HIGH-ORDER APPROXIMATIONS FOR NONCYCLIC AND CYCLIC ADSORPTION IN A BIPOROUS ADSORBENT

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Abstract – An accurate and realistic model for transient diffusion and adsorption in a biporous pellet is typically represented by two coupled second-order partial differential equations. The model, however, has been rarely used in practice because of its mathematical complexity and bulky numerical computation, and approximations of the model have been used instead. But the accuracy of the available approximations has been limited and not enough for detailed analysis and simulation of the mass transfer process. Therefore, in this study, we develop for the first time high-order approximations, of up to third order, for noncyclic and cyclic adsorption in a biporous pellet, respectively. The approximations are in the form of a state equation which consists of first-order differential equations; the number of the equations is the same as the approximation order. The approximations are easy to use and their accuracy dramatically increases with increasing approximation order, so that the second- or the third-order approximations can effectively substitute the complex biporous diffusion model.

Key words : LDF Equation, Biporous Adsorbent, Diffusion and Adsorption, Approximation

INTRODUCTION

Adsorbents commonly used in dynamic sorptive separation processes are made of microporous powder and hence have bi-disperse pore structures: micropores in the powder particles and macropores formed between the particles in pelleting. For these two distinctly different pores in the adsorbents, the realistic mass transfer model for the adsorbents should account for the mass transfer in the macropores and in the micropores separately, resulting in a biporous diffusion model. Because of its complexity and bulky numerical computations, however, the biporous diffusion model has rarely been used in the simulation and analysis of transient adsorption processes. Instead, various approximations of the mass transfer have been used with varying degrees of success.

The well-known approximation is the Glueckauf linear driving force (LDF) equation [1955]:

$$\frac{d\bar{q}}{d\tau} = 15\frac{\theta_p}{\theta}(f-\bar{q})$$ (1)

This approximation has been widely adopted to represent the finite mass transfer between the adsorbent and its surrounding [Kim et al., 1995; Xiu, 1996]. Since the LDF equation is based on a monoporous diffusion model, it involves the diffusional time constant, θ_p, which is defined with an overall effective diffusivity, D_p. It is well known that in principle two diffusivities, the macropore diffusivity and the micropore diffusivity, are needed to describe the mass transfer in biporous adsorbents. Apparently the LDF equation is not compatable with the biporous diffusion model unless there is a way of combining the two diffusivities into a single overall diffusivity. Furthermore it has been shown that the LDF approximation is equivalent to assuming a parabolic concentration profile in adsorbents [Liaw et al., 1979; Do and Rice, 1986], a valid assumption only when the time rate change of the concentration at the outer surface of the pellet, f, is slow. Kim [1989] has also found that the LDF equation is a truncated series solution of a monoporous diffusion model, represented in terms of time derivatives of f. Consequently, the LDF equation is not valid in rapidly changing processes where the concentration profile is not parabolic, and the time derivatives in the remainder of the series solution grow larger than the terms in the LDF equation.

Recently Kim [1997] developed a first-order approximation for cyclic adsorption in a biporous adsorbent:

$$\frac{d\bar{p}}{d\tau} = Af - B\bar{q}$$ (2)

where $\bar{p} = \bar{q} - c_0 + (A/B)c_0$, the constant c_0 is the time average of f over a period T, and A and B are coefficients which are functions of the cycle speed $w(=2\pi/T)$. As the cycle period increases, the approximation has been shown to approach the LDF equation when the time constant for τ, θ, is defined with an overall diffusivity, D_p, determined from the formula by Kim [1990]. This in fact suggests that the LDF, although based on the monoporous diffusion model, can be used as a first-order approximation for adsorption in biporous adsorbents for long cycle periods or noncyclic adsorption. For short cycle periods, however, the LDF equation as well as other approximations based on the monoporous diffusion model [Nakao and Suzuki, 1983; Kim, 1996] all have failed to predict the responses of biporous adsorbents with reasonable accuracy, whereas the approximation, Eq. (2), based on the biporous diffusion model has been found to be reliable.

