R&D NOTE

Analytical Breakthrough Curves for Inert Core Adsorbent with Sorption Kinetics

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From the kinetics viewpoint, the general rate model is the most general model of fixed-bed adsorber. In this model, the axial dispersion and all the mass-transfer resistances are taken into account, namely (1) the external mass transfer of adsorbate from the bulk phase to the external surface of the adsorbent; (2) the diffusion transport through the pores of the adsorbent; and (3) the adsorption−desorption kinetics at the active sites. The effects of various mass-transfer resistances on the breakthrough curves can be predicted separately by the general rate model. Based on the works of Rosen (1952) and Massaldi and Gottifredi (1972), the exact time domain solution of the general rate model under the linear adsorption kinetics has been derived to predict the breakthrough curves when the fixed-bed adsorber is packed with the conventional spherical/cylinder adsorbent (Rasmuson, 1981; Xiu, 1996). The solutions just mentioned are invalid for predicting the breakthrough curves in the case of inert core adsorbent.

Binding-ligand inert core adsorbents are being widely used for bioseparations, for example, the expanded bed for proteins separation (Bertrand et al., 1998; Owen and Chase, 1999; Ozyurt et al., 2002), and it may be used in fast, high-performance liquid chromatography (HPLC) due to its short diffusion path, which results in low intraparticle diffusion resistance for biological macromolecules (Lee, 1997; Rodrigues, 1997; Hunter and Carta, 2000). One example of such adsorbents is the Poroshell 5-μm particle with a thin layer of porous silica on a solid core used for fast, high-resolution protein separation (Agilent Technologies, 2001; Kirkland et al., 2000). Although the loading capacity of the columns packed with the inert core adsorbent is relatively low, the ability to quickly recover biological macromolecules with high biological activity overcomes this shortcoming; the latter is very important for the production of biological macromolecules in the pharmaceutical and biotechnology industries. In addition, for the rapid separation of biological macromolecules, the slow adsorption−desorption rate at the active sites caused by steric hindrance of biological macromolecules (Corsel et al., 1986; Cramer and Subramanian, 1990; Whitley et al., 1991; Frey and Vilfan, 2002) will affect the column behavior; therefore, the general rate model will be more effective for modeling the rapid separation process of biological macromolecules using the fixed-bed adsorber.

In this article, we extend the general rate model to the fixed-bed adsorber packed with inert core adsorbent. A general exact solution is derived under the linear adsorption kinetics to predict the breakthrough curves for the inert core adsorbent. The effects of the size of the inert core, the axial dispersion, external mass-transfer resistance, intraparticle diffusion resistance, and the adsorption−desorption rate on the breakthrough curves are evaluated by the exact solution. For simplification, a simple parabolic approximate solution is also derived.

Mathematical Model

The fixed-bed and the inert core adsorbent are shown in Figure 1. Here we consider an isothermal adsorption column packed with porous inert core particles. A step change in the concentration of an adsorbate was introduced to a flowing stream at time zero. The adsorption column was subjected to axial dispersion, external mass-transfer resistance, intraparticle diffusion resistance, and adsorption−desorption kinetics. The following assumptions are made: (1) Fick's law of diffusion governs both the axial dispersion in the bulk fluid phase within the column and the transport within the adsorbent particles; (2) the axial fluid velocity in the column is constant; (3) the adsorbent consists of a core of uniform thickness on a spherical particle that is inert and impenetrable to solution, and the outer layer undergoes negligible swelling or shrinking during sorption (Chanda and Rempel, 1999, 2001).

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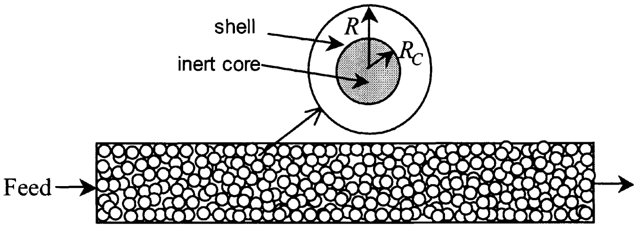

R: radius of adsorbent; R_C: radius of adsorbent core

Figure 1. Fixed-bed adsorber and inert-core adsorbent.

