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A new intraparticle mass transfer rate model for cyclic adsorption and desorption in a slab, cylinder or sphere

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Abstract A new intraparticle mass transfer rate model for cyclic adsorption and desorption in a slab, cylinder or sphere is proposed on the basis of the asymptotic behaviors of the adsorption rate for short and long cycle periods. Through comparison with the exact solution and the linear driving force (LDF) model, the new model is shown to provide a very good approximation for the instantaneous amount adsorbed as well as the adsorption rate for dimensionless half-cycle period $\tau_c = 0.001 \sim 1$ and is much better than the LDF model.

Keywords Cyclic adsorption · Rate model · Diffusion · Mass transfer · Mathematical modeling · Approximation

Nomenclature

A	Coefficient in Eq. (12)
K	LDF coefficient in Eq. (8)
n	Indicates the type of adsorbents, $n = 1, 2$ and 3 respectively for a slab, a cylinder and a sphere
Q	Dimensionless amount adsorbed defined by Eq. (23)
q	Adsorbed phase concentration in adsorbents
q_s	Value of q at adsorbent surface
$\bar{q}$	Amount adsorbed or volume-averaged value of q in adsorbents
$\bar{q}_0$	Value of $\bar{q}$ at the start of an adsorption or desorption step
x	Dimensionless spatial coordinate in adsorbents
y	Variable defined by Eq. (20)

Greek letters

$\Delta\bar{q}$	Net amount adsorbed in the adsorption step
τ	Dimensionless time
τ_c	Dimensionless half-cycle period

1 Introduction

In a cyclic adsorption and desorption process, the bulk phase mass balance equation is generally coupled with the intraparticle diffusion equation through the intraparticle mass transfer rate or adsorption/desorption rate. When an adsorbent (which may be a slab, a cylinder or a sphere) is subjected to a cyclic change in surface concentration (for simplicity a square wave with equal adsorption and desorption periods is assumed), the intraparticle diffusion equation may be written as

$$\frac{\partial q}{\partial \tau} = \frac{1}{x^{n-1}} \frac{\partial}{\partial x}\left(x^{n-1}\frac{\partial q}{\partial x}\right) \tag{1}$$

with boundary conditions

$$\frac{\partial q}{\partial x} = 0 \quad \text{at } x = 0 \tag{2}$$

$$q = q_s \quad \text{at } x = 1 \text{ for the adsorption step} \quad (0 \le \tau \le \tau_c) \tag{3}$$

$$q = 0 \quad \text{at } x = 1 \text{ for the desorption step} \quad (\tau_c \le \tau \le 2\tau_c) \tag{4}$$

where $n = 1, 2, 3$ respectively for a slab, cylinder, sphere and τ_c is the dimensionless half cycle period. The meanings of other symbols are given in the nomenclature.

At cyclic steady state the adsorption and desorption steps are related by (Carta 1993)

$$q(\tau, x) + q(\tau + \tau_c, x) = q_s \tag{5}$$

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Thus we will focus on the adsorption step only.

The instantaneous amount adsorbed or the average adsorbate concentration in the adsorbent is defined as

$$\bar{q} = n \int_0^1 q x^{n-1} dx \tag{6}$$

and the intraparticle mass transfer rate or adsorption/desorption rate is given by $\frac{d\bar{q}}{d\tau}$.

Since solving the intraparticle diffusion equation often means extensive numerical computations, approximate adsorption rate models are often used in practice. One well-known model is Glueckauf's (Glueckauf 1955) linear driving force (LDF) approximation for spherical adsorbents

$$\frac{d\bar{q}}{d\tau} = 15(q_s - \bar{q}) \tag{7}$$

For cyclic adsorption Nakao and Suzuki (1983) proposed the more general LDF model

$$\frac{d\bar{q}}{d\tau} = K(q_s - \bar{q}) \tag{8}$$

where the LDF coefficient K depends on the half-cycle period τ_c.

Other models for cyclic adsorption have been proposed and discussed by, for example, Buzanowski and Yang (1991), Gadre et al. (2005), Hsuen (2000), Kikkinides and Yang (1993), Kim (1996, 2009), Kim and Suh (1999), Sheng and Costa (1997), and Yao and Tien (1998).

The purpose of the present work is to present a new adsorption rate model for cyclic adsorption and desorption in a slab, a cylinder or a sphere which is constructed on the basis of the asymptotic behaviors of the adsorption rate for short and long cyclic periods. The new model is then compared with the exact solution and the LDF model.

