A film-diffusion-based adsorption kinetic equation and its application

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ABSTRACT

A convenient adsorption kinetic equation based on film diffusion mass transfer and Langmuir equilibrium was developed. The model shows a straight line passing through the origin in a plot similar to the Boyd plot and the slope of the line is related to the film mass transfer coefficient. It can be used to analyze if an adsorption process is controlled by film diffusion and, if so, to determine the film mass transfer coefficient. The model was applied to four adsorption systems and compared with the Weber, the Boyd (or Reichenberg) and the Vermeulen (or Urano) models.

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1. Introduction

Adsorption is an effective separation method widely used in water purification and wastewater treatment. The adsorption of an adsorbate from a liquid solution by a particulate adsorbent generally involves three steps (Chatzopoulos et al., 1993; Chatterjee and Schiewer, 2014; Dotto et al., 2014; Viegas et al., 2014; Yao and Chen, 2015; Moral-Rodriguez et al., 2016): (1) diffusion of the adsorbate across the liquid film surrounding the adsorbent particle (external film diffusion); (2) diffusion within the adsorbent particle (intraparticle diffusion) which may be due to pore diffusion or surface diffusion or a combination of both; (3) adsorption on the pore surface (surface reaction).

In most adsorption systems the surface reaction step is relatively fast and the controlling step is diffusion (film and/or intraparticle diffusion). If the film and the intraparticle diffusion resistances are of similar magnitude, the governing mass transfer equations which are partial differential equations have to be solved numerically in general and the mass transfer parameters (such as the film and intraparticle diffusion coefficients) are usually obtained by matching the numerical solution to experimental kinetic data (Chatzopoulos et al., 1993; Chatterjee and Schiewer, 2014; Dotto et al., 2014; Viegas et al., 2014; Yao and Chen, 2015; Moral-Rodriguez et al., 2016). On the other hand, if one (film or intraparticle) diffusion resistance is much larger than the other and is

thus controlling, the relevant mass transfer equations may be simplified and solved analytically, making it possible to determine the mass transfer parameters analytically.

The relative magnitude of film and intraparticle mass transfer resistances depends on adsorption conditions such as stirring speed and adsorbent size. High stirring can reduce or even eliminate film mass transfer resistance. Smaller particle size usually means lower intraparticle diffusion resistance.

For intraparticle diffusion controlled adsorption in spherical adsorbents, the following series solution is well known (Boyd et al., 1947; Crank, 1975; Chatterjee and Schiewer, 2014; Dotto et al., 2014; Viegas et al., 2014 Yao and Chen, 2015).

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_i n^2 \pi^2 t}{R^2}\right) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 Bt\right) \quad (1)$$

where q_t and q_e are respectively the instantaneous (at time t) and the equilibrium adsorbed phase concentration (adsorbed amount per unit mass of adsorbent), R the adsorbent radius, D_i the effective intraparticle diffusion coefficient. B is a parameter defined by

$$B = \frac{\pi^2 D_i}{R^2} \quad (2)$$

$$Bt = -\ln\left[1 - \left(\frac{q_t}{q_e}\right)^2\right] \qquad (7)$$

which, in the Boyd plot of Bt versus t, also shows a straight line passing through the origin. In fact the Boyd (or Reichenberg) model Eqs. (5) and (6) and the Vermeulen (or Urano) model Eq. (7) are very close to each other. This will be shown later on.

In the case of film diffusion controlled adsorption, a simple kinetic equation was shown by Furusawa and Smith (1973) and Choy et al. (2004) for linear adsorption equilibrium. But no simple kinetic equations are available for nonlinear adsorption equilibrium.

In the present study a convenient kinetic equation based on film diffusion mass transfer and Langmuir equilibrium is developed. Four adsorption systems are chosen to illustrate the usage of the model.