Based on the preceding assumptions, the fixed-bed adsorber can be described by the following set of equations. The material balance equation for bulk phase is

$$D_L \frac{\partial^2 C}{\partial Z^2} - \frac{u}{\epsilon_B}\frac{\partial C}{\partial Z} - \frac{\partial C}{\partial t} - \frac{(1-\epsilon_B)}{\epsilon_B}\frac{3}{R}\epsilon_S D_p \left(\frac{\partial c}{\partial r}\right)_{r=R} = 0 \tag{1}$$

where D_L is the axial dispersion coefficient; C is the concentration in the fluid phase; u denotes superficial velocity; c is the concentration in the adsorbent pore; D_p is pore diffusivity of adsorbate; ϵ_B denotes the fraction void volume in the column, hence, $(1-\epsilon_B)$ denotes the fractional volume taken up by the solid phase; ϵ_S is the shell porosity, Z is the axial distance from column entrance, r is the radial distance of the adsorbent, R is the radius of the adsorbent, and t is the time.

The mass balance in the adsorbent shell is

$$\epsilon_S \frac{\partial c}{\partial t} + \rho_S \frac{\partial q}{\partial t} = \epsilon_S D_p \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \quad (R_C \le r \le R) \tag{2}$$

where q is the concentration in adsorbed phase, ρ_S is the density of adsorbent shell, and R_C is the radius of adsorbent inert core.

Linear adsorption kinetics is assumed for reversible adsorption

$$\rho_S \frac{\partial q}{\partial t} = k_{ads}\left(c - \frac{q}{K}\right) \tag{3}$$

where k_{ads} is the kinetic constant for adsorption, and K is the Henry equilibrium constant.

Equation 3 is a standard Langmuir adsorption–desorption kinetic expression written with the additional assumption that solute loading is sufficiently low at all times so that the number of available sites for adsorption does not change as the solute moves through the column.

The initial and boundary conditions for Eqs. 1 and 2 are

$$C(Z,0) = 0 \tag{4}$$

$$C(0,t) = C_0 \quad \text{(step input)} \tag{5}$$

$$C(\infty,t) \quad \text{is limited} \tag{6}$$

$$c(r,Z,0) = 0 \tag{7}$$

$$q(r,Z,0) = 0 \tag{8}$$

$$\left(\frac{\partial c}{\partial r}\right)_{r=R_C} = 0 \tag{9}$$

$$\epsilon_S D_p \left(\frac{\partial c}{\partial r}\right)_{r=R} = k_f[C-(c)_{r=R}] \tag{10}$$

Arrange the preceding equations in dimensionless form as

$$\frac{1}{Pe}\frac{\partial^2 y}{\partial \zeta^2} - \frac{\partial y}{\partial \zeta} - \theta\frac{\partial y}{\partial \tau} - 3\theta\nu\left(\frac{\partial x}{\partial \xi}\right)_{\xi=1} = 0 \tag{11}$$

$$\frac{\partial x}{\partial \tau} + \xi_m \frac{\partial w}{\partial \tau} = \frac{\partial^2 x}{\partial \xi^2} + \frac{2}{\xi}\frac{\partial x}{\partial \xi} \quad (\xi_C \le \xi \le 1) \tag{12}$$

$$\frac{\partial w}{\partial \tau} = \psi(x-w) \tag{13}$$

$$y(\zeta,0) = 0 \tag{14}$$

$$y(0,\tau) = 1 \quad \text{(step input)} \tag{15}$$

$$y(\infty,\tau) \quad \text{is limited} \tag{16}$$

$$x(\xi,\zeta,0) = 0 \tag{17}$$

$$w(\xi,\zeta,0) = 0 \tag{18}$$

$$\left(\frac{\partial x}{\partial \xi}\right)_{\xi=\xi_C} = 0 \tag{19}$$

$$\left(\frac{\partial x}{\partial \xi}\right)_{\xi=1} = Bi[y-(x)_{\xi=1}]. \tag{20}$$

