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Review:

Mathematically modeling fixed-bed adsorption in aqueous systems^{*}

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Abstract: Adsorption is one of the widely used processes in the chemical industry environmental application. As compared to mathematical models proposed to describe batch adsorption in terms of isotherm and kinetic behavior, insufficient models are available to describe and predict fixed-bed or column adsorption, though the latter one is the main option in practical application. The present review first provides a brief summary on basic concepts and mathematic models to describe the mass transfer and isotherm behavior of batch adsorption, which dominate the column adsorption behavior in nature. Afterwards, the widely used models developed to predict the breakthrough curve, i.e., the general rate models, linear driving force (LDF) model, wave propagation theory model, constant pattern model, Clark model, Thomas model, Bohart-Adams model, Yoon-Nelson model, Wang model, Wolborska model, and modified dose-response model, are briefly introduced from the mechanism and mathematical viewpoint. Their basic characteristics, including the advantages and inherit shortcomings, are also discussed. This review could help those interested in column adsorption to reasonably choose or develop an accurate and convenient model for their study and practical application.

Key words: Column adsorption, Modeling, Fixed-bed adsorption, Breakthrough curve

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1 Introduction

Adsorption is a widely used method to treat industrial waste gas and effluent due to its low cost, high efficiency and easy operation. Particularly, the adsorption process is suitable for decontaminating those compounds of low concentration or high toxicity, which are not readily treated by biological processes. Based on the operation mode, adsorption can be generally classified into static adsorption and dynamic adsorption. Static adsorption, also called batch adsorption, occurs in a closed system containing a

desired amount of adsorbent contacting with a certain volume of adsorbate solution, while dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent. For column adsorption, how to determine the breakthrough curve is a very important issue because it provides the basic but predominant information for the design of a column adsorption system. Without the information of the breakthrough curve one cannot determine a rational scale of a column adsorption for practical application. There are two widely used approaches to obtain the breakthrough curve of a given adsorption system: direct experimentation or mathematical modeling. The experimental method could provide a direct and concise breakthrough curve of a given system. However, it is usually a time-consuming and economical undesirable process, particularly for the trace contaminants and long residence time. Also, it greatly depends upon the experimental conditions, such as ambient temperature and residence time.

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Comparatively, mathematical modeling is simple and readily realized with no experimental apparatus required, and thus, it has attracted increasing interest in the past decades.

Currently, a variety of mathematical models have been used to describe and predict the breakthrough curves of a column adsorption system in liquid or gaseous phase (Abu-Lail *et al.*, 2012; Cheknane *et al.*, 2012; Meng *et al.*, 2012; Nwabanne and Igbokwe, 2012; Yi *et al.*, 2012; Zhao *et al.*, 2012), but there is still lack of a comprehensive review of these models. The main objective of the present review is to introduce the modeling of dynamic adsorption in liquid phase. Different from the gas-solid adsorption, liquid-solid adsorption is more theoretically difficult to give an unambiguous description because the solvent accompanies more intricate interaction between the species involved. Moreover, the salvation effect results in a more complicated behavior of the process. To model a liquid-solid column adsorption, it is necessary to divide it into four basic steps (Fig. 1): (1) liquid phase mass transfer including convective mass transfer and molecular diffusion; (2) interface diffusion between liquid phase and the exterior surface of the adsorbent (i.e., film diffusion); (3) intrapellet mass transfer involving pore diffusion and surface diffusion; and, (4) the adsorption-desorption reaction (Crittenden and Weber, 1978; Crittenden *et al.*, 1986; Helfferich, 1995).

(1) Liquid phase mass transfer. Molecules or ions in the column can move in both axial and radial directions. For simplification, it is common to postulate that all cross-sections are homogeneous and the radial movement could be neglected. Thus, a macroscopic mass conservation equation is acquired to represent the relationship between the corresponding variations (i.e., concentration of the adsorbed adsorbate q ; concentration of the bulk solution C ; distance to the inlet z ; superficial velocity u ; and axial dispersion coefficient D_z (if the axial dispersion is not ignored)). Regarding a control volume as shown in Fig. 2, one has (Costa and Rodrigues, 1985; Tien, 1994; Fournel *et al.*, 2010)

$$\varepsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + (1 - \varepsilon) \rho_a \frac{\partial q}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2}, \quad (1)$$

where initial and boundary conditions are

$$\begin{aligned} t = 0 &\rightarrow C(z, t) = 0, \\ t = 0 &\rightarrow q(z, t) = 0, \\ z = 0 &\rightarrow C(0, t = 0) = 0, C(0, t > 0) = C_F, \\ z = H &\rightarrow \frac{\partial C}{\partial z} = 0. \end{aligned}$$

When the axial dispersion is ignored,

$$\varepsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + (1 - \varepsilon) \rho_a \frac{\partial q}{\partial t} = 0. \quad (2)$$

The initial and boundary conditions turn to

$$\begin{aligned} t = 0 &\rightarrow C(z, t) = 0, \\ z = 0 &\rightarrow C = C_F + \frac{D_z \varepsilon}{u} \frac{\partial C}{\partial z}, \\ z = H &\rightarrow \frac{\partial C}{\partial z} = 0, \end{aligned}$$

where ε is the bed porosity, t is the time, ρ_a is the adsorbent density, C_F is the initial concentration of the influent, and H is the bed height.

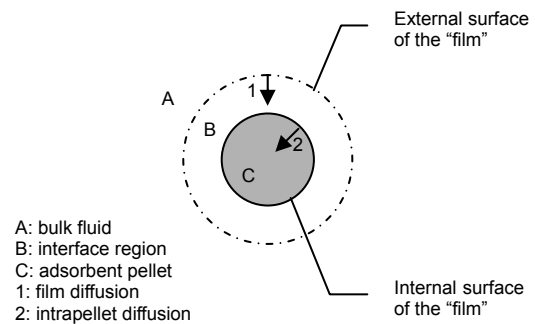


Fig. 1 Macroscopic adsorption process of an adsorbent pellet

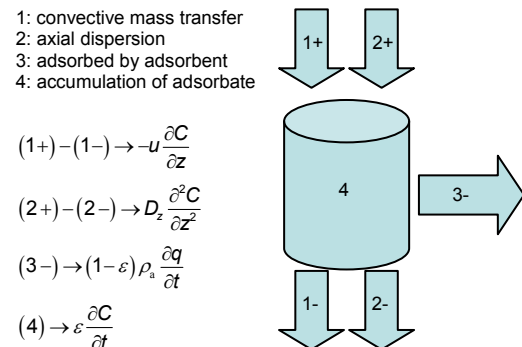


Fig. 2 Schematic diagram of the mass conservation of a control volume

Eqs. (1) and (2) are based on the following assumptions: (1) the process is isothermal; (2) no chemical reaction occurs in the column; (3) the packing material is made of porous particles that are spherical and uniform in size; (4) the bed is homogenous and the concentration gradient in the radial direction of the bed is negligible; (5) the flow rate is constant and invariant with the column position (Warchoř and Petrus, 2006); and, (6) the activity coefficient of each species is unity.

(2) Film diffusion. The driving force of film diffusion is the concentration gradient located at the interface region between the exterior surface of adsorbent pellets and the bulk solution. As the first step of adsorption, film diffusion predominates the overall uptake rate to some extent and even becomes the rate control step in some cases. The flux film diffusion can be expressed in linear form by multiplying its driving force and the phenomenological coefficient (Tien 1994; Fournel *et al.*, 2010):

$$\frac{dq}{dt} = J_f = k_f a(C - C_s), \quad (3)$$

where J_f is the mass transfer flux, a is the volumetric surface area, C_s is the adsorbate concentration at the exterior surface of adsorbent, and k_f is the film diffusion coefficient. It is generally known that increasing the flow rate will decrease the film thickness and resistance, whereas larger film resistance can be caused by packing with smaller adsorbent pellets due to the extension of the exterior surface area.

(3) Intrapellet diffusion and reaction. As shown in Fig. 3, surface diffusion and pore diffusion proceed in parallel accompanying with Knudsen diffusion and the adsorption reactions. Of note, when the pore size is only slightly larger than the diameter of adsorbate ions or molecules, the Knudsen diffusion begins to play a significant role as shown in Fig. 3b.

