A Half-Order Approximation for the Adsorption Dynamics in a Porous Particle

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Introduction

An accurate mathematical description for the dynamic mass transfer in a porous particle is the pore-diffusion model represented by a parabolic partial differential equation. In modeling of a packed-bed adsorber, the pore-diffusion model is coupled with interparticle balance equations. The model involves the spatial variables of the particle and the bed as independent variables. The number of independent variables is often proportionate with difficulty in solution of the model. To remove the spatial variable of the particle in the resulting model and at the same time to simplify the description of the pore diffusion, a number of approximations have been proposed for the pore-diffusion model. Glueckauf[1] first proposed a first-order ordinary differential equation model known as the linear driving force (LDF) model. The LDF model approximates that the mass-transfer rate between an adsorbent and its surrounding is proportional to the difference between the surface concentration and the mean concentration in the adsorbent particle. It has been shown that the simplification is valid only when the surface concentration of the particle changes slowly. Kim[2] proposed an improved first-order model having the time derivative of surface concentration. Lee and Kim[3] proposed high-order models to approximate the pore-diffusion model accurately for noncyclic and cyclic operations.

For the sinusoidal forcing of surface concentration, the amplitude ratio decreases by $1/\sqrt{\omega}$ as the angular frequency ω increases, and the phase angle goes to $-\pi/4$. All the previous approximations have been represented as integer-order differential equations, and, hence, have asymptotes of integer-powers of $j\omega$ where $j = \sqrt{-1}$. Consequently, they cannot accurately approximate the entire frequency response (the amplitude ratio and the phase angle), and each previous model has its own valid range in the frequency domain. The approximation formulas based on the Pade approximation method are developed around zero frequency, and, thus, show excellent accuracy for slowly changing operations.[3] On the other hand, for a fast cyclic operation, an approximation that fits the frequency region should be separately developed and used.[3]

To date, there has not been proposed any approximation that is valid throughout the entire frequency domain of the pore-diffusion model. In this study, we propose a half-order model based on the fractional calculus[4] to approximate the pore diffusion model in the entire frequency range.

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Pore-Diffusion Model

Consider the pore-diffusion model

$$\frac{\partial q(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q(r,t)}{\partial r}\right) \tag{1}$$

Here $q(r,t)$ is the dimensionless concentration, t is the dimensionless time, and r is the normalized radius ($r = 0$ at center, and 1 at external surface).[2] The initial and boundary conditions are

$$\begin{aligned} q(r,0) &= 0 \\ \left.\frac{\partial q(r,t)}{\partial r}\right|_{r=0} &= 0, \quad q(1,t) = f(t) \end{aligned} \tag{2}$$

where $f(t)$ is a forcing function at the surface.

The volume-average concentration $\bar{q}(t)$, is of main interest because the mass exchange rate between the particle and its surrounding can be conveniently expressed as $d\bar{q}(t)/dt$. The volume-average concentration is

$$\bar{q}(t) = 3\int_0^1 r^2 q(r,t)dr \tag{3}$$

and its Laplace transform is[1,3]

$$\bar{Q}(s) = 3\left(\frac{1}{\sqrt{s}}\coth\sqrt{s} - \frac{1}{s}\right)F(s) \equiv G(s)F(s) \tag{4}$$

where $\overline{Q}(s)$ and $F(s)$ are the Laplace transforms of $\overline{q}(s)$ and $f(t)$, respectively, and $G(s)$ is the transfer function relating them.

