Approximate Models for Nonlinear Adsorption in a Packed-Bed Adsorber

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Diffusion generally plays an important role in the adsorption processes. The diffusion in a porous adsorbent may be described by the pore-diffusion model with a constant effective diffusivity (Rice, 1982; Vermeulen et al., 1984; Park et al., 1987; Haynes, 1988). This model assumes that the adsorbate diffuses in the void fraction of the adsorbent and is adsorbed on the interior surface. An additional assumption is that the adsorption rate is much faster than the diffusion rate, so that equilibrium exists at every local position. The mass balance equation in a spherical adsorbent may be written as

$$\frac{\partial}{\partial t}(q+\epsilon_p c)=De\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \tag{1}$$

with the boundary condition on the external surface,

$$c=c_s \quad \text{or} \quad De\frac{\partial c}{\partial r}=k_f(c_b-c) \quad \text{at} \quad r=R \tag{2}$$

For a linear adsorption isotherm, Eq. 1 becomes

$$(\epsilon_p+K)\frac{\partial c}{\partial t}=De\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \tag{3}$$

In order to reduce computational efforts in solving Eq. 3, some simplifications have been made. Do and Rice (1986) assumed the concentration profile in an adsorbent to be parabolic. With this assumption, an ordinary differential equation for the rate of change in the volume-averaged concentration in an adsorbent can be obtained and is identical to the linear driving force expression (Glueckauf, 1955). The calculated results for a single particle with constant surface concentration were found to agree well with the analytical solutions except at beginning times. To overcome this limitation, a power-law model was proposed by Do and Mayfield (1987) and Do and Nguyen (1988). Although this model could provide better results, the assumption of invariant concentration on the external surface of a particle is in general not the case in fixed-bed operation. To cope with this deficiency, approximate expressions that are similar to the linear driving force equation but account for the rate of change in surface concentration were derived by Kim (1989). With these expressions, more accurate results could be obtained.

When the adsorption isotherm is nonlinear, the lefthand side of Eq. 1 becomes nonlinear. Under this situation, the above-mentioned simplifications may not be directly applied. The object of this note is to develop approximate models for obtaining the transient response for a nonlinear adsorption isotherm in a fixed-bed adsorber. This work may be regarded as an extension of previous work on linear adsorption.

Model Development

The mass balance equation in a spherical particle, Eq. 1, is written in dimensionless form as

$$\frac{\partial Q}{\partial \tau}=\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial C}{\partial x}\right) \tag{4}$$

where Q is the sum of the adsorbates in the void fraction and in the adsorbed phase. The corresponding boundary conditions are

$$\frac{\partial C}{\partial x}=0 \quad \text{at} \quad x=0, \tag{5}$$

$$C=C_s \quad \text{or} \quad \frac{\partial C}{\partial x}=Bi(C_B-C) \quad \text{at} \quad x=1 \tag{6}$$

Contrary to the linear isotherm case, the assumption of a parabolic profile to Q instead of to C is made in this work for mathematical simplicity. This assumption leads to the expression of Q as

$$Q=A+Bx^2 \tag{7}$$

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On the external surface of the particle, we have

$$Q_s = A + B \tag{8}$$

The volume-averaged sum can be written as

$$\overline{Q} = A + \frac{3}{5} B \tag{9}$$

and the mass flux across the external surface can be expressed by

$$\left.\frac{\partial Q}{\partial x}\right|_{x=1} = \left.\frac{dQ}{dC}\right|_{C_s} \left.\frac{\partial C}{\partial x}\right|_{x=1} = 2B \tag{10}$$

Integrating Eq. 4, the rate of change in $\overline{Q}$ becomes

$$\frac{\partial \overline{Q}}{\partial \tau} = 3 \left.\frac{\partial C}{\partial x}\right|_{x=1} = \frac{6B}{\left.\frac{dQ}{dC}\right|_{C_s}} \tag{11}$$

From Eqs. 8 and 9, we obtain the following relation:

$$2B = 5(Q_s - \overline{Q}) \tag{12}$$

Substituting Eq. 12 into Eq. 11, the approximate model assuming a parabolic profile to Q can be obtained, which has the expression

$$\frac{\partial \overline{Q}}{\partial \tau} = \frac{15(Q_s - \overline{Q})}{\left.\frac{dQ}{dC}\right|_{C_s}} \tag{13}$$