Generally speaking, the film diffusion driven solely by the concentration gradient can be expressed in a routine form (Eq. (3)), and the intrapellet diffusion, which is more complex and diverse, is the key-stone of modeling dynamic adsorption. Pore diffusion, surface diffusion and reaction are involved in intrapellet transfer simultaneously, and a set of equations could be set to consider all the possible mechanisms. Moreover, consideration of the heterogeneity

and Knudsen diffusion will tend to cause dramatic complexity and make the process very tedious. Hence, it is urgent to simplify such a process by making appropriate assumptions based on specific characteristics of the system, and several models were proposed based on different simplifications indeed.

Most mathematical models to predict a breakthrough curve have (or are acquired by) the same composition, i.e., (a) macroscopic mass conservation equation; (b) adsorption kinetic equation (sometimes including a set of equations); and (c) equilibrium relationship. Among these composition, (a) and (b) have been briefly discussed above. Logically, we introduce the equilibrium relationship (isotherm) in the following sections.

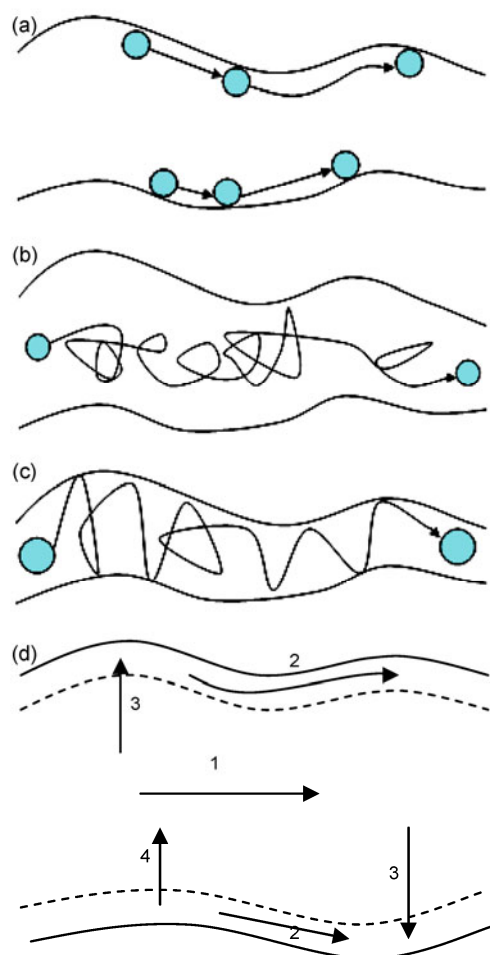


Fig. 3 Macroscopic schematic illustration of basic diffusion and adsorption steps inside the pore

(a) Surface diffusion; (b) Pore diffusion; (c) Pore diffusion with significant Knudsen diffusion; (d) Combination of intrapellet diffusion and adsorption. 1: pore diffusion; 2: surface diffusion; 3: adsorption; 4: desorption

2 Single-component isotherms

As we have illustrated, the general way to predict the breakthrough curve is to solve a set of partial differential equations which consist of a macroscopic mass conservation equation, uptake rate equation (sometimes including a set of equations), and isotherm equation. Obviously, as a prerequisite of modeling of the dynamic adsorption, the choice of the isotherm style will directly affect the effect of mathematic modeling. Although several methods have been adopted to determine the isotherm, the most widely used one is the conventional static method proceeding in a closed system. Actually, due to the complexity of the structure of adsorbent and the interaction between each corpuscle, isotherms can present diverse shapes. As shown in Fig. 4, Giles *et al.* (1960) classified different isotherms into four types (S, L, H and C types). Malek and Farooq (1996) suggested that there are three fundamental means to formulate an isotherm: dynamic equilibrium between adsorption and desorption, thermodynamic equilibrium between phases and species, and adsorption potential theory. Although researchers have developed various isotherm models in the past decades, it is clear that none of them fit well with all cases, and thus, one has to determine the best suitable isotherm experimentally. Morgenstern (2004) reviewed the means to derive the isotherm by both batch method and adsorption-desorption method. Here we do not intend to give a detailed discussion of various isotherms but only concisely introduce several widespread models.

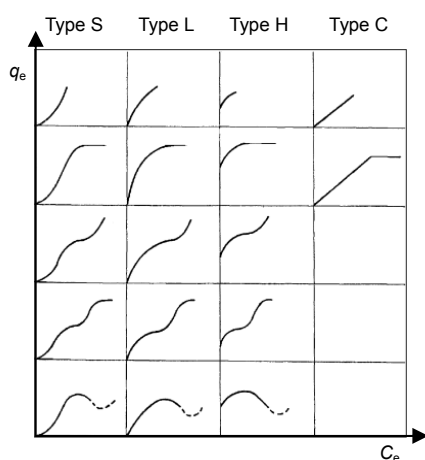


Fig. 4 Adsorption isotherms classified by Giles *et al.* (1960)

2.1 Langmuir isotherm

The Langmuir isotherm assumes: (1) the adsorption process takes place as monolayer adsorption (chemical adsorption); (2) the surface of adsorbent pellets or each adsorption site is homogeneous; and, (3) the adsorption heat does not vary with the coverage. In other words, in terms of the Langmuir isotherm, adsorption takes place when a free adsorbate molecule collides with an unoccupied adsorption site and each adsorbed molecule has the same percentage to desorption (Langmuir, 1916). The model can be written as

$$q_e = \frac{q_m b C_e}{1 + b C_e}, \quad (4)$$

where q_e is the value of q at equilibrium, q_m is the maximum adsorptive capacity, C_e is the concentration of adsorbate in liquid phase at equilibrium, and b is the Langmuir constant. Certainly, we can obtain a linear form of the Langmuir model

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}, \quad (5)$$

where

$$b = k_a / k_d, \quad (6)$$

where k_a refers to the adsorption rate coefficient of the Langmuir kinetic model, and k_d is the desorption rate coefficient (Azizian, 2004). Despite the reversible adsorption nature of the Langmuir model, it sometimes fits irreversible adsorption well. Because of its simple form and well fitting performance, the Langmuir isotherm has become one of the most popular models in adsorption studies.

2.2 Freundlich isotherm

Another most widely used model is the Freundlich isotherm. Comparing with the Langmuir isotherm, the Freundlich isotherm does not have much limitation, i.e., it can deal with both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption. Especially, this model frequently succeeds in depicting the adsorption behavior of organic compounds and reactive matters. The Freundlich isotherm is expressed as

$$q_e = KC_e^{1/n}, \quad (7)$$

and its linear form is

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e, \quad (8)$$

where K and n are the parameters to be determined. Though the Freundlich isotherm is one of the earliest empirical correlation, it could be deduced from the assumption that $Q_a = Q_{a,0} - a_f \ln \theta$, where Q_a is the differential heat of adsorption, θ is the coverage, $Q_{a,0}$ is the value of Q_a at $\theta=0$, and a_f is a constant. According to (Haghseresht and Lu, 1998), the surface heterogeneity and type of adsorption can be roughly estimated by the Freundlich parameters.

2.3 Other isotherms

Besides the above two isotherms, adsorption equilibrium can also be described by other isotherms such as the Sips model (Sips, 1948), Toth model (Toth, 1971), and the Brunauer-Emmett-Teller (BET) model (Brunauer *et al.*, 1938). One must note that the lower prevalence of these isotherms do not mean less functionality, e.g., the Dubinin-Radushkevich isotherm is able to calculate the mean adsorption free energy from which the prediction of adsorption type is available (Dubinin and Radushkevich, 1947); the Temkin isotherm allows one to estimate the effect of temperature (Temkin and Pyzhev, 1940). The single-component isotherms have been summarized in several studies (Foo and Hameed, 2010). Depending on the linear expression of each isotherm, all the isotherm parameters could be acquired by linear regression, and several commonly used error functions are outlined in Table 1.