2.   Theory

The mass transfer rate across the external film surrounding a spherical adsorbent can be written as (Chatterjee and Schiewer, 2014; Viegas et al., 2014 Yao and Chen, 2015; Moral-Rodriguez et al., 2016)

$$\frac{dq_t}{dt} = \frac{3k_f}{R\rho_p}(c_b - c_s) \qquad (8)$$

where k_f is the external film mass transfer coefficient, ρ_p the adsorbent particle density, c_b and c_s the adsorbate concentration 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. In the present study it is assumed that the adsorption isotherm can be expressed by the Langmuir equation

$$q_s = \frac{q_m b c_s}{1 + b c_s} \qquad (9)$$

where q_m and b are the Langmuir isotherm parameters. For adsorption under film diffusion control with no or negligible intraparticle diffusion resistance, $q_s \approx q_t$. Then c_s can be expressed as

$$c_s = \frac{q_s}{b(q_m - q_s)} \approx \frac{q_t}{b(q_m - q_t)} \qquad (10)$$

For a batch adsorption process the bulk phase mass balance may be written as

$$c_b = c_0 - \frac{mq_t}{V} \qquad (11)$$

where c_o is the initial bulk phase concentration, m the adsorbent mass, and V the solution volume. When adsorption reaches equilibrium, Eq. (11) becomes

$$c_e = c_0 - \frac{mq_e}{V} \qquad (12)$$

where c_e and q_e are respectively the equilibrium values of c_b and q_t and are related in the present study by the Langmuir equation

$$q_e = \frac{q_m b c_e}{1 + b c_e} \qquad (13)$$

Nomenclature	
A	parameter defined by Eq. (16), h^{-1}
B	parameter defined by Eq. (2), h^{-1}
b	Langmuir isotherm parameter in Eq. (9), L/mg
c_0	initial bulk phase concentration, mg/L
c_b	bulk phase concentration at time t, mg/L
c_e	equilibrium value of c_b, mg/L
c_s	liquid phase concentration at adsorbent surface, mg/L
D_i	effective intraparticle diffusion coefficient, mm^2/h
k_f	film mass transfer coefficient, mm/h
m	adsorbent mass, g
q_e	equilibrium value of q_t, mg/g
q_m	Langmuir isotherm parameter in Eq. (9), mg/g
q_s	adsorbed phase concentration at adsorbent surface, mg/g
q_t	adsorbed phase concentration or amount adsorbed by unit mass of adsorbent at time t, mg/g
R	adsorbent radius, mm
t	time, h
V	volume of bulk solution, L
ρ_p	adsorbent particle density, g/L

For short adsorption time when $q_t/q_e < 0.3$, Eq. (1) can be approximated by (Boyd et al., 1947; Crank, 1975; Chatterjee and Schiewer, 2014)

$$\frac{q_t}{q_e} = \frac{6}{\pi^{3/2}}\sqrt{Bt} \quad \text{(small t)} \qquad (3)$$

which is usually called the Weber (or Weber–Morris) model and the plot of q_t versus the square root of t is known as the Weber (or Weber-Morris) plot (Weber and Morris, 1963; Kapur and Mondal, 2013). If the Weber plot shows a straight line passing through the origin (for $q_t/q_e < 0.3$), this means that the adsorption process is controlled by intraparticle diffusion.

Reichenberg (1953) showed that Eq. (1) can be well approximated by

$$\frac{q_t}{q_e} = \frac{6}{\pi^{3/2}}\sqrt{Bt} - \frac{3}{\pi^2}Bt \qquad (4)$$

or

$$Bt = \pi\left(1 - \sqrt{1 - \frac{\pi}{3}\frac{q_t}{q_e}}\right)^2 \qquad (5)$$

for $q_t/q_e < 0.85$ and

$$Bt = -\ln\frac{\pi^2}{6} - \ln\left(1 - \frac{q_t}{q_e}\right) \qquad (6)$$

for $q_t/q_e > 0.85$. Eqs. (5) and (6) are known as the Boyd or Reichenberg model (Chatterjee and Schiewer, 2014; Viegas et al., 2014). The plot of Bt versus t is called the Boyd plot (Viegas et al., 2014) where a straight line passing through the origin means that the adsorption process is controlled by intraparticle diffusion. Otherwise the adsorption process is controlled by film diffusion or by both film and intraparticle diffusions (Chatterjee and Schiewer, 2014; Viegas et al., 2014). From the slope of the straight line in the Boyd plot the effective intraparticle diffusion coefficient can be calculated by Eq. (2).

Another well-known approximate equation for intraparticle diffusion controlled adsorption is the Vermeulen (Vermeulen, 1953; Outokesh and Naderi, 2014; Wassie and Srivastava, 2016) or Urano