If the adsorption isotherm is linear, Eq. 13 reduces to the expression of the linear driving force model. The boundary condition on the external surface to the present model is

$$\frac{5(Q_s - \overline{Q})}{\left.\frac{dQ}{dC}\right|_{C_s}} = Bi(C_B - C_s) \quad \text{at} \quad x = 1 \tag{14}$$

When the profile of Q is assumed to be quartic,

$$Q = A + Bx^2 + Dx^4 \tag{15}$$

then we have

$$Q_s = A + B + D \tag{16}$$

and

$$\overline{Q} = A + \frac{3}{5} B + \frac{3}{7} D \tag{17}$$

Because three unknowns A, B, and D are present, besides Eqs. 16 and 17 an additional equation is required to determine them. For a linear isotherm, this additional equation, suggested by Do and Rice (1986), is the mass balance equation, Eq. 1, at the central point of the particle. But such an approach introduces a new variable, the concentration at the center. Because of the presence of C_s in the model, for the sake of convenience the additional equation is considered to be the mass balance equation on the surface, that is

$$\frac{\partial Q_s}{\partial \tau} = \left.\frac{1}{x^2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial C}{\partial x}\right)\right|_{x=1} \tag{18}$$

From the chain rule and Eqs. 14 to 16, the following expressions may be obtained

$$\left.\frac{\partial C}{\partial x}\right|_{x=1} = \frac{2B + 4D}{\left.\frac{dQ}{dC}\right|_{C_s}} \tag{19}$$

$$\left.\frac{1}{x^2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial C}{\partial x}\right)\right|_{x=1} = \frac{6B + 20D}{\left.\frac{dQ}{dC}\right|_{C_s}} - \frac{\left.\frac{d^2Q}{dC^2}\right|_{C_s}}{\left.\frac{dQ}{dC}\right|_{C_s}} \left(\left.\frac{\partial C}{\partial x}\right|_{x=1}\right)^2 \tag{20}$$

$$6B + 20D = 10 \left.\frac{\partial C}{\partial x}\right|_{x=1} \left.\frac{dQ}{dC}\right|_{C_s} - 35(Q_s - \overline{Q}) \tag{21}$$

$$\frac{\partial Q_s}{\partial \tau} = \left.\frac{dQ}{dC}\right|_{C_s} \frac{\partial C_s}{\partial \tau} \tag{22}$$

Substituting Eq. 21 into Eq. 20 and combining with Eqs. 18 and 22, the rate of change in surface concentration can be obtained as

$$\frac{\partial C_s}{\partial \tau} = \frac{10 \left.\frac{\partial C}{\partial x}\right|_{x=1}}{\left.\frac{dQ}{dC}\right|_{C_s}} - \frac{35(Q_s - \overline{Q}) + \left.\frac{d^2Q}{dC^2}\right|_{C_s} \left(\left.\frac{\partial C}{\partial x}\right|_{x=1}\right)^2}{\left(\left.\frac{dQ}{dC}\right|_{C_s}\right)^2} \tag{23}$$

The rate of change in $\overline{Q}$ is obtained by integration of Eq. 4 and is written by

$$\frac{\partial \overline{Q}}{\partial \tau} = 3 \left.\frac{\partial C}{\partial x}\right|_{x=1} \tag{24}$$

Combining Eqs. 23 and 24 with the boundary condition on the surface results in the basic equations of the present model, which are

$$\frac{\partial C_s}{\partial \tau} = \frac{10Bi(C_B - C_s)}{\left.\frac{dQ}{dC}\right|_{C_s}} - \frac{35(Q_s - \overline{Q}) + \left.\frac{d^2Q}{dC^2}\right|_{C_s} [Bi(C_B - C_s)]^2}{\left(\left.\frac{dQ}{dC}\right|_{C_s}\right)^2} \tag{25}$$

and

$$\frac{\partial \overline{Q}}{\partial \tau} = 3Bi(C_B - C_s) \tag{26}$$

When the adsorption isotherm is linear, Eq. 25 reduces to

$$\frac{\partial C_s}{\partial \tau} = \frac{10Bi(C_B - C_s)}{K} - \frac{35(Q_s - \overline{Q})}{K^2} \tag{27}$$

Combining Eq. 27 with Eq. 26 gives the following expression:

$$\frac{\partial \overline{C}}{\partial \theta} = 10.5(C_s - \overline{C}) + 0.3\frac{\partial C_s}{\partial \theta} \tag{28}$$

Equation 28 is identical to that derived by Kim (1989).