It is difficult to solve the partial differential equation of Eq. 1 when it is coupled with additional balance equations. The well-known approximation of Eq. 1 is the linear driving force model

$$\frac{d\bar{q}(t)}{dt} = 15(f(t) - \bar{q}(t)) \tag{5}$$

It is corresponding to the approximation of transfer function $G(s)$[5]

$$G_{LDF}(s) = \frac{15}{s+15} \tag{6}$$

Equations 5 and 6 are valid only for slowly changing $f(t)$. Kim[2] proposed an improved first-order model having the term $df(t)/dt$

$$\frac{d\bar{q}(t)}{dt} = \frac{21}{2}(f(t) - \bar{q}(t)) + \frac{3}{10}\frac{df}{dt} \tag{7}$$

The transfer function of the model is

$$G_2(s) = \frac{3s+105}{10s+105} \tag{8}$$

A high-order model by Lee and Kim is

$$\frac{d\bar{q}}{dt} = -105\bar{q} + u + 42f(t)$$
$$\frac{du}{dt} = 945(f(t) - u) \tag{9}$$

Its transfer function is

$$G_3(s) = \frac{42s+945}{s^2+105s+945} \tag{10}$$

As the approximation order increases, the accuracy of the approximate model increases dramatically for slowly changing $f(t)$, and also the applicable frequency range in cyclic operations is significantly extended as shown in Figure 1. As the frequency increases, however, the amplitude ratio $|G(j\omega)|$ decreases by the rate of $1/\omega^{0.5}$, and the phase angle $\angle G(j\omega)$ approaches to $-\pi/4$. These asymptotes cannot be met by rational transfer functions like Eqs. 6, 8 and 10.

Half-order approximation

A simple fractional order system satisfying the amplitude and phase angle asymptotes is

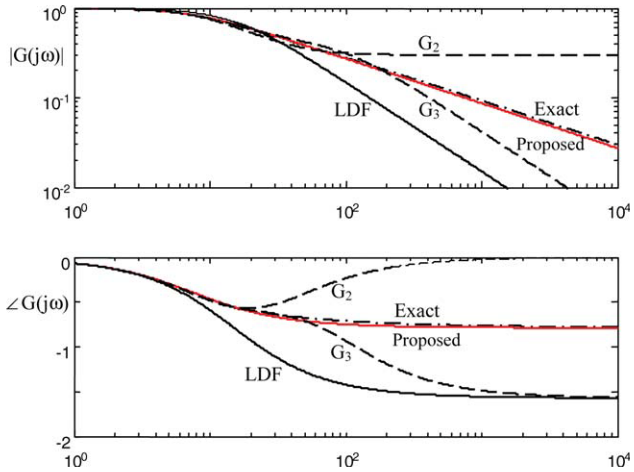

Figure 1. Bode plots of transfer functions.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$G_{HOS}(s) = \frac{1}{\sqrt{\frac{2}{15}s+1}} \tag{11}$$

Taylor series for $G(s)$, $G_{LDF}(s)$ and $G_{HOS}(s)$ are[5]

$$G(s) = 1 - \frac{1}{15}s + \frac{1}{157.5}s^2 - \frac{1}{1575}s^3 + \cdots$$
$$G_{LDF}(s) = 1 - \frac{1}{15}s + \frac{1}{225}s^2 - \frac{1}{3375}s^3 + \cdots$$
$$G_{HOS}(s) = 1 - \frac{1}{15}s + \frac{1}{150}s^2 - \frac{1}{1350}s^3 + \cdots \tag{12}$$

Compared to $G_{LDF}(s)$, the Taylor series of $G_{HOS}(s)$ is closer to that of $G(s)$. Frequency responses in Figure 1 show that the approximation by $G_{HOS}(s)$ is excellent. The relative errors of amplitude ratios are less than 7%, and the phase errors are less than 3° throughout frequencies.