3 Multi-component isotherms

When a variety of pollutants is present with the target pollutant in solution, the equilibrium relationship of any component may not fit the single-component isotherms since competitive adsorption occurs between different species. In order to solve the problem, multi-component isotherms were developed, among which the ideal adsorbed solution theory (IAST) model based on the equivalence of the spreading pressure, π , of each component is one of the most reliable iso-

therms (Myers and Prausnitz, 1965; Radke and Prausnitz, 1972; Hand *et al.*, 1985). Namely,

$$\pi_i = \pi_j. \quad (9)$$

The spreading pressure is a surface chemistry terminology referring to the difference of surface tension of the solvent-solid interface and solutions-solid interface. According to the Gibbs adsorption formula

$$\Gamma_i = \frac{1}{RT} \frac{d\pi_i}{\ln a_i}, \quad (10)$$

where Γ_i is the adsorptive capacity per surface area of species i , R is the ideal gas constant, T is the temperature, and a_i is the activity of solute i . Assuming that the activity coefficient of each solute is unity, and a_i could be substituted by C_i which refers to the concentration of solute i . Thus, we can rewrite Eq. (10) as (Myers and Prausnitz, 1965)

$$\pi_i(C_i) = \frac{RT}{a} \int_0^{C_i} \frac{q_i}{C_i} dC_i, \quad (11)$$

or

$$\pi_i(q_i) = \frac{RT}{a} \int_0^{q_i^*} \frac{d \log C_i}{d \log q_i} dq_i, \quad (12)$$

where q_i^* and C_i^* are respectively the solid phase and liquid phase concentrations of species i to generate the surface tension that is equal to π_i . Eqs. (13)–(18)

Table 1 Lists of some widely used error functions

Method	Expression
Sum squares errors	$\sum_{i=1}^n (X_{\text{cal}} - X_{\text{exp}})_i^2$
Mean sum of the percent errors	$\frac{100}{n} \sum_{i=1}^n \left \frac{X_{\text{cal}} - X_{\text{exp}}}{X_{\text{exp}}} \right _i$
Hybrid fractional error function	$\frac{100}{n-p} \sum_{i=1}^n \left \frac{X_{\text{cal}} - X_{\text{exp}}}{X_{\text{exp}}} \right _i$
Marquardt's percent standard deviation	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{X_{\text{cal}} - X_{\text{exp}}}{X_{\text{exp}}} \right)_i^2}$

n is the number of data point, p is the number of parameter, X_{cal} is the calculated value of parameter X , and X_{exp} is the measured value of parameter X by the experiment

are indispensable to solve the IAST model (Myers and Prausnitz, 1965; Radke and Prausnitz, 1972; Lo and Alok, 1996)

$$C_i = z_i C^*, \quad (13)$$

$$\frac{1}{q_T} = \sum_i^N z_i / q_i, \quad (14)$$

$$q_i = z_i q, \quad (15)$$

$$q_T = \sum_i^N q_i, \quad (16)$$

$$\sum_i^N z_i = 1, \quad (17)$$

$$q_i = f(C_i), \quad (18)$$

where z_i is the molar fraction of species i , and N is the number of the species in mixture. Eq. (18) denotes the isotherm of a single-compound solution of solute i . Sometimes modification of the IAST model is required to better represent some specific adsorption systems such as solutions containing humic substances (Weber and Smith, 1987). Some other isotherms are shown in Table 2.

4 Modeling of fixed-bed adsorption

As one of the most prevalent techniques for separation and purification, fixed-bed adsorption has been widely applied for its high efficiency and easy operation. How to optimize the design and operation conditions of the fixed-bed adsorption is obviously an important issue to be focused on. Given the fact that experimental determination of the adsorption performance under diverse conditions is usually expensive and time-consuming, development of mathematical models to predict fixed-bed adsorption is necessary. An ideal model should be mathematically convenient, be able to give an exact estimation of the breakthrough behavior, and evaluate the effect of each variable on adsorption.

A dynamic adsorption model usually consists of a macroscopic mass conservation equation, uptake rate equation(s) and isotherm. Considering the different components of the adsorption systems (solvents, adsorbate, adsorbent), variable operation conditions and specific demands of accuracy and calculative simplicity, it is an important but challenging task to propose a general use model, because most

Table 2 Lists of some multi-component isotherms

Expression	Description	Reference
$q_{e,i} = \frac{q_m b_i C_{e,i}}{1 + \sum_i^N b_i C_{e,i}}$	Multi-component Langmuir isotherm	(Silva <i>et al.</i> , 2010)
$q_{e,i} = \frac{q_m b_i (C_{e,i})^{k_i}}{1 + \sum_i^N b_i (C_{e,i})^{k_i}}$	Multi-component Langmuir-Freundlich isotherm	(Ruthven, 1984)
$q_{e,1} = \frac{q_{m,2} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} + \frac{(q_{m,1} - q_{m,2}) b_1 C_{e,1}}{1 + b_1 C_{e,1}}$	Assume the maximum adsorptive capacity of species 1 is higher than species 2 and the surplus part is treated as single-component adsorption	(Jain and Snoeyink, 1973)
$q_{e,2} = \frac{q_{m,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}}$		
$q_{e,1} = \frac{q_m b_1 C_{e,1} [1 + (K' / b_1) C_{e,2}]}{1 + b_1 C_{e,1} + b_2 C_{e,2} + 2K C_{e,1} C_{e,2}}$	Postulate formation of Ad-M ₁ -M ₂ , Ad is the adsorbent, and M ₁ and M ₂ represent species 1 and 2.	(Chong and Volesky, 1995)
$q_{e,2} = \frac{q_m b_2 C_{e,2} [1 + (K' / b_2) C_{e,1}]}{1 + b_1 C_{e,1} + b_2 C_{e,2} + 2K'' C_{e,1} C_{e,2}}$		
$q_1 = \frac{n_1 R_{sm} K_1 C_1^{n_1}}{1 + K_1 C_1^{n_1} + K_2 C_2^{n_2}}, \quad q_2 = \frac{n_2 R_{sm} K_2 C_2^{n_2}}{1 + K_1 C_1^{n_1} + K_2 C_2^{n_2}}$	Assume that adsorption of species M ₁ and M ₂ follows	(Xue <i>et al.</i> , 2009)
$K_1 = \frac{[R_s M_{1n_1}]}{[M_1]^{n_1} [R_s]}, \quad K_2 = \frac{[R_s M_{2n_2}]}{[M_2]^{n_2} [R_s]}$	$n_1 M_1 + R_s \rightleftharpoons R_s M_{1n_1}$ $n_2 M_2 + R_s \rightleftharpoons R_s M_{2n_2}$	

b_i, K', K'' and k_i are the model constants, R_s refers to the an active adsorption site, and R_{sm} is the total amount of the active adsorption sites

models derived from different assumptions are only suitable for a limited situation but fail to describe others. In this section, some widely used models are presented and discussed to choose proper models when needed. Note that, toward the solution of unknown composition, a full illustration of modeling was provided elsewhere (Crittenden *et al.*, 1985) and here, we do not intend to discuss that case.

4.1 General rate models

Based on the assumption that the rate of intrapellet diffusion is described by Fick's Law, some different expressions of general rate models were developed, such as the pore diffusion model (PDM), homogeneous surface diffusion model (HSDM), and pore and surface diffusion model (PSDM).

PDM can be described as (Du *et al.*, 2008)

$$\varepsilon \frac{\partial C}{\partial t} + \rho \frac{\partial q}{\partial t} = \frac{\rho D_{ep}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right), \quad (19)$$

with the initial and boundary conditions as

$$\begin{aligned} 0 \leq z \leq H, 0 \leq r \leq r_p, t = 0 \rightarrow q &= 0, \\ r = 0 \rightarrow \frac{\partial q}{\partial r} &= 0, \\ r = r_p \rightarrow D_{ep} \left(\frac{\partial q}{\partial r} \right)_{r=r_p} &= k_f a (C - C_s), \end{aligned}$$

where ρ is the bed density, r_p is the radius of adsorbent pellets, D_{ep} refers to the effective pore diffusion coefficient, and r is the distance to the centre of the pellet.

The basic mathematic form of HSDM is (Tien, 1994)

$$\varepsilon \frac{\partial C}{\partial t} + \rho \frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right), \quad (20)$$

with its initial and boundary conditions as

$$\begin{aligned} 0 \leq z \leq H, 0 \leq r \leq r_p, t = 0 \rightarrow q &= 0, \\ r = 0 \rightarrow \frac{\partial q}{\partial r} &= 0, \\ r = r_p \rightarrow \rho D_s \left(\frac{\partial q}{\partial r} \right)_{r=r_p} &= k_f a (C - C_s), \end{aligned}$$

where D_s is the surface diffusion coefficient.

In addition, PSDM can be represented as (Liu *et al.*, 2010)

$$\varepsilon \frac{\partial C}{\partial t} + \rho \frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) + \frac{\rho D_{ep}}{r^2} \left(r^2 \frac{\partial q}{\partial r} \right), \quad (21)$$

with its specific initial and boundary conditions of

$$\begin{aligned} 0 \leq z \leq H, 0 \leq r \leq r_p, t = 0 \rightarrow q &= 0, \\ r = 0 \rightarrow \frac{\partial q}{\partial r} &= 0, \\ r = r_p \rightarrow \left[\left(D_{ep} + D_s \rho \frac{dq}{dC} \right) \frac{\partial C}{\partial r} \right]_{r=r_p} &= k_f a (C - C_s). \end{aligned}$$

Due to the fact that $\rho \frac{\partial q}{\partial t}$ is usually much higher than $\varepsilon \frac{\partial C}{\partial t}$, the latter term was neglected in most cases.