Results and Discussions

In order to check the validity of the approximate models proposed above, the breakthrough curves for a fixed-bed adsorber were calculated. When the Langmuir isotherm is considered, the sum of adsorbates can be written as

$$Q = \frac{KC}{1 + \beta C} + \epsilon_p C \tag{29}$$

Because the amount of adsorbate in the adsorbed phase is generally larger than that in the void fraction, Eq. 29 may be reduced to

$$Q \cong \frac{KC}{1 + \beta C} \tag{30}$$

Substituting Eq. 30 into Eq. 3, we have

$$\frac{\partial C}{\partial \theta} = (1 + \beta C)^2 \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial C}{\partial x}\right) \tag{31}$$

where $\theta = \tau / K$. The mass balance equation for the flowing phase may be expressed by

$$\epsilon_b \frac{\partial c_b}{\partial t} + u\frac{\partial c_b}{\partial z} = \frac{3(1 - \epsilon_b)}{R} k_f (c_s - c_b) \tag{32}$$

In dimensionless form, Eq. 32 becomes

$$\frac{\partial C_B}{\partial Z} = \alpha Bi(C_s - C_B) \tag{33}$$

The initial and boundary conditions are

$$C_B = Q = \overline{Q} = 0 \quad \text{at} \quad \theta = 0 \tag{34}$$

$$C_B = 1 \quad \text{at} \quad Z = 0 \tag{35}$$

Equations 31 to 35 are the basic equations of the pore-diffusion model. The numerical solutions to this model were obtained by applying the orthogonal collocation method to the radial direction x and the cross-integral scheme (Hansen, 1971) and the modified Adams predictor-corrector method to both the Z and θ directions.

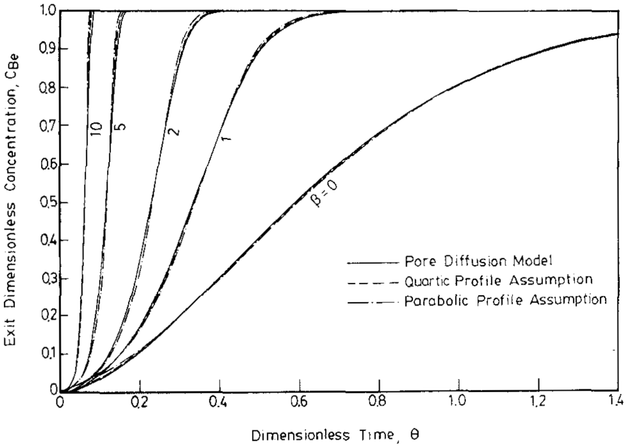

Figure 1. Comparison of proposed models with pore-diffusion model for $Bi = 5$, $\alpha = 2$.

For the approximate model with a parabolic profile assumption, Eqs. 13 and 14 are written as

$$\frac{\partial \overline{Q}'}{\partial \theta} = 15(1 + \beta C_s)^2 \left(\frac{C_s}{1 + \beta C_s} - \overline{Q}'\right) \tag{36}$$

$$5(1 + \beta C_s)^2 \left(\frac{C_s}{1 + \beta C_s} - \overline{Q}'\right) = Bi(C_B - C_s) \tag{37}$$

where $\overline{Q}' = \overline{Q}/K$. Equations 36 and 37 combined with Eqs. 33 and 35 can then be solved by the cross-integral scheme and the modified Adams predictor-corrector method to obtain the breakthrough curves.

When the approximate model is taken with a quartic profile assumption, Eqs. 25 and 26 become

$$\frac{\partial C_s}{\partial \theta} = 10(1 + \beta C_s)^2 Bi(C_B - C_s) - 35(1 + \beta C_s)^4 \left(\frac{C_s}{1 + \beta C_s} - \overline{Q}'\right) + 2\beta(1 + \beta C_s)[Bi(C_B - C_s)]^2 \tag{38}$$

$$\frac{\partial \overline{Q}'}{\partial \theta} = 3Bi(C_B - C_s) \tag{39}$$

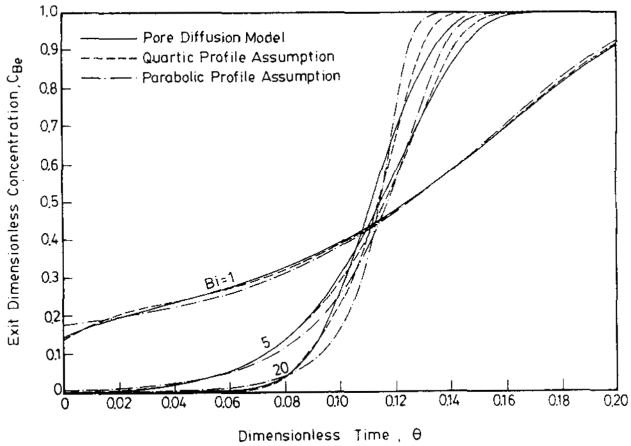

Figure 2. Comparison of proposed models with pore-diffusion model for $\alpha = 2$, $\beta = 5$.