The dimensionless variables are

$x = \frac{c}{C_0}$, $w = \frac{q}{KC_0}$, $y = \frac{C}{C_0}$ dimensionless concentrations

in adsorbent pore, adsorbed phase, and bulk fluid phase

$\xi = \frac{r}{R}$ dimensionless radial distance

$\zeta = \frac{Z}{L}$ dimensionless axial distance

and the model parameters are

$\nu = \left(\frac{1-\epsilon_B}{\epsilon_B}\right)\epsilon_S$ porosity ratio

$\xi_m = \frac{K\rho_S}{\epsilon_S}$ capacity factor

$Bi = \dfrac{k_f R}{\epsilon_S D_p}$ Biot number

$\theta = \dfrac{L D_p \epsilon_B}{u R^2}$ ratio of time constants for convection in outer fluid and pore diffusion

$Pe = \dfrac{uL}{\epsilon_B D_L}$ Pelect number based on adsorber length

$\tau = \dfrac{D_p t}{R^2}$ dimensionless contact time

$\psi = \dfrac{k_{ads} R^2}{D_p K \rho_S}$ dimensionless adsorption rate constant

Exact analytical solution

According to Eq. 13, in the Laplace domain we have

$$\overline{w} = \frac{\psi \bar{x}}{p + \psi} \tag{21}$$

in which the overbar indicates the Laplace transform, and p is the Laplace transform parameter.

Combined Eq. 13 with Eq. 12

$$\frac{\partial^2 \bar{x}}{\partial \xi^2} + \frac{2}{\xi}\frac{\partial \bar{x}}{\partial \xi} - \lambda^2 \bar{x} = 0 \quad (\xi_C \le \xi \le 1) \tag{22}$$

where

$$\lambda = \sqrt{\frac{\xi_m \psi p}{\psi + p} + p} \tag{23}$$

Taking the boundary condition, Eq. 19, into account the solution of Eq. 22 is

$$\bar{x} = \frac{\sinh[\lambda(\xi - \xi_C)] + \lambda \xi_C \cosh[\lambda(\xi - \xi_C)]}{[\cosh(\lambda \xi_C) - \lambda \xi_C \sinh(\lambda \xi_C)]} \left(\frac{m_1}{\lambda \xi} \right) \tag{24}$$

where the integration constant m_1 is calculated from Eq. 20 as

$$m_1 = Bi\bar{y} \frac{\lambda[\cosh(\lambda \xi_C) - \lambda \xi_C \sinh(\lambda \xi_C)]}{\lambda(1 + Bi\xi_C - \xi_C)\cosh[\lambda(1 - \xi_C)] + (\lambda^2 \xi_C + Bi - 1)\sinh[\lambda(1 - \xi_C)]} \tag{25}$$

Thus

$$\left(\frac{\partial \bar{x}}{\partial \xi} \right)_{\xi = 1} = \frac{\lambda(1 - \xi_C)\coth[\lambda(1 - \xi_C)] + (\lambda^2 \xi_C - 1)}{\lambda(1 + Bi\xi_C - \xi_C)\coth[\lambda(1 - \xi_C)] + (\lambda^2 \xi_C + Bi - 1)} Bi\bar{y} \tag{26}$$

Inserting Eq. 26 into Eq. 11, we have the following equation in the Laplace domain

$$\frac{1}{Pe}\frac{\partial^2 \bar{y}}{\partial \zeta^2} - \frac{\partial \bar{y}}{\partial \zeta} - \theta[p + 3\nu G(p)]\bar{y} = 0 \tag{27}$$

where

$$G(p) = \frac{Bi Y_D(p)}{Bi + Y_D(p)} \tag{28}$$

$$Y_D(p) = \frac{\lambda \coth[\lambda(1 - \xi_C)] + \lambda^2 \xi_C}{\lambda \xi_C \coth[\lambda(1 - \xi_C)] + 1} - 1 \tag{29}$$

in which $Y_D(p)$ is the particle transfer function.