With distinct rate control step(s) of different systems, the appropriate type of the general rate models should be applied, including the film-pore diffusion model, film-surface diffusion model and film-pore/surface diffusion model. Reasonably, the film diffusion can be neglected when the film mass transfer resistance is quite small (i.e., negligible concentration gradient in the film). However, additional experiments should be performed to ensure that film diffusion is not a rate control step. Note that among Eqs. (19)–(21), the term of the surface reaction rate is not involved in most cases because it is much faster than other diffusion steps. Sometimes the surface reaction should be considered when it significantly affects the total adsorption rate or even becomes the sole rate control step. Plazinski *et al.* (2009) made a comprehensive review of sorption kinetics including surface reaction mechanism.

When a proper liquid phase continuity equation (Eq. (1) or (2)), film diffusion equation (Eq. (3)), intrapellet diffusion equation, and isotherm equation are available, it is possible to generate the breakthrough curve by solving these partial differential equations. Note that several parameters in the general rate models can be determined both theoretically and experimentally. The theoretical method is based on some basic correlations (Roberts *et al.*, 1985;

Crittenden *et al.*, 1986; Weber and Smith, 1987; Wolborska, 1989b; Tien, 1994; Sperlich *et al.*, 2005; Worch, 2008) and part of them are listed in Table 3, whereas the accuracy of estimation values of the parameters is not satisfactory. Especially, to our knowledge, there is no reliable method to theoretically predict the tortuosity τ and surface diffusion coefficient D_s , which are indispensable when using the general rate models. Thus, for trustworthy prediction, it is inevitable to use the experimental method to determinate these parameters.

To directly solve the general rate models is usually a time-consuming and computationally troubled work. Some convenient methods such as the finite difference method and orthogonal collocation method (Mathews and Weber, 1977; Kaczmariski and Antos, 1996; McKay, 2001; Finlayson, 2003; Lee and McKay, 2004) were developed to obtain the numerical solution with the aid of several computational softwares.

Except for PDM, HSDM and PSDM, some other models based on Fick's law were also available and summarized in Table 4.

Table 3 Some basic correlations to determine the parameters of the general rate models

Parameter	Correlation	Condition	Reference
Bulk liquid diffusivity of the adsorbate, D_M	$D_M \eta / T = 7.4 \times 10^{-8} (\beta M)^{0.5} / V_m^{0.6}$	—	(Wilke and Chang, 1955)
	$D_M = \frac{0.01498 T^{1.81} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P(T_{C_i} T_{C_j})^{0.1405} (V_{m_i}^{0.4} V_{m_j}^{0.4})^2}$	—	(Puértolas <i>et al.</i> , 2010)
	$D_M = \frac{3.595 \times 10^{-14} T}{\eta M^{0.53}}$	—	(Worch, 1993)
Film (external) diffusivity, k_f	$Sh = \frac{1.1}{\varepsilon} Pe^{1/3}$	—	(Tan <i>et al.</i> , 1975)
	$Sh = \frac{1.09}{\varepsilon} Pe^{1/3}$	$0.0016 < \varepsilon Re < 55$; $950 < Sc < 70000$	(Wilson and Geankoplis, 1966)
	$Sh = 2 + 1.58 Re^{0.4} Sc^{1/3}$	$0.001 < Re < 5.8$	(Ohashi <i>et al.</i> , 1981)
	$Sh = 2 + 1.21 Re^{0.5} Sc^{1/3}$	$5.8 < Re < 500$	
	$Sh = 2 + 0.59 Re^{0.6} Sc^{1/3}$	$Re > 500$	
	$Sh = 2.4 \varepsilon Re^{0.3} Sc^{0.42}$	$0.08 < Re < 125$; $150 < Sc < 1300$	(Williamson <i>et al.</i> , 1963)
	$Sh = \frac{0.325}{\varepsilon Re^{0.36} Sc^{1/3}}$	—	(Ko <i>et al.</i> , 2003)
	$Sh = 2 + 1.1 Re^{0.6} Sc^{1/3}$	$3.0 < Re < 10000$	(Wakao and Funazkri, 1978)
	$Sh = 1.85 [(1 - \varepsilon) / \varepsilon]^{1/3} Re^{1/3} Sc^{1/3}$	$Re [\varepsilon / (1 - \varepsilon)] < 100$	(Kataoka <i>et al.</i> , 1972)
	$Sh = (2 + 0.644 Re^{1/2} Sc^{1/3}) [1 + 1.5(1 - \varepsilon)]$	—	(Chern and Chien, 2002)
	$Sh = \left[2 + (Sh_L^2 + Sh_T^2)^{0.5} \right] [1 + 1.5(1 - \varepsilon)]$	$Re Sc > 500$; $Sc < 12000$	(Gnielinski, 1978)
	$Sh_L = 0.644 Re^{1/2} Sc^{1/3}$		
	$Sh_T = (0.037 Re^{0.8} Sc) / \left[1 + 2.443 Re^{-0.1} (Sc^{2/3} - 1) \right]$		
Knudsen diffusion coefficient, D_k	$D_k = 9700 r_{ap} \sqrt{\frac{T}{M}}$	—	(Scott and Dullien, 1962)
Pore diffusion coefficient, D_p	$D_p = \varepsilon D_M / \tau$	—	—
Effective pore diffusion coefficient, D_{ep}	$\frac{1}{D_{ep}} = \frac{1}{D_p} + \frac{1}{D_k}$	—	—

η is the dynamic viscosity, r_{ap} is the average pore radius of adsorbent, M is the molecular weight, β is the association constant of the solvent and $\beta=2.6$ for water and 1.5 for ethanol, V_m is the molar volume of solute at normal boiling point, and T_c is the critical temperature

Table 4 Lists of some general rate type models

Modification	Assumption	Equation	Reference
Macropore diffusion and micropore diffusion (in series)	Postulating each adsorbent pellet is composed of a core with micropore ($0 < r < r_c$) and outer region with macropore ($r_c < r < r_p$)	<p>Diffusion equation of macropore region:</p> $\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[(D_e)_{\text{Ma}} r^2 \frac{\partial q}{\partial r} \right], \quad r_c \leq r \leq r_p;$ <p>Diffusion equation of micropore region:</p> $\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[(D_e)_{\text{mi}} r^2 \frac{\partial q}{\partial r} \right], \quad 0 \leq r \leq r_c;$ <p>Mass conservation at the interface:</p> $(D_e)_{\text{Ma}} \left(\frac{\partial q}{\partial r} \right)_{r \rightarrow r_c^+} = (D_e)_{\text{mi}} \left(\frac{\partial q}{\partial r} \right)_{r \rightarrow r_c^-}$	(Tien, 1994)
Macropore diffusion and micropore diffusion (in parallel)	The so-called branched pore kinetic model applies to adsorption processes controlled by the pore-surface diffusion. Divide the adsorbent pellet into two regions, micropore and macropore region, and assume both of them array parallel	<p>Diffusion equation of macropore:</p> $f \frac{\partial q_{\text{Ma}}}{\partial t} = f \frac{1}{r^2} \frac{\partial}{\partial r} \left[(D_e)_{\text{Ma}} r^2 \frac{\partial q_{\text{Ma}}}{\partial r} \right] - R_b;$ <p>Diffusion equation of micropore:</p> $(1-f) \frac{\partial q_{\text{mi}}}{\partial t} = (1-f) \frac{1}{r^2} \frac{\partial}{\partial r} \left[(D_e)_{\text{mi}} r^2 \frac{\partial q_{\text{mi}}}{\partial r} \right] + R_b;$ <p>Total adsorption amount:</p> $q = f q_{\text{Ma}} + (1-f) q_{\text{mi}};$ <p>Transfer rate of solute from macropore to micropore:</p> $R_b = k_b (q_{\text{Ma}} - q_{\text{mi}})$	(Peel <i>et al.</i> , 1981; Yang and Al-Duri, 2001; Ko <i>et al.</i> , 2002)
Shrinking core theory model	This model used to describe the intrapellet adsorption is controlled by pore diffusion, supposing adsorption firstly occurs at the outer region of adsorbent, then the mass transfer zone moves inward together with the extending of saturated outer region and shrinking of unloaded core (Fig. 5)	<p>The mass transfer flux at the solid-liquid phase interface:</p> $J = 4\pi r_p^2 k_f (C - C_e);$ <p>Diffusion in the pore of adsorbent (Fick's Law):</p> $J = \frac{4\pi C_e r_p r_c D_{\text{ep}}}{r_p - r_c};$ <p>The velocity of the mass transfer zone:</p> $\frac{dr_c}{dt} = -\frac{J}{4\pi r_c^2 \rho q_c};$ <p>The mean concentration of adsorbed solute:</p> $\bar{q} = q_c [1 - (r_c / r_p)^3]$	(Ko <i>et al.</i> , 2001; Quek and Al-Duri, 2007; Traylor <i>et al.</i> , 2011)
HSDM involved additional reaction	When additional reaction occurs in adsorption process, the conventional HSDM considering only the diffusion mechanism is no longer suitable. For this matter, modification were made to meet the demand	<p>Diffusion and reaction combined equation:</p> $\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial q}{\partial r} \right) - R_r;$ <p>For example, when R_r is expressed by</p> $R_r = K_r (q - q_e);$ <p>The diffusion-reaction rate equation is written as</p> $\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial q}{\partial r} \right) - K_r (q - q_e)$	(Abuzaid and Nakhla, 1997)
General rate model with nonuniform size of particles	This method thinks about the nonuniformity of the size of adsorbent pellets by adding a distribution equation of the particle size	<p>The function of volume particle size distribution for spherical particles is expressed as</p> $f_1(d) = \frac{1}{\sqrt{2\pi}\sigma_s} \exp \left[-\frac{(d-d_a)^2}{2\sigma_s^2} \right],$ <p>or</p> $f_2(d) = \frac{f_1(d)}{1 - \int_{-\infty}^{d_{\min}} f_1(d) \delta d - \int_{d_{\max}}^{\infty} f_1(d) \delta d},$ $\int_{d_{\min}}^{d_{\max}} f_2(d) \delta d = 1$	(Yun <i>et al.</i> , 2004; Du <i>et al.</i> , 2007; 2008)