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Although the first-order approximations are adequate in elucidating the essential features of the mass transfer, they may not be accurate enough for a detailed analysis and optimization. In this regard, high-order approximations, precise enough and yet much easier to use than the pore diffusion model, are thus necessary. Recently, Lee and Kim [1998] developed methods for high-order approximations for adsorption and diffusion in a particle with a unimodal pore size distribution. The methods are extended in this study to develop high-order approximations for biporous diffusion and adsorption.

THEORY

Consider adsorption and diffusion in a spherical pellet with bidisperse porous structure. An adsorbate diffuses into the pellet through the macropores, the interparticle void, and then into microparticles, which are assumed to be spheres of uniform size. Further assume that the diameters of the micropores are comparable with the diameter of the diffusing molecules. In this case, the diffusing molecules are under the force field exerted by the atoms consisting the pore walls, and distinguishing the adsorbed molecules and the molecules moving from one adsorption site to another is not physically reasonable. This approach is usually adopted in formulating diffusion and adsorption in zeolite crystals and carbon molecular sieves [Hashimoto et al., 1976; Chiang et al., 1984].

The mass balance equations are

Macropore:

$$\varepsilon_a \frac{\partial C_a}{\partial t} = \varepsilon_a D_a \frac{1}{r_a^2} \frac{\partial}{\partial r_a}\left(r_a^2 \frac{\partial C_a}{\partial r_a}\right) - \frac{3(1-\varepsilon_a)}{R_b}D_b \left.\frac{\partial Q_b}{\partial r_b}\right|_{r_b=R_b} \quad (3)$$

Micropore:

$$\frac{\partial Q_b}{\partial t} = D_b \frac{1}{r_b^2} \frac{\partial}{\partial r_b}\left(r_b^2 \frac{\partial Q_b}{\partial r_b}\right) \quad (4)$$

Initial conditions:

$$C_a(r_a, t)=0, \quad Q_b(r_a, r_b, t)=0 \quad (5)$$

Boundary conditions:

$$\left.\frac{\partial C_a}{\partial r_a}\right|_{r_a=0}=0, \quad \left.\frac{\partial Q_b}{\partial r_b}\right|_{r_b=0}=0 \quad (6)$$

$$C_a(R_a, t)=F(t), \quad Q_b(r_a, R_b, t)=KC_a(r_a, t)$$

Here adsorption equilibrium is assumed at the outer surface of the microparticle and the equilibrium is linear with respect to the macropore concentration. F(t) is an arbitrary time-varying concentration at the outer surface of the biporous pellet.

Next we define dimensionless variables and parameters

$$\tau = \frac{t}{\theta}, \quad x = \frac{r_a}{R_a}, \quad y = \frac{r_b}{R_b}$$

$$c_a = \frac{C_a}{C_0}, \quad c_b = \frac{Q_b}{KC_0}, \quad f(\tau)=\frac{K_0 F(t)}{C_0}$$

$$H_a = \frac{\theta D_a}{R_a^2}, \quad H_b = \frac{\theta D_b}{R_b^2}, \quad K_0 = \varepsilon_a + (1-\varepsilon_a)K \quad (7)$$

Here K_0 is the apparent adsorption equilibrium constant in

the pellet, the equilibrium ratio of the adsorbate amount per unit volume of the pellet to the adsorbate concentration in the bulk surrounding the pellet. The time constant, θ, can be defined in any proper way, such as the space time of an adsorber or any time constant of the process involved.

Usually the volume-average concentration is of main interest since the mass exchange rate between the pellet and its surroundings can be conveniently represented by the time-derivative of the average concentration. The dimensionless volume-average concentration is

$$\bar{q} = 3\int_0^1 [\varepsilon_a c_a + 3(1-\varepsilon_a)K\int_0^1 c_b y^2 \, dy]x^2 \, dx \quad (8)$$

Now we need a Laplace transform of $\bar{q}$ to develop approximations for the mass exchange. The solution of the biporous model, Eq. (3)-(6) can be readily obtained in Laplace transform, and the Laplace-domain solution is substituted into Eq. (8) to give

$$\bar{Q} = \frac{3\varepsilon_a H_a}{s}(\sqrt{\alpha}\coth\sqrt{\alpha}-1)\frac{F(s)}{K_0}$$

$$\equiv G(s)F(s) \quad (9)$$

where

$$\alpha = \frac{s}{H_a}\left[1 + \frac{3(1-\varepsilon_a)}{\varepsilon_a}K\frac{H_b}{s}\left(\sqrt{\frac{s}{H_b}}\coth\sqrt{\frac{s}{H_b}}-1\right)\right] \quad (10)$$

G(s) is the transfer function of the biporous system, relating $\bar{Q}$ and F(s).