The solution in Laplace domain is

$$\bar{y} = \frac{1}{p}\exp(r_1 \zeta) \tag{30}$$

where the transfer function of the system relating outlet and inlet adsorbate concentration in the Laplace domain is

$$r_1 = \frac{Pe}{2} - \sqrt{\frac{1}{4}Pe^2 + \theta Pe[p + 3\nu G(p)]} \tag{31}$$

Finally, the solution in the time domain is as follows

$$y = \frac{1}{2} + \frac{1}{\pi}\int_0^\infty \exp\left(\frac{Pe\zeta}{2} - \zeta\sqrt{\frac{\sqrt{a^2 + b^2} + a}{2}} \right) \sin\left(\beta\tau - \zeta\sqrt{\frac{\sqrt{a^2 + b^2} - a}{2}} \right) \frac{d\beta}{\beta} \tag{32}$$

with

$$a = Pe\left(\frac{Pe}{4} + 3\theta\nu I_1 \right) \tag{33}$$

$$b = \theta Pe(\beta + 3\nu I_2) \tag{34}$$

$$I_1 = \frac{Bi^2 I_3 + Bi(I_3^2 + I_4^2)}{(Bi + I_3)^2 + I_4^2} \tag{35}$$

$$I_2 = \frac{Bi^2 I_4}{(Bi + I_3)^2 + I_4^2} \tag{36}$$

$$I_3 = \frac{\xi_C\left(\phi_1^2 + \phi_2^2\right)\left[\left(H_1^2 + H_2^2\right) + \xi_C(\phi_1 H_1 - \phi_2 H_2)\right] + \xi_C\left(\phi_1^2 - \phi_2^2\right) + (\phi_1 H_1 + \phi_2 H_2)}{\xi_C^2\left(\phi_1^2 + \phi_2^2\right)\left(H_1^2 + H_2^2\right) + 2\xi_C(\phi_1 H_1 + \phi_2 H_2) + 1} - 1 \tag{37}$$

$$I_4 = \frac{\xi_C^2\left(\phi_1^2 + \phi_2^2\right)(\phi_2 H_1 + \phi_1 H_2) + (\phi_2 H_1 - \phi_1 H_2) + 2\xi_C \phi_1 \phi_2}{\xi_C^2\left(\phi_1^2 + \phi_2^2\right)\left(H_1^2 + H_2^2\right) + 2\xi_C(\phi_1 H_1 + \phi_2 H_2) + 1} \tag{38}$$

$$H_1 = \frac{\sinh\left[2\phi_1(1 - \xi_C)\right]}{\cosh\left[2\phi_1(1 - \xi_C)\right] - \cos\left[2\phi_2(1 - \xi_C)\right]} \tag{39}$$

$$H_2 = \frac{\sin\left[2\phi_2(1 - \xi_C)\right]}{\cosh\left[2\phi_1(1 - \xi_C)\right] - \cos\left[2\phi_2(1 - \xi_C)\right]} \tag{40}$$

$$\phi_1 = \sqrt{\frac{\sqrt{c_1^2 + c_2^2} + c_1}{2}} \tag{41}$$

$$\phi_2 = \sqrt{\frac{\sqrt{c_1^2 + c_2^2} - c_1}{2}} \tag{42}$$

$$c_1 = \frac{\xi_m \psi \beta^2}{\psi^2 + \beta^2} \tag{43}$$

$$c_2 = \beta + \frac{\xi_m \psi^2 \beta}{\psi^2 + \beta^2} \tag{44}$$

When $\xi_C \to 0$, the preceding solutions, Eqs. 32–44, become those given by Rasmuson (1981).