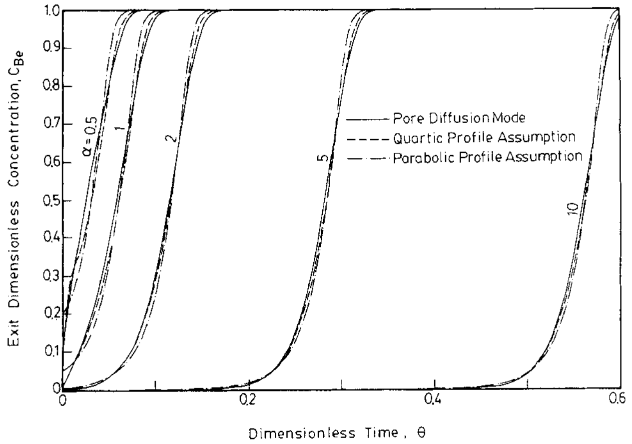

Figure 3. Comparison of proposed models with pore-diffusion model for $\beta = 5$, $Bi = 5$.

The numerical solutions to this model were obtained by solving Eqs. 33, 35, 38, and 39.

The numerical solutions to the pore-diffusion model and the proposed approximate models are shown in Figures 1 to 3. It can be seen that the breakthrough curves calculated by these two approximate models agree well with those of the pore-diffusion model. The quartic profile assumption in general provided more accurate prediction than did the parabolic profile assumption, especially at beginning times. This observation is similar to that for a linear isotherm as pointed out by Do and Rice (1986). To quantitatively justify the validity of the approximate models, the relative error is defined as follows:

$$E_R = \frac{\int_0^\infty (C_{B_e}|_{\text{approx}} - C_{B_e}|_{\text{pore}})^2 d\theta}{\int_0^\infty (1 - C_{B_e}|_{\text{pore}}) d\theta} = \frac{\int_0^\infty (C_{B_e}|_{\text{approx}} - C_{B_e}|_{\text{pore}})^2 d\theta}{\dfrac{\alpha}{3(1+\beta)}} \qquad (40)$$

where $C_{B_e}|_{\text{approx}}$ and $C_{B_e}|_{\text{pore}}$ are the effluent concentrations for the approximate model and the pore-diffusion model, respectively. This definition is similar to that proposed by Kim (1990) for studying effective diffusivity in a bidispersed particle. Table 1 shows the errors at various sets of parameters used in the present models and the linear driving force model (Raghavan et al., 1986). It is indicated that E_R increases with increasing the degree of nonlinearity. When β equal 0, a linear isotherm, all the approximate models behave similarly to the pore-diffusion model. Table 1 also indicates that the quartic profile assumption provided more accurate predictions than did the parabolic profile assumption and the linear driving force model.

Table 1. Deviation of approximate models from pore diffusion model

	$E_R \times 10^4$		
	Parabolic	Quartic	LDF
$\alpha = 2$, $Bi = 5$			
$\beta = 0$	0.69	0.01	0.69
1	2.17	0.06	1.51
2	4.93	0.29	2.57
5	14.74	2.64	6.95
10	27.48	8.54	12.54
20	40.68	17.16	18.52
$\alpha = 2$, $\beta = 5$			
$Bi = 1$	2.86	0.37	2.39
2	4.92	0.57	2.75
5	14.74	2.64	6.59
10	27.69	5.61	12.43
20	41.64	9.35	18.17
50	56.28	11.94	23.49
100	63.14	13.45	25.71
$Bi = 5$, $\beta = 5$			
$\alpha = 0.5$	100.00	45.12	92.10
1	36.76	11.93	22.39
2	14.74	2.64	6.59
5	5.78	1.74	2.57
10	2.89	0.87	1.40
20	1.45	0.44	0.70
50	0.58	0.17	0.28