To be continued

(Table 4)

General rate model with concentration-dependent surface diffusion coefficient	<p>To describe the change of surface diffusion coefficient under different coverage, functions of $D_s(q)$ were proposed. In case 3, according to (Cussler, 1976), the cross-term Fickian diffusivities, D_{12} and D_{21} are usually neglected because they are generally less than 10% of D_{11} and D_{22}</p>	<p>1. $D_s(q) = D_{s0} \exp \left[k_s \left(\frac{q}{q_m} \right) \right];$</p> <p>2. $D_s(q) = D_{s0} \frac{\partial \ln C}{\partial \ln q};$</p> <p>3. For binary system,</p> $\frac{\partial q_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \left(D_{s,ii} \frac{\partial q_i}{\partial r} + D_{s,ij} \frac{\partial q_j}{\partial r} \right) \right],$ $D_{s,ij}(q) = D_{s0,i} \left(\frac{q_i}{q_j} \right) \frac{\partial C_i}{C_i} / \frac{\partial q_j}{q_j}$	(Neretnieks, 1976; Ko et al., 2005; Lee et al., 2005; Jia and Lua, 2008)
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$(D_e)_{Ma}$: effective diffusion coefficient of macropore region; $(D_e)_{mi}$: effective diffusion coefficient of micropore region; R_b : branched pore kinetic model rate constant; q_{Ma} : adsorbed concentration of the macropore zone; q_{mi} : adsorbed concentration of the micropore zone; f : volume fraction of the macropore region; K_r : reaction rate coefficient; k_b : model kinetic coefficient; k_s : model constant; r_c : critical radius; σ_s : standard deviation of the particles; d : diameter of the adsorbent pellets; d_a : average diameter of the adsorbent pellets; D_{s0} : surface diffusion coefficient when the coverage is zero (self-diffusivity)

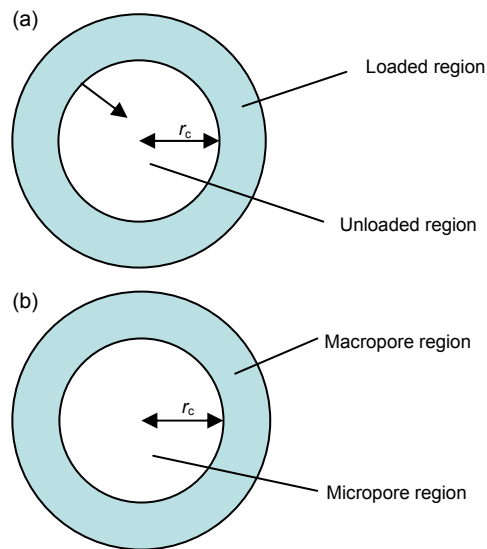


Fig. 5 Schematic diagram of branched pore kinetic model (a) and shrinking core theory model (b)

A review of surface diffusion is available elsewhere (Medved and Cerny, 2011), which might provide some ideas to modify the intrapellet diffusion models.

The prevalence of the conventional/modified general rate models is not only because they give good prediction of dynamic adsorption, but also involves a variety of parameters to determine the process variables. The variables could be optimized by keeping other parameters constant and comparing the breakthrough curves predicted by this model under different values of the target parameter “X”, for example, $0.5X$, X and $2X$ (Note that adjusting a

parameter may lead to variation in the phenomenological coefficient(s), and optimization based on modeling is not a precise method). However, the main limitation of these models is the complicated and time-consuming computation.

4.2 Linear driving force (LDF) model

The linear driving force (LDF) model proposed by (Glueckauf, 1955) formulates a lumped mass transfer coefficient to represent the intrapellet diffusion rate, as written in a linear form as

$$\frac{dq}{dt} = k_e (q_s - q_a), \quad (22)$$

where q_a is the average concentration of the adsorbed adsorbate, q_s is the loading of the adsorbate at the external surface of adsorbent, and k_e is the lump intrapellet diffusion kinetic coefficient. The original LDF model regards that q_s in equilibrium corresponds to the concentration of the bulk solution C . In other words, it neglected the concentration gradient in the interface region between the liquid phase and adsorbent, and k_e is a function of intrapellet diffusivity. When the mass transfer within the interface is involved, the film diffusion equation should be added into the LDF model, namely

$$\frac{dq}{dt} = k_f a (C - C_s). \quad (23)$$

Combining Eqs. (22) and (23) with the liquid phase mass conservation equation and proper isotherm, it is possible to predict the breakthrough curve. Hence, the LDF model can be used to estimate the coefficients k_e and k_f . Similar to the general rate models, these parameters can be acquired by the theoretical and experimental ways. For the theoretical way, a widely accepted expression is written as (Glueckauf, 1955)

$$k_e = \frac{15D_e}{r_p^2}. \quad (24)$$

When intrapellet diffusion is dominated by pore diffusion

$$k_e = \frac{15D_p}{f'(C)\rho r_p^2}. \quad (25)$$

While by surface diffusion

$$k_e = \frac{15D_s}{r_p^2}. \quad (26)$$

An empirical equation of the rate constant was developed previously (Heese and Worch, 1997; Worch, 2008)

$$k_e = 0.00129 \left[D_M C_F / (r_p^2 q_F) \right]^{1/2}, \quad (27)$$

where D_e is the effective intrapellet diffusion coefficient involving both surface diffusion and pore diffusion, $f'(C)$ is related to the isotherm. Except for D_s and D_e , all the parameters are available by directly measuring or referring to the corresponding isotherms.

Note that $\frac{dq}{dc}$ is not constant if the isotherm is nonlinear (i.e., does not obey Henry's Law). Hence, to obtain the value of D_e , an average value has to be applied to represent $f'(C)$. As for D_s , it can be reckoned by combining Eqs. (26) and (27):

$$\frac{15D_s}{r_p^2} = 0.00129 \left[D_M C_F / (r_p^2 q_F) \right]^{1/2}, \quad (28)$$

and then calculate D_e by

$$D_e = D_s + D_p / (f'(C)\rho). \quad (29)$$

The calculated kinetic parameters sometimes fit well with the experimental data, but conspicuous deviation may appear in other cases. For instance, the theoretical value is often much higher than the experimental result when the dissolved organic matter (DOM) is adsorbed. In that case, the theoretical method could just approximately reckon the adsorption performance, and the parameters have to be determined by the experimental breakthrough curves.

