Rate equations and isotherms for two adsorption models

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Received 24 December 2007; received in revised form 8 April 2008; accepted 8 April 2008

Abstract

The rate equations and isotherms for two adsorption models have been formulated and discussed. The rate equations obtained have been compared to those of pseudo-first-order model and pseudo-second-order model, respectively. Calculated results indicated that the rate equations of single site model and dual site model could be approximated by those of pseudo-first-order model and pseudo-second-order model, respectively, in a limited ranges of the values of $C_{A \cdot S_e}^*$ (or $C_{A \cdot S_2 e}^*$), K^* and t^*. The adsorption isotherm of single site model has been found to be the same as that of Langmuir type.

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Keywords: Adsorption; Dual site model; Isotherm; Rate equation; Single site model

1. Introduction

Ion exchange, electrolyte or liquid extraction, electrodyalysis, precipitation, cementation and reverse osmosis are the methods for treating wastewater containing low concentrations of heavy metals (Horacek *et al.*, 1994). However, adsorption onto low cost particulate offers an alternative option for the removal of metal ions in the water (Brown *et al.*, 2000).

The overall process for adsorbing the heavy metal ion A^{2+} onto the active site (or sites) of the pore surface of adsorbent can be broken down into three steps as pictured in Fig. 1. They are (1) mass transfer of metal ion A^{2+} from the bulk aqueous solution through an artificial film to the external surface of the adsorbent, (2) diffusion of metal ion A^{2+} from the pore mouth through the pore to the immediate vicinity of the active site and (3) adsorption of metal ion A^{2+} onto the active site (or sites) of the internal pore surface (Fogler, 1999). The overall rate of the adsorption is equal to the rate of the slowest step (called controlling step).

If the mass transfer in the film is the controlling step, the overall rate of adsorption is given by (Choy *et al.*, 2004)

$$\ln\left(\frac{C}{C_0} - \frac{1}{1 + mk_f}\right) = \ln\left(\frac{mk_f}{1 + mk_f}\right) - \frac{1 + mk_f}{mk_f}\beta S_s t \quad (1)$$

The values of m and S_s are calculated from the following equations:

$$m = \frac{w}{v} \quad (2)$$

$$S_s = \frac{6m}{d_p \rho_p (1 - \varepsilon_p)} \quad (3)$$

The meaning of the symbols appeared in the above equations and the following equations can be found in the section of nomenclature.

If the pore diffusion step is the slowest one, the rate expression can be depicted as (Morris and Weber, 1962)

$$\frac{C_A}{C_{Ao}} = k_d t^{0.5} \quad (4)$$

When the adsorption step controls the overall process, three kinds of rate equations have been found for different adsorption mechanisms. The first one is the Elovich equation (Aharoni and Tompkins, 1970) which is normally used in the case of chemisorption

$$q = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln\left(t + \frac{1}{ab}\right) \quad (5)$$

Two other types of rate equations have also been employed for the physisorption. The first one is the pseudo-first-order type (Lagergren, 1898):

