-first-order (PFO) kinetic model can be written as [15–18].

$$\frac{q}{q_e} = 1 - e^{-k_1 t} \tag{1}$$

where q is the adsorbed amount at time t, q_e the equilibrium value of q, and k_1 the pseudo-first-order rate constant. The pseudo-second-order (PSO) kinetic model may be expressed as [15–18].

$$\frac{q}{q_e} = \frac{k_2 q_e t}{1 + k_2 q_e t} \tag{2}$$

where k_2 is the pseudo-second-order rate constant.

In the present work we construct a new kinetic equation by taking a weighted average of the PFO and PSO models with the weighting factors being set as q/q_e and $1\text{-}q/q_e$ respectively.

$$\frac{q}{q_e} = \frac{q}{q_e}(1 - e^{-kt}) + \left(1 - \frac{q}{q_e}\right)\frac{at}{1 + at} \tag{3}$$

where a and k are new model parameters. Eq. (3) can be rearranged to give.

$$\frac{q}{q_e} = \frac{ate^{kt}}{1 + at + ate^{kt}} \tag{4}$$

which is the new weighted average (WA) kinetic model. The new model has three parameters, namely q_e, a and k, which are to be determined by fitting the model to kinetic data through a nonlinear regression method. The characteristics of the WA model are mainly reflected by the parameters a and k as discussed below.

From Eq. (4) the adsorption rate for the WA model can be obtained as.

$$\frac{dq}{dt} = \frac{aq_e e^{kt}(1 + kt + akt^2)}{(1 + at + ate^{kt})^2} \tag{5}$$

which, in view of Eq. (4), may be rewritten as.

$$\frac{dq}{dt} = \frac{ae^{kt}(1 + kt + akt^2)}{(1 + at)(1 + at + ate^{kt})}(q_e - q) \tag{6}$$

Let

$$F = \frac{ae^{kt}(1 + kt + akt^2)}{(1 + at)(1 + at + ate^{kt})} \tag{7}$$

Then Eq. (6) becomes.

$$\frac{dq}{dt} = F(q_e - q) \tag{8}$$

F can be regarded as an adsorption rate constant for the WA model. Eq. (7) shows that F is dependent on a and k. For small adsorption time or in the early adsorption stage Eq. (7) leads to.

$$F|_{t\to 0} = a \tag{9a}$$

For large adsorption time or in the late adsorption stage Eq. (7) gives.

$$F|_{t\to \infty} = k \tag{9b}$$

Thus the parameters a and k in the WA model can be considered respectively as the early- and late-stage adsorption rate constants. The effects of a and k on q/q_e for the WA model are shown in Fig. 1, where it is seen that a affects mainly the early adsorption stage (Fig. 1a) and k the late adsorption stage (Fig. 1b). It is thus expected that by adjusting a and k the WA model can fit adsorption kinetic data well in both early and late adsorption stages. It will be further shown later on that the WA model parameters are related to the mass transfer coefficients.

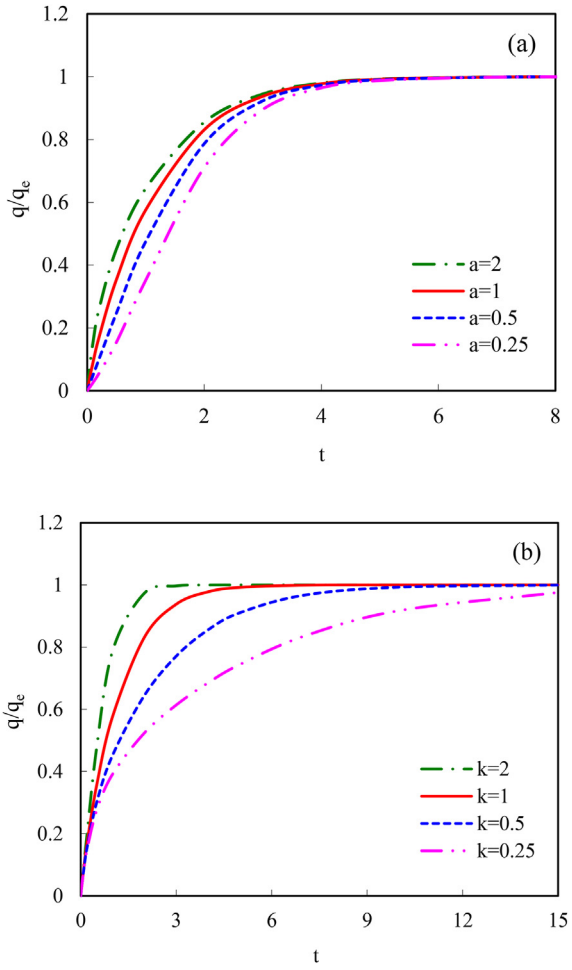

Fig. 1. Variation of q/q_e with t for the WA model (a) effect of a when $k = 1$ and (b) effect of k when $a = 1$.

2.2. Adsorption mass transfer model

For liquid phase adsorption in a spherical adsorbent, the film-surface diffusion (also known as the film-solid diffusion or homogeneous surface diffusion) model can be expressed as [7, 12–14].

$$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q_r}{\partial r}\right) \tag{10}$$

with the initial and boundary conditions.

$$t = 0,\ q_r = 0 \tag{11}$$

$$r = 0,\ \frac{\partial q_r}{\partial r} = 0 \tag{12}$$

$$r = R,\ \rho_p D_s \frac{\partial q_r}{\partial r} = k_f(c_b - c_s) \tag{13}$$

where r is the radial coordinate, R the adsorbent radius, q_r the adsorbed phase concentration at r, D_s the surface diffusion coefficient, k_f the film mass transfer coefficient, ρ_p the adsorbent particle density, c_b and c_s the adsorbate concentrations in the bulk solution and at the adsorbent surface respectively. c_s is related to the adsorbed phase concentration at the adsorbent surface q_s by the adsorption isotherm. The amount