Another expression of the LDF model is available by incorporating Eqs. (22) and (23)

$$\frac{\partial q}{\partial t} = k_o (q_s - q_a), \quad (30)$$

where k_o is the overall kinetic constant combining both the film diffusivity and the intrapellet diffusivity. Both expressions of the LDF model have widespread application (Murillo *et al.*, 2004; Borba *et al.*, 2006; Puértolas *et al.*, 2010; Silva *et al.*, 2010). Additionally, surface reaction was also involved in LDF in some cases (Szukiewicz, 2000; 2002). Computational software is often required to derive the numerical solution of the LDF model, especially when the isotherm is in the nonlinear form. Nevertheless, as compared to the general rate models, the LDF model could reduce the computational time significantly and its accuracy was generally acceptable. Hence, the LDF model has become one of the most widely used models now. For some recent developments of the LDF model one could refer to the work by Gholami and Talaie (2010). The limitations of the LDF model were also discussed elsewhere (Nakao and Suzuki, 1983; Do and Mayfield, 1987; Yao and Tien, 1993; Zhang and Ritter, 1997), such as the limited applicability of the conventional expression of k_e in many systems.

4.3 Wave propagation theory

A novel method to evaluate the service volume (or service time) was proposed by (Helfferich and Klein, 1970). They defined the wave velocity as the velocity of a given value of a variable and made an analog to explain the concept of wave (Helfferich and

Carr, 1993), from which one can easily deduce the “concentration velocity” as

$$u_c = \left(\frac{\partial z}{\partial t} \right)_c = - \frac{\left(\frac{\partial C}{\partial t} \right)_z}{\left(\frac{\partial C}{\partial z} \right)_t}, \quad (31)$$

where u_c is the velocity of the “concentration wave”. The liquid phase continuity equation applied in the wave propagation theory can be expressed as

$$\rho \frac{\partial q}{\partial t} + \varepsilon \frac{\partial C}{\partial t} + u_i \varepsilon \frac{\partial C}{\partial z} = 0, \quad (32)$$

where u_i is the interstitial velocity. Combining Eqs. (31) and (32), we can obtain:

$$u_c = \frac{u_i}{1 + \frac{\rho}{\varepsilon} \left(\frac{dq}{dC} \right)}. \quad (33)$$

Assuming the adsorption rate is infinite (i.e., Local equilibrium), $\frac{dq}{dC}$ is available to be calculated by the corresponding isotherm

$$q_e = f(C_e). \quad (34)$$

Especially, for a self-sharpening wave, the wave velocity is calculated by

$$u_c = \frac{u_i}{1 + \frac{\rho}{\varepsilon} \left(\frac{\Delta q}{\Delta C} \right)}. \quad (35)$$

For better understanding of the terminologies “self-sharpening” and “non-sharpening”, one can refer to some previous works where the chromatographic phenomena were discussed in detail (Helfferich and Klein, 1970; Helfferich, 1984; Helfferich and Carr, 1993; Helfferich and Whitley, 1996; Chern and Huang, 1999). From the wave velocity the breakthrough volume (or service time) can be calculated, for the self-sharpening wave (Chern and Huang, 1999)

$$\frac{V_{bk}}{V_b} = \varepsilon \left(1 + \frac{\rho}{\varepsilon} \frac{\Delta q}{\Delta C} \right) = \varepsilon \left(1 + \frac{\rho}{\varepsilon} \frac{q_F - q}{C_F - C} \right); \quad (36)$$

for non-sharpening wave

$$\frac{V_{bk}}{V_b} = \varepsilon \left(1 + \frac{\rho}{\varepsilon} \frac{dq}{dC} \right), \quad (37)$$

where V_{bk} is the breakthrough volume, and V_b is the bed volume. Apparently, this ingenious method brings considerably mathematical convenience to predict an adsorption system and the only information needed is the isotherm. Once the isotherm information ($\frac{dq}{dC}$ or $\Delta q/\Delta C$) is available, the service time can be directly calculated by Eq. (36) or Eq. (37). On the other hand, the hypothesis of the infinite mass transfer velocity is too arbitrary when the flow rate is not so slow, and the results calculated from the wave theory may deviate from the experimental data notably. Moreover, when the molecular diffusion cannot be neglected or Eq. (2) is used as the liquid phase continuity equation, the service time cannot be acquired by the wave velocity.

4.4 Constant pattern theory

Even though the wave propagation theory has limited range of application due to the harsh premise, wave propagation is still an interesting concept in modeling. Luckily, the constant pattern theory including the “wave” velocity offers another approach to predict the breakthrough curve. When one assumes that a self-sharpening wave moves at a constant rate in column, τ , the adjusted time, can be represented as (Chern and Chien, 2002; Pan *et al.*, 2005)

$$\tau = t - \frac{z}{u_c}. \quad (38)$$

The liquid phase continuity equation is

$$\rho \frac{\partial q}{\partial t} + \varepsilon \frac{\partial C}{\partial t} + u_i \varepsilon \frac{\partial C}{\partial z} = 0. \quad (39)$$

Substituting Eq. (38) into Eq. (39), we can obtain

$$\left(1 - \frac{u_i}{u_c}\right)C + \frac{\rho}{\varepsilon}q = 0. \quad (40)$$

Thus, an important relationship can be deduced

$$\frac{C_1}{C_2} = \frac{q_1}{q_2}, \quad (41)$$

or

$$\frac{C}{C_F} = \frac{q}{q_F}. \quad (42)$$

Combining with the isotherm $q_e = f(C_e)$ leads to

$$C_e = f^{-1}(Cq_F / C_F). \quad (43)$$

The overall mass transfer equation can be expressed as

$$\rho \frac{dq}{d\tau} = \varepsilon K_L a (C - C_e), \quad (44)$$

where K_L is the overall kinetic constant, and $a = 3(1 - \varepsilon)/r_p$. After integrating Eq. (43) with Eq. (44) and rearranging, we obtain

$$t = t_{1/2} + \frac{\rho q_F}{\varepsilon K_L a C_F} \int_{C_{F/2}}^C \frac{1}{C - f^{-1}(q_F C / C_F)} dC, \quad (45)$$

where $t_{1/2}$ is the time when the concentration of adsorbate in the effluent reaches half of that in the feeding solution, q_F is the value of q in equilibrium with C_F . Combining Eq. (45) with a specific isotherm, the breakthrough curve can be generated, for example, with the Langmuir isotherm

$$t = t_{1/2} + \frac{\rho q_m}{\varepsilon K_L a C_F} \left[\ln 2x + \frac{1}{1 + bC_F} \ln \frac{1}{2(1-x)} \right], \quad (46)$$

or with the Freundlich isotherm

$$t = t_{1/2} + \frac{\rho K C_F^{n-1}}{\varepsilon K_L a} \int_{1/2}^x \frac{1}{x - x^{1/n}} dx. \quad (47)$$

Rewriting

$$\left(\frac{dx}{dt}\right)_{x=0.5} = \frac{\varepsilon K_L a}{\rho K C_F^{n-1}} (x - x^{1/n}), \quad (48)$$

where $x = C/C_F$. In some cases the constant pattern model works in a transcendental way. This is because, when film diffusion is the only rate control step of adsorption, the value of K_L is close to the external diffusion coefficient k_f , which could be estimated by the corresponding correlation listed in Table 4. Unfortunately, adsorbent of microporous structure usually has great intrapellet resistance, leading to the limited application of the method. Chern *et al.* (2002) related the volumetric film diffusion mass transfer coefficient to the volumetric flow rate Q

$$k_f a = k_1 + k_2 Q^{1/2}. \quad (49)$$

Kananpanah *et al.* (2009) also proposed that

$$k_f a = k_1 + k_2 Q^{n'}, \quad (50)$$

$$k_f a = k_1 e^{k_2 Q}, \quad (51)$$

$$k_f a = k_1 + k_2 e^{k_3 Q}, \quad (52)$$

where specific parameters k_1 , k_2 , k_3 and n' can be acquired by fitting the experimental data. Eqs. (49)–(52) pave a way to predict the performance under different volumetric flow rates, but it is not suitable to predict the performance of the adsorption systems with no experimental data. The main functions of the constant pattern theory are: (1) to determine valuable information such as ρ , ε , q_F , C_F , and isotherm; (2) to read $t_{1/2}$ through dynamic adsorption; and, (3) to determine $K_L a$ by proper methods. For instance, when the isotherm follows the Freundlich model, according to Eq. (48), $K_L a$ can be obtained from the tangent slope of x vs. t at $x = 1/2$. When the Langmuir isotherm is better to describe the equilibrium relationship, $K_L a$ can be calculated by the slope of the plot of $\ln 2x + [1/(1 + bC_F)] \ln [1/(2 - 2x)]$ vs. t (Eq. (46)); and, (4) to generate the complete breakthrough curve by integrating $K_L a$ into a corresponding equation. The constant pattern model gives outstanding prediction of the breakthrough curve in numerous studies. Yet, when the adsorption rate is dominated by the intrapellet diffusion, prediction by this model sometimes deviates from the real situation.