The time-domain expressions for the fractional order system, Eq. 11, is

$$\bar{q}(t) = \int_0^t g_{HOS}(t-\tau)f(\tau)d\tau$$
$$= \int_0^t g_{HOS}(\tau)f(t-\tau)d\tau \tag{13}$$

where $g_{HOS}(t)$ is the inverse of Laplace transform $G_{HOS}(s)$[5]

$$g_{HOS}(t) = \sqrt{\frac{15}{2\pi}}\frac{1}{\sqrt{t}}\exp\left(-\frac{15}{2}t\right) \tag{14}$$

The mass exchange rate is

$$\frac{d\bar{q}}{dt} = \int_0^t g_{HOS}(t-\tau)\frac{df(\tau)}{d\tau}d\tau \tag{15}$$

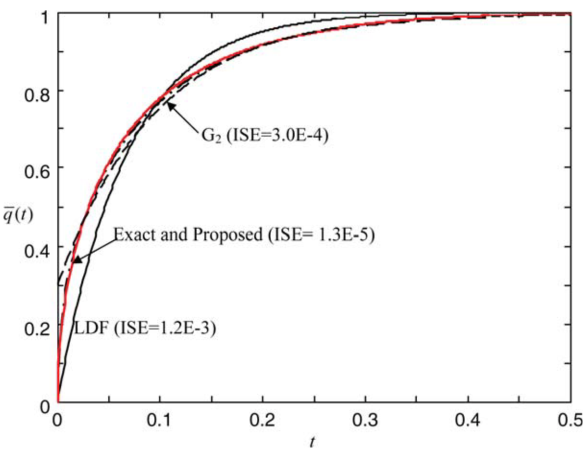

Figure 2. Step responses and integral of square errors (ISE).

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Simulations

The half-order approximation of Eq. 11 is examined for practical applications. The step response ($f(t) = 1,\ t > 0$) is

$$\bar{q}(t) = \int_0^t g_{HOS}(\tau) f(t-\tau) d\tau = \int_0^t g_{HOS}(\tau) d\tau$$
$$= \sqrt{\frac{15}{2\pi}} \int_0^t \frac{1}{\sqrt{\tau}} \exp\left(-\frac{15}{2}\tau\right) d\tau = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{15t/2}} \exp(-v^2) dv,$$
$$= erf\left(\sqrt{\frac{15t}{2}}\right) \quad (16)$$

Figure 2 shows the step responses of the previous approximations and the proposed one. The integral of squared errors (ISE) of the approximations are also listed in the figure. We can see that the ISE value of the proposed half-order model is one-hundredth of that of the LDF model.

For a square wave cyclic forcing with a period p

$$f(t) = \begin{cases} 1, & mp < t < mp + h \\ 0, & mp + h < t < mp + p \end{cases} \quad (17)$$

the response of the proposed approximation is, for $mp < t < mp + p$

$$\bar{q}(t) = \int_0^t g_{HOS}(t-\tau) f(\tau) d\tau = \int_0^h g_{HOS}(t-\tau) d\tau$$
$$+ \int_p^{p+h} g_{HOS}(t-\tau) d\tau + \cdots + \int_{mp}^t g_{HOS}(t-\tau) d\tau$$
$$= \sum_{k=0}^{m} \left(erf\left(\sqrt{\frac{15(t-kp)}{2}}\right) - erf\left(\sqrt{\frac{15(t-kp-h)}{2}}\right) \right) \quad (18)$$

Here square roots of negative values in Eq. 18 are set to zero. Arranging Eq. 18, we have

$$\bar{q}(t+p) = \sum_{k=0}^{m+1} \left(erf\left(\sqrt{\frac{15(t+p-kp)}{2}}\right) - erf\left(\sqrt{\frac{15(t+p-kp-h)}{2}}\right) \right)$$
$$= erf\left(\sqrt{\frac{15(t+p)}{2}}\right) - erf\left(\sqrt{\frac{15(t+p-h)}{2}}\right)$$
$$+ \sum_{k=1}^{m+1} \left(erf\left(\sqrt{\frac{15(t+p-kp)}{2}}\right) - erf\left(\sqrt{\frac{15(t+p-kp-h)}{2}}\right) \right)$$
$$= \bar{q}(t) + erf\left(\sqrt{\frac{15(t+p)}{2}}\right) - erf\left(\sqrt{\frac{15(t+p-h)}{2}}\right) \quad (19)$$

Hence, $\psi = erf\left(\sqrt{\frac{15(t+p)}{2}}\right) - erf\left(\sqrt{\frac{15(t+p-h)}{2}}\right)$ the term determines how much time is needed to reach the cyclic steady state from the zero initial steady state. Figure 3 shows responses for the square wave forcing with $p = 0.02$ and $h = 0.01$. We can see that all the approximate models yielding rational transfer functions, regardless of its approximations order, fails to describe this cyclic response, while the proposed half-order model provides an excellent cyclic response.