We approximate G(s) by a rational funtion.

$$G_n(s) = \frac{b_{n-1}s^{n-1} + b_{n-2}s^{n-2} + \cdots + b_0}{a_n s^n + a_{n-1}s^{n-1} + \cdots + a_1 s + 1} \quad (0<n) \quad (11)$$

The method of determining the 2n coefficients is different for noncyclic and cyclic adsorption and well described in Lee and Kim [1998].

The Laplace domain approximation, Eq. (11), can be represented by a time-domain state equation [Kailath, 1980]:

$$\frac{dz(\tau)}{d\tau} = \begin{pmatrix} -\frac{a_{n-1}}{a_n} & 1 & 0 & \cdots & 0 \\ -\frac{a_{n-2}}{a_n} & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -\frac{a_1}{a_n} & 0 & 0 & \cdots & 1 \\ -\frac{1}{a_n} & 0 & 0 & \cdots & 0 \end{pmatrix}z(\tau) + \begin{pmatrix} \frac{b_{n-1}}{a_n} \\ \frac{b_{n-2}}{a_n} \\ \vdots \\ \frac{b_1}{a_n} \\ \frac{b_0}{a_n} \end{pmatrix}f(\tau) \quad (12)$$

where $z(\tau)=(z_1, z_2, \cdots, z_n)^T$, and $z(0)=(0, 0, \cdots, 0)^T$. An approximation of $\bar{q}$ based on $G_n(s)$ is now given by

$$\bar{q}(\tau)=z_1(\tau) \quad (13)$$

n is the order of the state equation and also equal to the number of the first-order differential equations.

1. Approximations for Noncyclic Forcing

Here the coefficients are determined by the method of Pade approximation [Bender and Orzsag, 1978], in which the coeffi-

cients are chosen to make the first 2n terms of the Taylor series expansion of $G_n(s)$ coincide with the first 2n terms of the Taylor expansion of $G(s)$. In Table 1, the first six coefficients of the series are listed, with which the Pade approximation of up to third order can be readily obtained. We list the Pade approximations and the corresponding state equations in Table 2.

2. Approximations for Cyclic Forcing

In this case, the surface concentration, $f(\tau)$, is periodic with a period T. Also the response of the biporous pellet to this change becomes periodic with the same period. Hence the forcing function and the response can be expanded in Fourier series.

$$f(\tau)=c_0+\sum_{k=1}^{\infty}(c_k\cos kw\tau+d_k\sin kw\tau)\quad w=\frac{2\pi}{T}\quad (14)$$

$$\bar{q}(\tau)=c_0G(0)+\sum_{k=1}^{\infty}|G(jkw)|\,[c_k\cos(kw\tau+\angle G(jkw)]$$
$$+d_k\sin(kw\tau+\angle G(jkw))]\quad (15)$$

where c_k and d_k are the Fourier coefficients of $f(\tau)$, $j=\sqrt{-1}$, $|G(jkw)|$ is the amplitude ratio, and $\angle G(jkw)$ is the phase lag.

For cyclic forcing, Lee and Kim [1998] proposed the method of frequency matching between $G(s)$ and its approximation $G_n(s)$. In this method, $G_n(s)$ is determined by the condition that equates $G(s)$ and $G_n(s)$ at $s=jkw$ (k=1, 2, ···, n). The condition gives 2n algebraic equations: n equations from equating the real parts of $G(jkw)$ and $G_n(jkw)$ and another n equations from

Table 1. Taylor series coefficients of G(s)