If the adsorption rate is much faster than the diffusion rate, that is, ψ is so large that equilibrium exists at all local positions in the adsorbent, adsorption equilibrium may be assumed, that is, $x = w$ (Lloyd and Warner, 1990). In this case, Eqs. 32–36 are still valid for the existing solution, provided that Eqs. 37–44 are replaced by the following equations

$$I_3 = \phi \frac{2\xi_C \phi\left[\left(H_1^2 + H_2^2\right) + \xi_C \phi(H_1 - H_2)\right] + (H_1 + H_2)}{2\xi_C^2 \phi^2\left(H_1^2 + H_2^2\right) + 2\xi_C \phi(H_1 + H_2) + 1} - 1 \tag{45}$$

$$I_4 = \phi \frac{2\xi_C^2 \phi^2 (H_1 + H_2) + (H_1 - H_2) + 2\xi_C \phi}{2\xi_C^2 \phi^2\left(H_1^2 + H_2^2\right) + 2\xi_C \phi(H_1 + H_2) + 1} \tag{46}$$

$$H_1 = \frac{\sinh\left[2\phi(1 - \xi_C)\right]}{\cosh\left[2\phi(1 - \xi_C)\right] - \cos\left[2\phi(1 - \xi_C)\right]} \tag{47}$$

$$H_2 = \frac{\sin\left[2\phi(1 - \xi_C)\right]}{\cosh\left[2\phi(1 - \xi_C)\right] - \cos\left[2\phi(1 - \xi_C)\right]} \tag{48}$$

$$\phi = \sqrt{\frac{(1 + \xi_m)\beta}{2}} \tag{49}$$

Parabolic-profile approximate solution

In order to reduce the complexity of the exact analytical solution, the parabolic concentration profile in the adsorbent has been assumed (Liaw et al., 1979; Rice, 1982; Xiu, 1996; Xiu et al., 1997). In this work, a possible approximation for the parabolic profile in the adsorbent shell is

$$x(\xi, \zeta, \tau) = d_1(\zeta, \tau) + d_s(\zeta, \tau)\xi^2 \quad (\xi_C \le \xi \le 1) \tag{50}$$

Applying the boundary conditions, along with the definition of volume-averaged x, $(x)_{av}$, one obtains

$$\left(\frac{\partial x}{\partial \xi}\right)_{\xi = 1} = \frac{1}{I_5}\left[y - \frac{(x)_{av}}{\left(1 - \xi_C^3\right)}\right] \tag{51}$$

where

$$I_5 = \frac{5\left(1 - \xi_C^3\right) - 3\left(1 - \xi_C^5\right)}{10\left(1 - \xi_C^3\right)} + \frac{1}{Bi} \tag{52}$$

When the governing diffusion equation (Eq. 12) is volume-averaged, we have

$$\frac{\partial (x)_{av}}{\partial \tau} + \xi_m \frac{\partial (w)_{av}}{\partial \tau} = \frac{3}{I_5}\left[y - \frac{(x)_{av}}{\left(1 - \xi_C^3\right)}\right] \quad (\xi_C \le \xi \le 1) \tag{53}$$

Combined with Eq. 13 in the Laplace domain, we finally have the same solution as Eqs. 30 and 31, in which

$$G(p) = \frac{1}{I_5}\left[1 - \frac{1}{1 + \left(\dfrac{\xi_m \psi p}{\psi + p} + p\right)\dfrac{\left(1 - \xi_C^3\right) I_5}{3}}\right] \tag{54}$$

The time-domain solution has the same form as the general solution, Eqs. 32–34, in which I_1, I_2, I_3, and I_4 should be replaced by the following equations

$$I_1 = \frac{1}{I_5}\left(1 - \frac{I_3}{I_3^2 + I_4^2}\right) \tag{55}$$

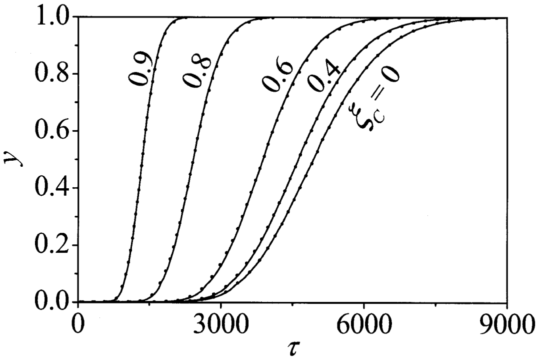

Figure 2. Effect of ξ_C on $y-\tau$ curves at $\theta = 10$, $Pe = 10^2$, $Bi = 10^2$, and $\psi = 10^{-1}$.