For a general forcing function of $f(t)$, the convolution integral of Eq. 13 or Eq. 15 needs to be evaluated. As the weighting function $g_{HOS}(\tau)$ decreases very fast as τ increases (Figure 4), we can limit the integration interval without a significant loss of accuracy. Consider the term $\xi = \int_\delta^t g_{HOS}(\tau) f(t-\tau) d\tau$,

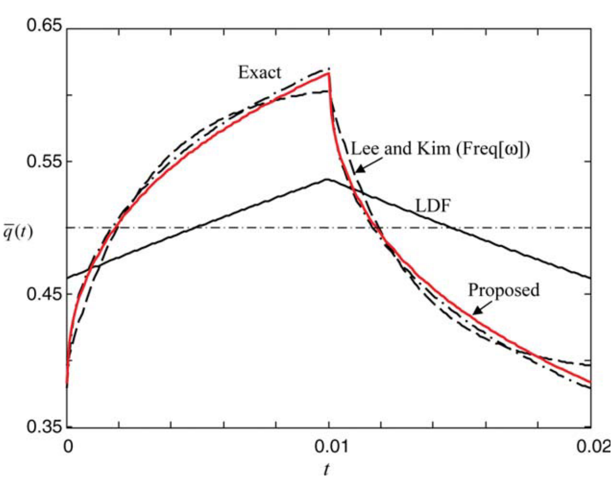

Figure 3. Responses at the cyclic steady state (p = 0.02, h = 0.01).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

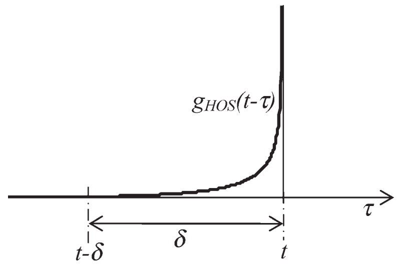

Figure 4. A weighting function $g_{HOS}(t\text{-}\tau)$ for the convolution integral.

$$|\xi| = \left| \int_{\delta}^{t} g_{HOS}(\tau) f(t-\tau) d\tau \right| = \left| \int_{0}^{t-\delta} g_{HOS}(t-\tau) f(\tau) d\tau \right|$$
$$\leq \int_{0}^{t-\delta} g_{HOS}(t-\tau) |f(\tau)| d\tau \leq |f_{\max}| \int_{0}^{t-\delta} g_{HOS}(t-\tau) d\tau$$
$$= |f_{\max}| \left(1 - erf\left(\sqrt{\frac{15\delta}{2}} \right) \right) \quad (20)$$

where $|f_{\max}|$ is the absolute maximum of $f(t)$ for the time between 0 and $t\text{-}\delta$. As δ increases, ξ decreases fast. For example, the term $\left(1 - erf\left(\sqrt{15\delta/2}\right)\right)$ is 0.0062 for $\delta = 0.5$ and 0.000108 for $\delta = 1$. Hence

$$\bar{q}(t) = \int_{0}^{\delta} g_{HOS}(\tau) f(t-\tau) d\tau + \xi \approx \int_{0}^{\delta} g_{HOS}(\tau) f(t-\tau) d\tau$$
$$= \sqrt{\frac{15}{2\pi}} \int_{0}^{\delta} \frac{1}{\sqrt{\tau}} \exp\left(-\frac{15}{2}\tau\right) f(t-\tau) d\tau \quad (21)$$

Because $f_{\max}$ is known during simulations, we can obtain δ for a given error bound of Eq. 20, and Eq. 21 can be integrated with a program in Press et al.[6] effectively. Figure 5 shows effects of δ on the responses at the cyclic steady state. For most practical applications, $\delta = 0.5$ would be sufficient.