	Coefficient
s^0	$A_0=1$
s^1	$A_1=-\dfrac{1}{15}\left[\dfrac{K_0}{\varepsilon_a H_a}+\dfrac{K_0-\varepsilon_a}{H_b K_0}\right]$
s^2	$A_2=\dfrac{2}{315}\dfrac{K_0^2}{(\varepsilon_a H_a)^2}+\dfrac{2}{225}\dfrac{(1-\varepsilon_a)K}{(\varepsilon_a H_a)H_b}+\dfrac{2}{315}\dfrac{(1-\varepsilon_a)K}{H_b^2 K_0}$
s^3	$A_3=-\dfrac{1}{1575}\dfrac{(1-\varepsilon_a)K}{K_0 H_b^3}-\dfrac{1}{23625}\dfrac{(-34\varepsilon_a K_0+27 K_0^2+7\varepsilon_a^2)}{(H_a\varepsilon_a)K_0 H_b^2}$
	$\quad-\dfrac{2}{1575}\dfrac{K_0(1-\varepsilon_a)K}{(H_a\varepsilon_a)^2 H_b}-\dfrac{1}{1575}\dfrac{K_0^3}{(H_2\varepsilon_a)^3}$
s^4	$A_4=\dfrac{2}{31185}\dfrac{(1-\varepsilon_a)K}{K_0 H_b^4}+\dfrac{2}{70875}\dfrac{(1-\varepsilon_a)K(5K(1-\varepsilon_a)+3\varepsilon_a)}{K_0\varepsilon_a H_a H_b^3}$
	$\quad+\dfrac{2}{165375}\dfrac{(1-\varepsilon_a)K(17(1-\varepsilon_a)K+10\varepsilon_a)}{(\varepsilon_a H_a)^2 H_b}$
	$\quad+\dfrac{4}{23625}\dfrac{K_0^2(1-\varepsilon_a)K}{(\varepsilon_a H_a)^3 H_b}+\dfrac{2}{31185}\dfrac{K_0^4}{(\varepsilon_a H_a)^4}$
s^5	$A_5=-\dfrac{1382}{212837625}\dfrac{(1-\varepsilon_a)K}{H_b^5 K_0}$
	$\quad-\dfrac{2}{81860625}\dfrac{(1-\varepsilon_a)K\{691(1-\varepsilon_a)K+350\varepsilon_a\}}{(\varepsilon_a H_a)H_b^4 K_0}$
	$\quad-\dfrac{2}{7441875}\dfrac{(1-\varepsilon_a)K\{112K^2(1-\varepsilon_a)^2+150K\varepsilon_a(1-\varepsilon_a)+45\varepsilon_a^2\}}{(\varepsilon_a H_a)^2 H_b^3 K_0}$
	$\quad-\dfrac{2}{2480625}\dfrac{K_0(1-\varepsilon_a)K\{41K(1-\varepsilon_a)+20\varepsilon_a\}}{(\varepsilon_a H_a)^3 H_b}$
	$\quad-\dfrac{2}{93555}\dfrac{K_0^3 K(1-\varepsilon_a)}{(\varepsilon_a H_a)^4 H_b}-\dfrac{1382}{212837625}\dfrac{K_0^5}{(\varepsilon_a H_a)^5}$

Table 2. Approximations for noncyclic adsorption

Pade [1] $a_1=-\dfrac{A_1}{A_0}$, $b_0=1$

$$\frac{d\bar{q}}{d\tau}=\frac{15}{\left[\dfrac{K_0}{\varepsilon_a H_a}+\dfrac{K_0-\varepsilon_a}{H_b K_0}\right]}(f-\bar{q})$$

Pade [2] $a_1=\dfrac{-A_1A_2+A_3}{A_1^2-A_2}$, $a_2=\dfrac{-A_1A_3+A_2^2}{A_1^2-A_2}$