Solid lines: exact solution; dotted lines: parabolic approximation.

$$I_2 = \frac{1}{I_5}\left(\frac{I_4}{I_3^2 + I_4^2}\right) \tag{56}$$

$$I_3 = 1 + \frac{(1-\xi_C^3)I_5}{3}\left(\frac{\xi_m \psi \beta^2}{\psi^2 + \beta^2}\right) \tag{57}$$

$$I_4 = \frac{(1-\xi_C^3)I_5}{3}\left(\beta + \frac{\xi_m \psi^2 \beta}{\psi^2 + \beta^2}\right) \tag{58}$$

Discussion and Summary

The integrand of Eq. 32 for both the exact analytical solution and the parabolic-profile approximate solution is the product of an exponential decaying function and a periodic sine function. Integration should be performed over each half-period of the sine wave that was developed by Rasmuson (1985). Usually, the capacity factor, ξ_m, changes from 10^2 to 10^4; in the following discussion, we selected $\xi_m = 10^3$, $\nu = 0.5$, and $\zeta = 1$ (the point at which the breakthrough curve is measured) as an example.

The exact analytical solution, Eq. 32 with Eqs. 33–44, is a general solution by which the breakthrough curves for the inert core adsorbent ($\xi_C > 0$) and conventional adsorbent ($\xi_C = 0$) can be predicted under the linear adsorption kinetics. Figure 2 shows the effect of the parameter ξ_C, which characterizes the inert core adsorbent, on the breakthrough curves. The breakthrough points for the column packed with the inert core adsorbent occur earlier than for one packed with the conventional adsorbent; the shape of the breakthrough curves for the adsorbent with the inert core will become sharper.

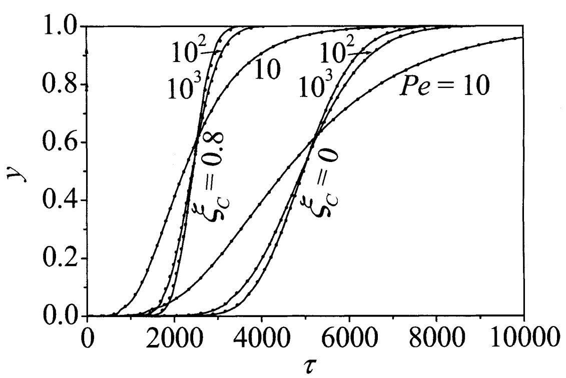

Figure 3. Effects of Pe on $y-\tau$ curves for shell-core adsorbent at $\theta = 10$, $Bi = 10^2$, and $\psi = 10^{-1}$.

Solid lines: exact solution; dotted lines: parabolic approximation.

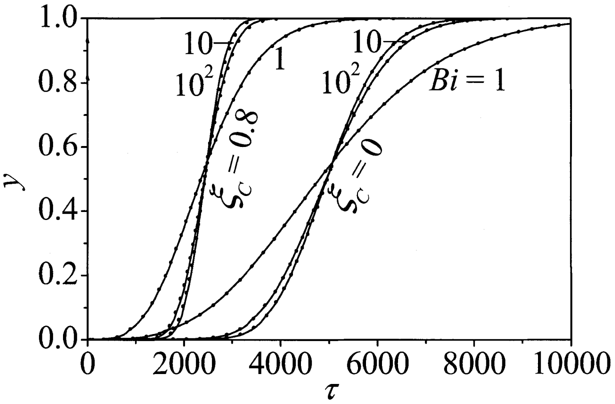

Figure 4. Effects of Bi on $y-\tau$ curves for shell-core adsorbent at $\theta = 10$, $Pe = 10^3$, and $\psi = 10^{-1}$.