4.5 Clark model

As is well known, granular active carbon (GAC) is one of the most popular adsorbents with micropore structure. US EPA even initiated a series of field studies to evaluate the performance of GAC and acquired sufficient data. Based on the data from US EPA, Clark (1987) developed a model to predict the performance of GAC-organic compounds adsorption system. The Clark model was deduced based on the following equations and assumptions (Clark, 1987).

(1) Liquid phase continuity equation is

$$J = \frac{Q_A AC - Q_A A(C - \Delta C)}{A \Delta z}. \quad (53)$$

(2) The shape of the mass-transfer zone is constant and all the adsorbates are removed at the end of the column,

$$Q_A C = u_a q_F. \quad (54)$$

(3) The isotherm fits the Freundlich type:

$$q_e = KC^{1/n}. \quad (55)$$

(4) Expression of the adsorption rate is

$$J = Q_A \frac{dC}{dz} = K_T (C - C_e), \quad (56)$$

where J is the mass-transfer rate per unit reactor volume, A is the column cross-section area, Q_A is the volumetric flow rate per unit of cross-section area, u_a is the mass velocity of the adsorbent to maintain the mass-transfer zone stationary, ΔC is the incremental change of concentration, and Δz is the differential reactor height.

The final expression of Clark model is

$$\left(\frac{C_{in}^{n-1}}{1 + B e^{-r't}} \right)^{1/(n-1)} = C, \quad (57)$$

$$B = \left(\frac{C_{in}^{n-1}}{C_b^{n-1}} - 1 \right) e^{r't_b}, \quad (58)$$

$$r' = (n-1) \frac{K_T}{Q_a} \frac{dz}{dt}, \quad (59)$$

where C_b is the breakthrough concentration, t_b is the service time, and C_{in} is the constant influent value on the carbon bed. The following procedures should be completed prior to using the model.

- (1) Determine n by the batch experiment;
- (2) Rearrange Eq. (58) into

$$\ln \left[\left(\frac{C_F}{C} \right)^{n-1} - 1 \right] = -r't + \ln B. \quad (60)$$

(3) The slope and intercept of the plot $\ln[(C_F/C)^{1/n} - 1]$ vs. t allow one to solve r' and B , respectively;

(4) Generate the whole breakthrough curve.

It is clear that the mass conservation equation in the column is different from those discussed above. We find that Eq. (53) actually disregards the accumulation of adsorbate concentration. In other words, it does not reflect the time difference between C and $C + \Delta C$. If taking a controlled volume V (the volume passing through any cross-section per unit time) into consideration and postulating the uniformity of the control volume and negligible molecular diffusion, we obtain

$$\varepsilon V C_{z,t} - \rho V J \Delta t = \varepsilon V C_{z+\Delta z, t+\Delta t}. \quad (61)$$

When $\Delta t \rightarrow 0$, then

$$\varepsilon V C_{z,t} - \rho V J dt = \varepsilon V C_{z+dz, t+dt}. \quad (62)$$

Additionally

$$C_{z+dz, t+dt} = C_{z,t} + \frac{\partial C}{\partial z} dz + \frac{\partial C}{\partial t} dt. \quad (63)$$

Cancelling Vdt of Eq. (62) and combining Eq. (63)

$$\rho J = -u_t \varepsilon \frac{\partial C}{\partial z} - \varepsilon \frac{\partial C}{\partial t}. \quad (64)$$

Obviously, Eq. (64) is the same with Eq. (32), while deleting the term of $dt \frac{\partial C}{\partial t}$ will lead to Eq. (53). The same conclusion can also be made when

assuming $\rho_a(1-\varepsilon)\left(\frac{\partial q}{\partial t}\right) + u\left(\frac{\partial C}{\partial z}\right) \gg \varepsilon\left(\frac{\partial C}{\partial t}\right)$.

However, the Clark model has successfully predicted a variety of systems and even those not following this assumption. As mentioned above, the dynamic adsorption is such a complicated process that it is almost impossible to give a complete description of each variable. Actually, even the “most theoretically rigorous” general rate models are still simplified from the real situations, such as the distribution of adsorbent pellets with different size in the column, the wall effect, the mass transfer caused by momentum transfer and heat transfer. Moreover, by mathematical fitting, each phenomenological coefficient could be adjusted to the optimal values, which would compensate for the inherent shortages of the model to some extent. Thus, it is still rational to suppose the Clark model has good performance under different conditions.

4.6 Thomas model

The Thomas model is another one frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming the second-order reversible reaction kinetics and the Langmuir isotherm (Han *et al.*, 2008; Ghasemi *et al.*, 2011). Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small (Aksu and Gönen, 2004). The Thomas model is given by

$$\ln\left(\frac{C_F}{C} - 1\right) = \frac{k_{Th}q_F m}{Q} - k_{Th}C_F t, \quad (65)$$

where k_{Th} is the Thomas rate constant, m is the mass of adsorbent in the column. With several couples of m and Q , k_{Th} and q_F values derived through a plot of $\ln[(C_F/C)-1]$ vs. t , further prediction and design is then available. Eq. (65) can also be expressed as

$$\ln\left(\frac{C_F}{C} - 1\right) = k'(t - t_1), \quad (66)$$

where $k' = k_{Th}C_F$ and $t_1 = q_F m / (QC_F)$. The general version of Eq. (66) is represented as (Pearl, 1977; Lin *et al.*, 2002)

$$\ln\left(\frac{C_F}{C} - 1\right) = b_0 + b_1 t + b_2 t^2 + \dots = \sum_i b_i t^i. \quad (67)$$

This equation is applied when $\ln[(C_F/C)-1]$ vs. t is not in linear form. By fitting the experimental data, the corresponding parameters b_i can be calculated. Generally, it is adequately accurate to employ the former three terms. It is worth noting that q_F derived from the experiment is often conspicuously different from the value acquired by equilibrium calculation, and the bed adsorptive capacity is often determined from the dynamic adsorption (Brauch and Schlunder, 1975; McKay, 1984; McKay and Al-Duri, 1988; Ko *et al.*, 2000).

4.7 Bohart-Adams model and bed depth service time (BDST) model

Bohart and Adams (1920) came up with the Bohart-Adams (B-A) model when they proceeded with their work of analyzing the typical chlorine-charcoal transmission curve. They hypothesized that the uptake rate of chlorine is proportional to the concentration of the chlorine existing in the bulk fluid and the residual adsorptive capacity of charcoal, from which the following two equations are obtained:

$$\frac{\partial C}{\partial z} = -\frac{k_B q_r C}{u}, \quad (68)$$

$$\frac{\partial q_r}{\partial t} = -k_B q_r C, \quad (69)$$

where q_r is the residual adsorptive capacity, and k_B is the kinetic constant of the Bohart-Adam model.

Additionally

$$\begin{cases} t = 0 \rightarrow \frac{q_r}{q_m} = 1, \\ z = 0 \rightarrow \frac{C}{C_F} = 1. \end{cases}$$

Finally, the basic form of the B-A model was obtained:

$$\ln\left(\frac{C_F}{C} - 1\right) = \ln\left[\exp\left(k_B q_m \frac{H}{u}\right) - 1\right] - k_B C_F t. \quad (70)$$

If $\exp(k_B q_m H/u)$ is much larger than 1, Eq. (70) can be reduced and rearranged as

$$t = \frac{q_m}{C_F u} H - \frac{1}{k_B C_F} \ln\left(\frac{C_F}{C} - 1\right). \quad (71)$$

Eq. (71) is the so-called bed depth service time model proposed by Hutchins (1973). Note that the B-A model (or bed depth service time (BDST) model) involves several important variables of adsorption system such as C_F , u , q_m , and H , and approximate estimation of the effect of each parameter from both models is achievable. As two widely used models in practice, the B-A and BDST models succeeded in predicting several breakthrough curves and optimizing the parameters, although it is relatively rough (Ayoob *et al.*, 2007; Bhakat *et al.*, 2007; Maji *et al.*, 2007; Han *et al.*, 2008; Srivastava *et al.*, 2008).