$b_0=1$, $b_1=A_1+a_1$

$$\frac{d\bar{q}}{d\tau}=\frac{1}{a_2}(b_1f-a_1\bar{q})+z_2$$

$$\frac{dz_2}{d\tau}=\frac{1}{a_2}(f-\bar{q})$$

Pade [3] $D=-A_4A_2+A_4A_1^2+A_3^2-2A_1A_2A_3+A_2^3$

$$a_1=\frac{1}{D}(A_1A_3^2-A_3A_4+A_1A_2A_4-A_2^2A_3+A_5A_2-A_5A_1^2)$$

$$a_2=\frac{1}{D}(-A_2^2A_4+A_2A_3^2+A_1A_2A_5+A_4^2-A_1A_3A_4-A_3A_5)$$

$$a_3=\frac{1}{D}(2A_2A_3A_4-A_2^2A_5-A_1A_4^2+A_1A_3A_5-A_3^3)$$

$b_0=1$

$b_1=A_1+a_1$

$b_2=A_2+A_1a_1+a_2$

$$\frac{d\bar{q}}{d\tau}=\frac{1}{a_3}(b_2f-a_2\bar{q})+z_2$$

$$\frac{dz_2}{d\tau}=\frac{1}{a_3}(b_1f-a_1\bar{q})+z_3$$

$$\frac{dz_3}{d\tau}=\frac{1}{a_3}(f-\bar{q})$$

equating the corresponding imaginary parts. With these 2n equations, the 2n coefficients of $G_n(s)$ can be readily determined as shown in Table 3. As noted by Lee and Kim, when thus determined $G_n(s)$ is replaced with $G(s)$ in Eq. (15), the resulting approximation of $\bar{q}$ is shifted approximately by a constant from $\bar{q}$ because $G_n(0)\neq G(0)$. The correction by a constant is

$$\bar{q}(\tau)=z_1(\tau)+c_0G(0)-c_0G_n(0)\quad (16)$$

DISCUSSION

1. Noncyclic Adsorption

We compare the step responses of the approximations in Fig. 1(a) and (b). As we see, the error of approximation is decreasing rapidly with increasing order of the approximation. The third-order approximation is seen to be almost identical to the exact response, except at extremely small times.

The first-order approximation, shown in Table 2, can be made identical to the LDF equation if

$$\frac{K_0}{\varepsilon_a H_a}+\frac{K_0-\varepsilon_a}{H_b K_0}=1\quad (17)$$

This gives that

$$\frac{R_a^2}{D_a}+\frac{(1-\varepsilon_a)K}{K_0^2}\frac{R_b^2}{D_b}=\frac{\theta}{K_0}=\frac{R_a^2}{D_p}\quad (18)$$

Table 3. Coefficients of approximations for cyclic adsorption

Appro-ximation	Coefficients*
Freq [ω]	$\begin{bmatrix} a_1 \\ b_0 \end{bmatrix} = \begin{bmatrix} Y_1\omega & 1 \\ -X_1\omega & 0 \end{bmatrix}^{-1} \begin{bmatrix} X_1 \\ Y_1 \end{bmatrix}$
Freq [ω, 2ω]	$\begin{bmatrix} a_1 \\ a_2 \\ b_0 \\ b_1 \end{bmatrix} = \begin{bmatrix} Y_1\omega & X_1\omega^2 & 1 & 0 \\ -X_1\omega & Y_1\omega^2 & 0 & \omega \\ 2Y_2\omega & 4X_2\omega^2 & 1 & 0 \\ -2X_2\omega & 4Y_2\omega^2 & 0 & 2\omega \end{bmatrix}^{-1} \begin{bmatrix} X_1 \\ Y_1 \\ X_2 \\ Y_2 \end{bmatrix}$
Freq [ω, 2ω, 3ω]	$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ b_0 \\ b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} Y_1\omega & X_1\omega^2 & -Y_1\omega^3 & 1 & 0 & -\omega^2 \\ -X_1\omega & Y_1\omega^2 & X_1\omega^3 & 0 & \omega & 0 \\ 2Y_2\omega & 4X_2\omega^2 & -8Y_2\omega^3 & 1 & 0 & -4\omega^2 \\ -2X_2\omega & 4Y_2\omega^2 & 8X_2\omega^3 & 0 & 2\omega & 0 \\ 3Y_3\omega & 9X_3\omega^2 & -27Y_3\omega^3 & 1 & 0 & -9\omega^2 \\ -3X_3\omega & 9Y_3\omega^2 & 27X_3\omega^3 & 0 & 3\omega & 0 \end{bmatrix}^{-1} \begin{bmatrix} X_1 \\ Y_1 \\ X_2 \\ Y_2 \\ X_3 \\ Y_3 \end{bmatrix}$

*Freq [ω, ⋯, Nω]= $\dfrac{b_{N-1}s^{N-1} + \cdots + b_0}{a_N s^N + \cdots + a_1 s + 1}$, X_k=Re(G(jkw)),
Y_k=Im (G(jkw)).