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (6)$$

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Nomenclature

a	constant appeared in Eq. (5) (mg/g s)
$\bar{a}$	quantity defined by Eq. (21) $(\text{mg}^{(1-1/n)}/\text{L}^{1/n}/\text{g})$
$\bar{a}^*$	dimensionless quantity defined by Eq. (34)
a_R	Redlich–Peterson constant appeared in Eq. (11) $(\text{L}^{\beta}/\text{mg}^{\beta})$
b	constant appeared in Eq. (5) (g/mg)
$\bar{b}$	quantity defined by Eq. (22)
$\bar{b}^*$	dimensionless quantity defined by Eq. (35)
$\bar{c}$	quantity defined by Eq. (23) $(\text{mg}^{(2-1/n)}/\text{L}^{1/n-2}/\text{g})$
$\bar{c}^*$	dimensionless quantity defined by Eq. (36)
C	concentration of adsorbate in aqueous solution at time t (mg/L)
C_0	initial concentration of adsorbate in aqueous solution (mg/L)
C_A	concentration of A^{2+} in aqueous solution at time t (mg/L)
C_{Ae}	concentration of A^{2+} at equilibrium (mg/L)
C_{Ao}	initial concentration of A^{2+} in aqueous solution (mg/L)
$C_{A \cdot S}$	concentration of A^{2+} attached on site at time t (mg/L)
$C_{A \cdot Se}$	concentration of A^{2+} attached on site at equilibrium (mg/L)
$C_{A \cdot S}^*$	dimensionless concentration of A^{2+} attached on site at time t
$C_{A \cdot Se}^*$	dimensionless concentration of A^{2+} attached on site at equilibrium
$C_{A \cdot S_2}$	concentration of A^{2+} attached on dual sites at time t (mg/L)
$C_{A \cdot S_2 e}$	concentration of A^{2+} attached on dual sites at equilibrium (mg/L)
$C_{A \cdot S_2 e}^*$	dimensionless concentration of A^{2+} attached on dual site at equilibrium
C_t	concentration of total site (or sites) (number of site/L)
C_V	concentration of vacant site (or sites) (number of site/L)
d_p	adsorbent diameter (cm)
k_F	Freundlich constant appeared in Eq. (9) $(\text{mg}^{(1-1/n)}/\text{L}^{1/n}/\text{g})$
k_L	Langmuir equilibrium constant appeared in Eq. (8) (L/mg)
k_{LF}	Langmuir–Freundlich constant appeared in Eq. (10) $(\text{L}^{1/n}/\text{mg}^{1/n})$
k_R	Redlich–Peterson equilibrium constant appeared in Eq. (11) (L/g)
k_b	desorption rate constant appeared in Eq. (12) (1/s)
k_d	rate constant appeared in Eq. (4) $(1/\text{s}^{0.5})$
k_f	adsorption rate constant appeared in Eq. (12) (1/s number of site)
k_1	rate constant appeared in Eqs. (6) and (27) (1/s)
k_2	rate constant appeared in Eq. (7) (g/mg s)
K	equilibrium constant appeared in Eq. (15)
K^*	dimensionless equilibrium constant
m	mass of adsorbent per unit volume of adsorbent free slurry (g/L)
n	Freundlich exponent, appeared in Eq. (9)
q	amount of A^{2+} adsorbed at time t (mg/g)
q_e	amount of A^{2+} adsorbed at equilibrium (mg/g)
Q_o	amount of A^{2+} required for the formation of a monolayer (mg/g)
r	adsorption rate constant appeared in Eq. (13) (mg/L s)
S_s	outer surface area of adsorbent per unit volume of adsorbent-free slurry (1/cm)
t	time (s)
t^*	dimensionless time
w	weight of adsorbent (g)
v	volume of adsorbent free solution (L)

Greek symbols

α	Redlich–Peterson exponent appeared in Eq. (11)
β	mass transfer coefficient appeared in Eq. (1) (cm/s)
ε_p	porosity of adsorbent particle
ρ_p	density of adsorbent particle (mg/L)

and the second one is the pseudo-second-order type (Ho and Mckay, 1999a):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

As the adsorption lasts long enough, it reaches equilibrium. The data obtained at this stage are normally correlated by the following adsorption isotherms, which depict the capability of the adsorbent.

Langmuir isotherm (Langmuir, 1918)
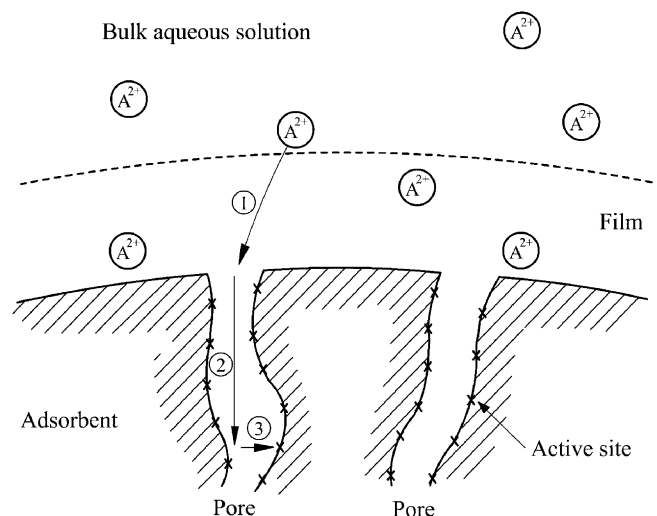
$$q_e = \frac{k_L Q_o C_{Ae}}{1 + k_L C_{Ae}} \tag{8}$$

Fig. 1. Steps in adsorbing heavy metal ion A^{2+} on adsorbent from aqueous solution.