Notation

A, B, D = parameters in parabolic and quartic profile assumptions
Bi = Biot number, $k_f R/De$
C = dimensionless concentration in the void fraction of an adsorbent particle, C_i/C_{b0}
C_s = dimensionless surface concentration, C_s/C_{b0}
C_B = dimensionless concentration in the bulk phase, C_b/C_{b0}
C_{B_e} = dimensionless concentration at the column exit position, C_{be}/C_{b0}
c = concentration in the void fraction of an adsorbent particle, mol/cm^3
c_b = concentration in the bulk phase, mol/cm^3
c_{b0} = concentration at the column inlet position, mol/cm^3
c_{be} = concentration at the column exit position, mol/cm^3
c_s = concentration on the surface of an adsorbent particle, mol/cm^3
De = effective diffusivity, cm^2/s
E_R = relative error, Eq. 40
K = constant in Langmuir isotherm
k_f = interphase mass transfer coefficient, cm/s
L = length of packed-bed adsorber, cm
Q = dimensionless sum of the adsorbates in void fraction and adsorbed phase, $q/C_{b0} + \epsilon_p C/C_{b0}$
$\bar{Q}$ = dimensionless averaged sum of adsorbates
$\bar{Q}'$ = $\bar{Q}/K$
Q_s = dimensionless sum of adsorbate on the surface of an adsorbent particle, $Q|_{x=1}$
q = adsorbed amount in an adsorbent, mol/cm^3
R = radius of adsorbent particle, cm
r = radial coordinate, cm
t = time, s
u = superficial velocity, cm/s
x = dimensionless radial coordinate, r/R
Z = characteristic coordinate, z/L
z = axial coordinate, cm

Greek letters

α = $3L(1-\epsilon_b)De/R^2u$
β = constant in Langmuir isotherm
ϵ_b = void fraction in a packed-bed adsorber
ϵ_p = void fraction in an adsorbent particle
θ = dimensionless time coordinate, τ/K
τ = dimensionless time, tDe/R^2

Literature Cited

Do, D. D., and P. L. J. Mayfield, "A New Simplified Model for Adsorption in a Single Particle," *AIChE J.*, **33**, 1397 (1987).

Do, D. D., and T. S. Nguyen, "A Power Law Adsorption Model and Its Significance," *Chem. Eng. Commun.*, **72**, 171 (1988).

Do, D. D., and R. G. Rice, "Validity of the Parabolic Profile Assumption in Adsorption Studies," *AIChE J.*, **32**, 149 (1986).

Glueckauf, E., "Theory of Chromatography. 10: Formula for Diffusion into Spheres and Their Application to Chromatography," *Trans. Farad. Soc.*, **51**, 1540 (1955).

Hansen, K. W., "Analysis of Transient Models for Catalytic Tubular Reactors by Orthogonal Collocation," *Chem. Eng. Sci.*, **26**, 1555 (1971).

Haynes, H. W., Jr., "The Experimental Evaluation of Catalyst Effective Diffusivity," *Catal. Rev.-Sci. Eng.*, **30**, 563 (1988).

Kim, D. H., "Linear Driving Force Formulas for Diffusion and Reaction in Porous Catalysts," *AIChE J.*, **35**, 343 (1989).

Kim, D. H., "Single Effective Diffusivities for Dynamic Adsorption in Bidisperse Adsorbents," *AIChE J.*, **36**, 302 (1990).

Park, I. S., J. M. Smith, and B. J. McCoy, "Intraparticle Diffusion Coefficients in Packed Columns: Measurements by Arrested-Flow Gas Chromatography," *AIChE J.*, **33**, 1102 (1987).

Raghavan, N. S., M. M. Hassan, and D. M. Ruthven, "Numerical Simulation of a PAS System Using a Pore Diffusion Model," *Chem. Eng. Sci.*, **41**, 2787 (1986).

Rice, R. G., "Approximate Solutions for Batch, Packed-Tube, and Radial-Flow Adsorbers—Comparison with Experiment," *Chem. Eng. Sci.*, **37**, 83 (1982).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 242 (1984).

Vermeulen, T., M. D. LeVan, N. K. Hiester, and G. Klein, "Adsorption and Ion Exchange," *Perry Chemical Engineers' Handbook*, 6th ed., 16 (1984).

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Corrections

An R&D note "Closure Equations for Single and Multiple Reactions in a CSTR" by A. Chatterjee and J. M. Tarbell, which was published in the February 1991 issue (p. 277), was not included in the Table of Contents. Our apologies to the authors.

We would like to acknowledge Karlton K. Shen-Tu for finding a typographical error in an article published in the June 1961 issue (see p. 268 of February 1991 issue).