Eq. (17) defines the time constant, θ, for the first-order approximation to become the LDF equation. Since the LDF equation is based on the monoporous diffusion model with an overall effective diffusivity, D_p, it involves the associated time constant, $\theta_p(=K_0 D_p/R_a^2)$. In principle the monoporous diffusion model and the biporous diffusion model are incompatible with each other and cannot be used interchangeably. Nevertheless, if we define D_p for the biporous pellet as in Eq. (18), then $\theta_p=\theta$ and the first-order approximation becomes the original dimensionless LDF equation. It is noted that the formula for D_p, Eq. (18), has been developed by Kim [1990] in an attempt to describe the performance of an adsorber packed with biporous adsorbents using the simpler monoporous diffusion model.

2. Cyclic Adsorption

The first-order approximation for cyclic adsorption is identical to the approximation developed by Kim [1997] since both approximations are based on the first partial sum of the series, Eq. (15). However, the method of determining the coefficients in the present approximation is much easier than the previous method which involves a slowly convergent double summation and numerical solution of a transcendental equation to evaluate each term in the summation. In the present method, the evaluation of the real and imaginary parts of the transfer function at a specified frequency and solution of the algebraic equations shown in Table 3 are all that is needed to evaluate the coefficients. Furthermore, the previous method by Kim could not be extended to develop higher-order approximations.

Unlike the case of noncyclic adsorption, the first-order approximation for the biporous diffusion model and that for the monoporous diffusion model with D_p of Eq. (17) are in general quite different in their predictions. Only when the cycle period is long enough so that complete adsorption and desorption oc-
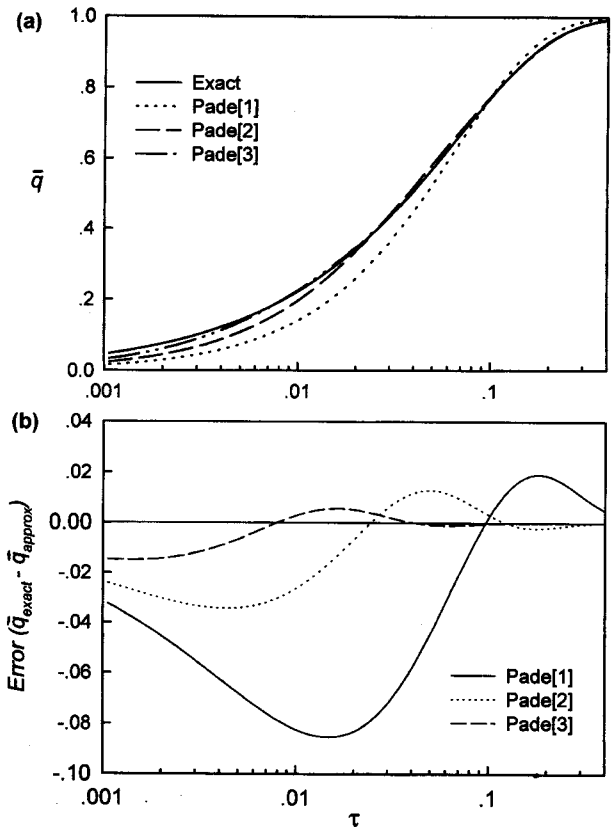
Fig. 1. (a) Comparison of step responses, (b) errors of approximations (H_a=400, H_b=2.404, K=100, ε_a=0.3).
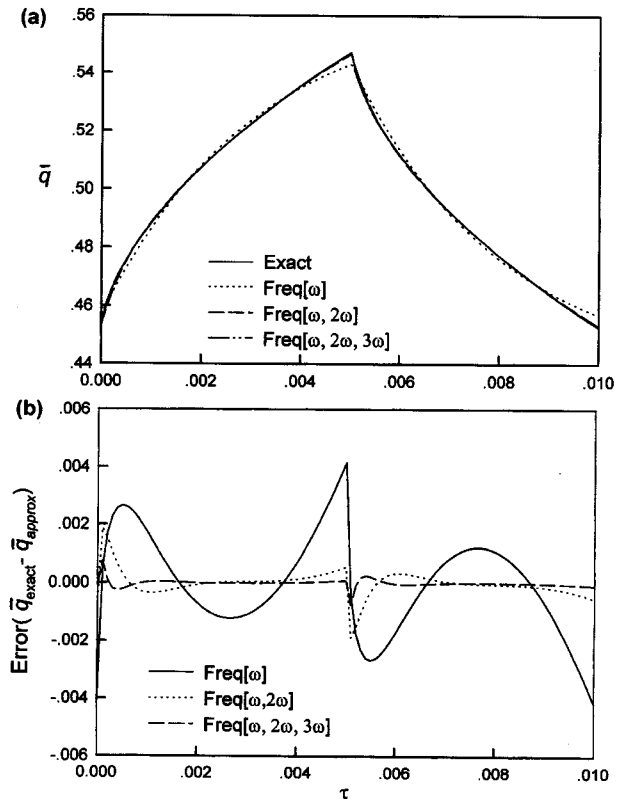