Both the B-A and BDST models have seven parameters, among which C_F and u can be determined before the dynamic adsorption experiment. For the B-A model, the height of the fixed bed (i.e., the height of packing adsorbent), H , is a constant and can be directly measured. Subsequently, different C and corresponding t are obtained through the dynamic adsorption experiment, and then a plot of $\ln(C_F/C-1)$ vs. t should theoretically be a straight line. After linear regression, q_m and k_B can be calculated from the tangent slope and intercept, respectively. In terms of calculated q_m and k_B , prediction of adsorption performance at different process variables is available based on Eq. (70). As for the application of the BDST model, similar to the B-A model, after determining the demand concentration of the effluent solution, q_m and k_B can be worked out by a straight line of t vs. H . Then, the adsorption efficiency under various conditions can be predicted. Actually, q_m and k_B are not constant when the variable(s) is changed, which may lead to unsatisfactory prediction. Especially, at 50% breakthrough, $C/C_F=0.5$ and $t=t_{1/2}$, and Eq. (71) changes to

$$t_{1/2} = \frac{q_m H}{C_F u}. \quad (72)$$

Hence, q_m can be calculated by plotting $t_{1/2}$ vs. H . By rearranging Eq. (71) into proper form or giving specific values to parameters, the BDST model is frequently employed as a powerful tool to find the optimal operation condition. More recently, Ko *et al.* (2000) came up with a method to optimize the BDST model, where the bed adsorptive capacity q_m is substituted by a modified correlation,

$$q_t = q_m [1 - \exp(-a_r \sqrt{t})]. \quad (73)$$

Integrating into Eq. (68)

$$t = m' [1 - \exp(-a_r \sqrt{t})] z + b', \quad (74)$$

where q_t is the adsorptive capacity of column at time t , a_r is the rate parameter, $m' = q_m / (C_F u)$, and $b' = -[1/(k_B C_F)] \ln[(C_F/C)-1]$. This method provides a way to approximately evaluate the significance of both film diffusion and intraparticle diffusion. The intraparticle mass transfer rate is proportional to the square-root of the residence time when the sorption process is controlled by intraparticle diffusion (McKay, 1979),

$$\frac{a_1}{a_2} = \sqrt{\frac{t'_1}{t'_2}} = \sqrt{\frac{u_2}{u_1}}. \quad (75)$$

According to the correlation proposed by (Wilson and Geankoplis, 1966),

$$Sh = \frac{1.09}{\varepsilon} Pe^{1/3}. \quad (76)$$

Namely

$$\frac{a_1}{a_2} = \left(\frac{u_1}{u_2} \right)^{2/3} = \left(\frac{u_2}{u_1} \right)^{-2/3}. \quad (77)$$

Combining Eq. (75) and Eq. (77), one can obtain

$$\frac{a_1}{a_2} = \left[\left(\frac{u_2}{u_1} \right)^{1/2} \right]^{p_i} \left[\left(\frac{u_2}{u_1} \right)^{-2/3} \right]^{p_f} = \left(\frac{u_2}{u_1} \right)^{p'}, \quad (78)$$

where p_i , p_f reflect the fractions of the overall uptake rate influenced by intraparticle diffusion and film diffusion, respectively. Thus,

$$\begin{cases} 0.5 p_i - \frac{2}{3} p_f = p', \\ p_i + p_f = 1, \end{cases}$$

where p' is determined by fitting the experimental data so that p_i and p_f are acquired subsequently.

4.8 Yoon-Nelson model

The Yoon-Nelson model is extremely concise in form, supposing that the decrease in the probability of each adsorbate to be adsorbed is proportional to the probability of its adsorption and breakthrough on the adsorbent (Yoon and James, 1984). It can be represented by

$$\ln \frac{C}{C_F - C} = K_{YN}t - t_{1/2}K_{YN}, \quad (79)$$

where K_{YN} is the Yoon-Nelson rate constant. By plotting $\ln[C/(C_F - C)]$ vs. t , K_{YN} and theoretical $t_{1/2}$ are reckoned. The Yoon-Nelson model not only has a more simple form than other models, but also requires no detailed data concerning the characters of adsorbate and adsorbent, as well as the parameters of the fixed bed (Hamdaoui, 2006). Also, as limited by its rough form, the Yoon-Nelson model is less valuable or convenient to obtain process variables and to predict adsorption under variety conditions.

4.9 Wang model

Wang *et al.* (2003) developed a mass transfer model to describe the breakthrough curve of solutions containing Co or Zn ions in the fixed bed on the basis of the following assumptions

- (1) The adsorption process remains isothermal;
- (2) The mass transfer equation is written as

$$-\frac{dy}{dt} = k_w xy, \quad (80)$$

where k_w is the kinetic constant, y is the fraction of the adsorbed metal ions, and x is the fraction of metal ions passing through the fixed bed, with $x+y=1$.

- (3) The breakthrough curve is symmetrical; and,
- (4) There is negligible axial dispersion in the column.

Presuming $y=y_w$ at $t=t_w$ and integrating Eq. (80), one can obtain

$$\ln[x(1-x_a)/x_a(1-x)] = k_w(t_a - t). \quad (81)$$

Let $w=0.5$, then $y_w=y_{1/2}=x_{1/2}$, $t_w=t_{1/2}$. Combining the above parameters with Eq. (81)

$$t = t_{1/2} - \frac{1}{k_w} \ln\left(\frac{1}{1-x}\right), \quad (82)$$

where x can be expressed as

$$x = C / C_F. \quad (83)$$

Substituting Eq. (83) into Eq. (82), t should be in direct proportion to $\ln[(C_F/C)-1]$. A plot of $\ln[(C_F/C)-1]$ vs. t produces the slope and intercept value as $1/k_w$ and $t_{1/2}$, respectively. Then the entire breakthrough curve can be obtained based on Eq. (82). This model was successfully applied in some cases (Wang *et al.*, 2003; Araneda *et al.*, 2011). Meanwhile, similar to the Yoon-Nelson model, it cannot provide sufficient information of an adsorption system.

4.10 Other models

4.10.1 Wolborska model

Wolborska (1989a) and Wolborska and Pustelnik (1996) analyzed the adsorption of *p*-nitrophenol on activated carbon and found that the initial segment of the breakthrough curve is controlled by film diffusion with constant kinetic coefficient, and the concentration profile of the initial stage moves axially in the column at a constant velocity. Moreover, the width of concentration profile in the column and the final breakthrough curve were nearly constant. Based on above observations, they developed a model to describe the breakthrough at low concentration region, which was written as

$$\ln \frac{C}{C_F} = \frac{\beta_L C_F \varepsilon}{\rho q_F} t - \frac{\beta_L H}{u}, \quad (84)$$

where β_L is the film diffusivity, which can be determined from the initial linear section of the breakthrough curve in the semi-logarithmic system through experiment or correlations.

4.10.2 Modified dose-response model

This model was initially developed for pharmacology studies and recently used to describe adsorption of metals in some cases (Yan *et al.*, 2001; Senthilkumar *et al.*, 2006; Araneda *et al.*, 2011). The modified dose-response model can be written as

$$\frac{C}{C_F} = 1 - \frac{1}{1 + \left(\frac{C_F Q t}{q_F m} \right)^{a'}} \quad (85)$$

After rearrangement, it could be written as

$$\ln \frac{C}{C_F - C} = a' \ln(C_F Q t) - a' \ln(q_F m), \quad (86)$$

where a' is the model parameter. Similar to other models, a' and q_F could be determined by plotting $\ln[C/(C_F - C)]$ vs. $\ln(C_F Q t)$.

5 Conclusions

Fixed-bed or column adsorption is the most popular option in practical application of adsorption process, and due to the complexity of a column adsorption system and lack of solid theory, its mathematical modeling is obviously more difficult than batch adsorption. To choose or develop a suitable model, accuracy and convenience should be considered simultaneously. Currently, although some effort had been made to complete these models (especially the general rate models and LDF model), each model has its inherent shortages and requires further development. The general rate models (and “general rate type” models) and LDF model generally fit well with the experimental data for most cases, but they are relatively time-consuming. Other models including the wave propagation theory, Bohart-Adams model, Yoon-Nelson model, Thomas model, Wang model, Wolborska model, and modified dose-response model could be applicable without isotherm information, but they are derived from specific situations and limited in space. The Clark model is suitable to describe column adsorption obeying the Freundlich isotherm and do not show conspicuously better accuracy than the above models. The constant pattern model is relatively convenient to apply and gives satisfactory prediction, but it cannot be readily employed for adsorption predominated by intrapellet diffusion. In addition, experimental work is always required to determine the isotherm and dynamic model as well as the related parameters. Moreover, when the breakthrough curve deviates from the ideal S shape, prediction derived from any model usually cannot meet our demand.

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Introducing editorial board member:

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