Half-order approximation for first-order reactions

In the presence of a first-order reaction in the catalyst particle, the mass balance equation becomes

$$\frac{\partial q(r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q(r,t)}{\partial r} \right) - \phi^2 q(r,t) \quad (22)$$

where ϕ is the Thiele modulus.[2] The transfer function for this system is

$$H(s) = 3\left(\frac{1}{\sqrt{s+\phi^2}} \coth\sqrt{s+\phi^2} - \frac{1}{s+\phi^2} \right) \quad (23)$$

When compared to the transfer function in the absence of reaction (Eq. 4), it is seen that s in Eq. 4 is substituted with $s + \phi^2$ in Eq. 23. This is equivalent to shift $G(s)$ to the left by ϕ^2 on the s axis, i.e. $G(s+\phi^2) = H(s)$. As the half-order model $G_{HOS}(s)$ approximates closely on the entire domain, the half-order approximation of $H(s)$, $H_{HOS}(s)$, can also be obtained by shifting on the s axis

$$H_{HOS}(s) = \frac{1}{\sqrt{\frac{2}{15}(s+\phi^2) + 1}} \quad (24)$$

It can be rearranged as

$$H_{HOS}(s) = \frac{1}{\sqrt{\frac{2}{15}s + \frac{2}{15}\phi^2 + 1}} = \frac{1}{\sqrt{\frac{2}{15}\phi^2 + 1}} \frac{1}{\sqrt{\frac{2}{15+2\phi^2}s + 1}} \quad (25)$$

It is the same form as Eq. 11, and its inverse in the time-domain can be easily obtained as

$$h_{HOS}(t) = \sqrt{\frac{15}{2\pi}} \frac{1}{\sqrt{t}} \exp\left(-\frac{2\phi^2 + 15}{2} t \right) \quad (26)$$

Substitution of g_{HOS} with h_{HOS} in Eqs. 13 and 15, and in the presence of a first-order reaction can be readily obtained. This simple extension to the case of a first-order reaction is not feasible with previous approximations of integer order, since their transfer functions are valid only in the vicinity of $s = 0$.

Conclusion

A simple half-order model is proposed to approximate the pore-diffusion model describing the mass-transfer dynamics in a particle. It is shown to approximate the entire frequency response of the pore-diffusion model and can be used for any operation pattern. Implementation issues for the half-order system are investigated. The half-order model is extended to the case of a first-order reaction in the particle.

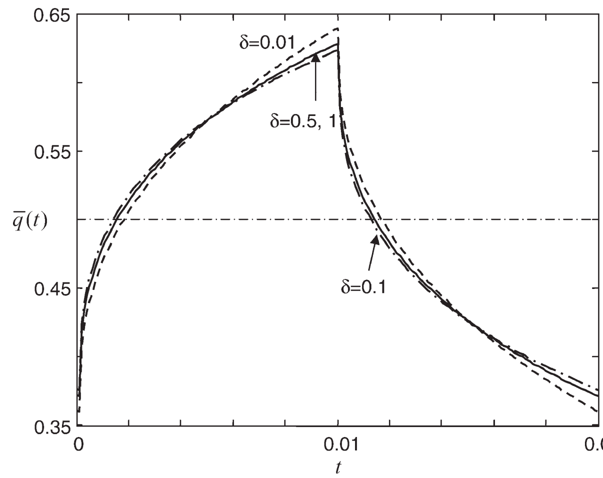

Figure 5. Effects of δ on the responses at the cyclic steady state (p = 0.02, h = 0.01).

Acknowledgments

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