Solid lines: exact solution; dotted lines: parabolic approximation.

The effects of the axial dispersion, external mass-transfer resistance, intraparticle diffusion resistance, and the adsorption–desorption rate on the breakthrough curves for the inert core adsorbent can be predicted by the exact analytical solution; the typical results are demonstrated in Figures 3 to 5. The model parameter Pe is usually below 10^3 in a fixed-bed adsorber; the effect of the axial dispersion on the breakthrough curves is not negligible, as shown in Figure 3. The parameter Bi stands for the ratio of the internal resistance to the external resistance for mass transfer in the adsorbent; the effect of Bi on the breakthrough curves is evidence under the given conditions, as shown in Figure 4. The global adsorption rate is controlled by the combined effects of diffusion through the shell void along with the local adsorption rate. The parameter ψ stands for the relative importance of the rate of adsorption and the rate of the pore diffusion. The

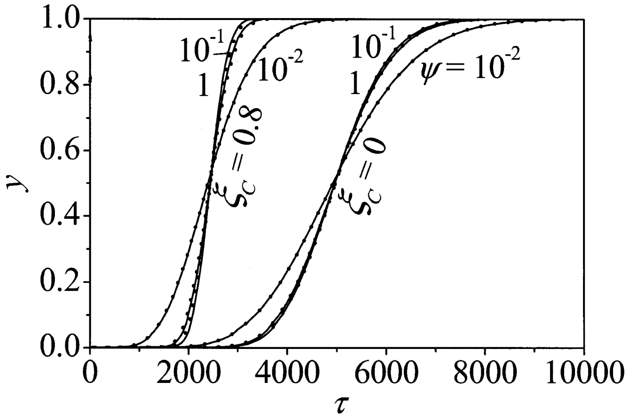

Figure 5. Effect of ψ on $y-\tau$ curves for shell-core adsorbent at $\theta = 10$, $Pe = 10^3$, and $Bi = 10^2$.

Solid lines: exact solution; dotted lines: parabolic approximation.

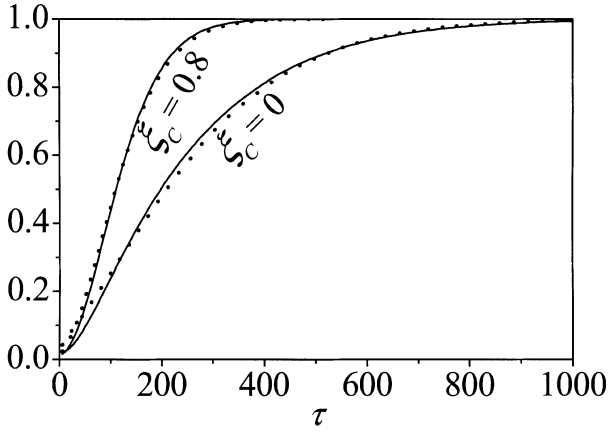

Figure 6. Effect of ξ_C on $y-\tau$ curves for short column ($\theta = 0.5$) at $Pe = 10^3$, $Bi = 10^2$, and $\psi = 10^{-1}$.

Solid lines: exact solution; dotted lines: parabolic approximation.

effect of ψ on the breakthrough curves is shown in Figure 5; it is evident that the effect of ψ can be neglected only when $\psi \geq 10^{-1}$.

Figures 2 to 5 also present the breakthrough curves predicted by the simple parabolic approximate solution; the accuracy of the approximate solution is acceptable—except for the very short column where the intraparticle diffusion resistance is important—and the deviation between the exact analytical solution and the parabolic approximate solution is significant, as shown in Figure 6.

In conclusion, the exact analytical solution derived based on the general rate model can predict the breakthrough curves for the inert core adsorbent where the linear adsorption kinetics coupled with the axial dispersion, external film diffusion resistance, and intraparticle-diffusion resistance. The simple parabolic approximate solution is acceptable for prediction of the breakthrough curves.

Acknowledgments

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