Fig. 2. (a) Comparison of responses, (b) errors of approximations (H_a=400, H_b=2.404, K=100, ε_a=0.3 T=0.01).

cur within a cycle, Kim [1997] has shown that the first-order approximations for both diffusion models tend to the LDF equation and hence become identical. Consequently, in cyclic adsorptions, the use of correct pore structure in formulating the intraparticle mass transfer is particularly important when the cycle time is short.

Fig. 2(a) and 2(b) show, respectively, the responses and the errors of the approximations for a square wave forcing:

$$f(\tau) = \begin{cases} 1 & \text{when } 0 \le \tau < 0.005 \\ 0 & \text{when } 0.005 \le \tau < 0.01 \end{cases} \quad f(\tau) = f(\tau + 0.01) \quad (19)$$

As can be seen in the figures, the approximation error decreases dramatically with increasing order and the responses of the second- and third-order approximations are seen to virtually coincide with the exact response.

CONCLUSION

High-order approximations for adsorption and diffusion in biporous adsorbents are presented. Depending on the type of the concentration forcing at the outer surface of the adsorbent, noncyclic and cyclic, approximations of up to third order are obtained, respectively. The approximations are structually simple, easy to use, and yet very accurate in their predictions. Hence the approximations provide a useful alternative to the complex biporous diffusion model in modeling or simulation of adsorbers packed with biporous adsorbents.

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NOMENCLATURE

A_i : ith coefficient of Taylor series of $G(s)$
a_i, b_i : coefficients in approximation of $G(s)$, Eq. (11)
c_i, d_i : Fourier coefficients of $f(\tau)$
$C_a(t)$: concentration in macropore [mol/m^3]
D_a : effective macropore diffusivity based on void area [m^2/sec]
D_b : effective micropore diffusivity [m^2/sec]
D_p : overall effective diffusivity [m^2/sec]
$F(s)$: Laplace transform of $f(\tau)$
$f(\tau)$: dimensionless concentration of at the outer surface of adsorbent
$Freq[w, \cdots, Nw]$: approximation for cyclic adsorption from frequency response matching at $w, \cdots, Nw$
$G(s)$: transfer function defined in Eq. (9)
$G_n(s)$: approximation of the transfer function, Eq. (11)
H_a, H_b : diffusivity parameters defined in Eq. (7)
K : adsorption equilibrium constant in microparticle, dimensionless
K_0 : apparent adsorption equilibrium constant, defined in Eq. (7)
$Pade[n]$: nth-order Pade approximation

Q_b : concentration in microparticle [mol/m^3]
$\bar{q}$: dimensionless volume-average concentration in pellet, defined in Eq. (8)
R_a : radius of pellet [m]
r_b : radial variable in particle [m]
r_a : radial variable in pellet [m]
s : Laplace domain variable
t : time [s]
T : dimensionless cycle period
$z_i(\tau)$: concentration variables in the state equation, Eq. (12)

Greek Letters

α : defined in Eq. (10)
ε_a : macropore porosity in pellet
θ : time constant [s]
θ_p : diffusional time constant of monoporous diffusion $(=K_0R_a^2/D_p)$
τ : dimensionless time $(=t/\theta)$
w : frequency $(=2\pi/T)$

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