2 Model development

It is noted that for long cycle periods (large τ_c) a cyclic adsorption process is similar to a batch adsorption process. In this case the penetration solution valid for short adsorption or desorption time (after the start of an adsorption or desorption step) is given by (Crank 1956)

$$\frac{\bar{q} - \bar{q}_0}{q_s - \bar{q}_0} = 2n\sqrt{\frac{\tau}{\pi}} \tag{9}$$

By differentiating Eq. (9) with respect to τ and eliminating $\sqrt{\tau}$ through Eq. (9) the adsorption rate is obtained as

$$\frac{d\bar{q}}{d\tau} = \frac{2n^2}{\pi} \frac{(q_s - \bar{q}_0)^2}{\bar{q} - \bar{q}_0} \tag{10}$$

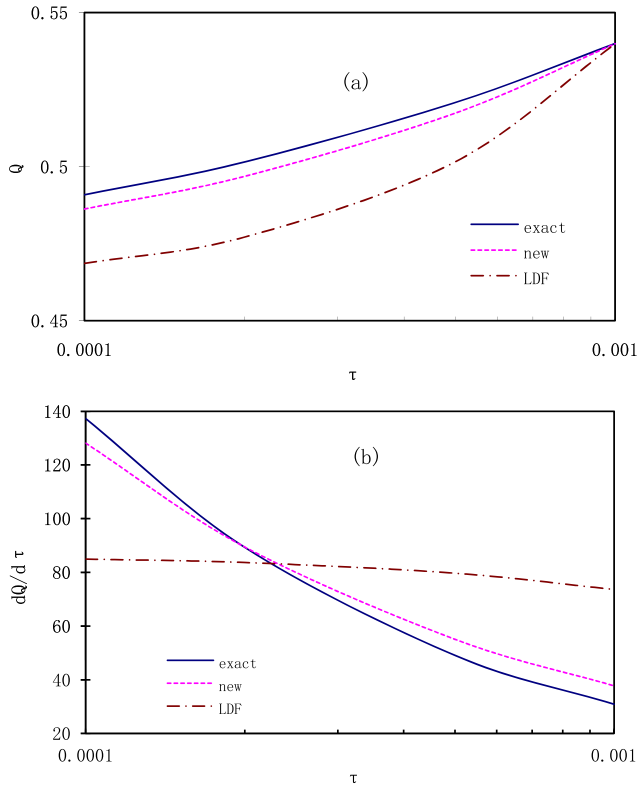


Fig. 1 Comparison of (**a**) Q and (**b**) $dQ/d\tau$ as a function of τ calculated by the new model with the exact solution and the LDF model ($K = 160$) for spherical adsorbents ($n = 3$) with $\tau_c = 0.001$

Equation (10) can be considered as a short time (when $\bar{q} \to \bar{q}_0$) approximation of the following adsorption rate (asymptotic rate for long cyclic periods) expression

$$\frac{d\bar{q}}{d\tau} = \frac{2n^2}{\pi} \frac{q_s - \bar{q}_0}{\bar{q} - \bar{q}_0}(q_s - \bar{q}) \tag{11}$$

For short cycle periods (small τ_c) we assume an adsorption rate expression similar to Eq. (10)

$$\frac{d\bar{q}}{d\tau} = A\frac{(q_s - \bar{q}_0)^2}{\bar{q} - \bar{q}_0} \tag{12}$$

where A is a coefficient to be determined. The integration of Eq. (12) with $\bar{q} = \bar{q}_0$ at $\tau = 0$ gives

$$\frac{\bar{q} - \bar{q}_0}{q_s - \bar{q}_0} = \sqrt{2A\tau} \tag{13}$$

For short cycle periods Alpay and Scott (1992) and Scott (1994) gave the net amount adsorbed in the adsorption step

$$\frac{\Delta\bar{q}}{q_s} \equiv \frac{\bar{q}(\tau_c) - \bar{q}_0}{q_s} = 0.8568n\sqrt{\tau_c} \tag{14}$$

From Eqs. (5), (13)and (14) one can obtain

$$A = 2\left(\frac{0.8568n}{1 + 0.8568n\sqrt{\tau_c}}\right)^2 = \frac{1.468n^2}{(1 + 0.8568n\sqrt{\tau_c})^2} \tag{15}$$

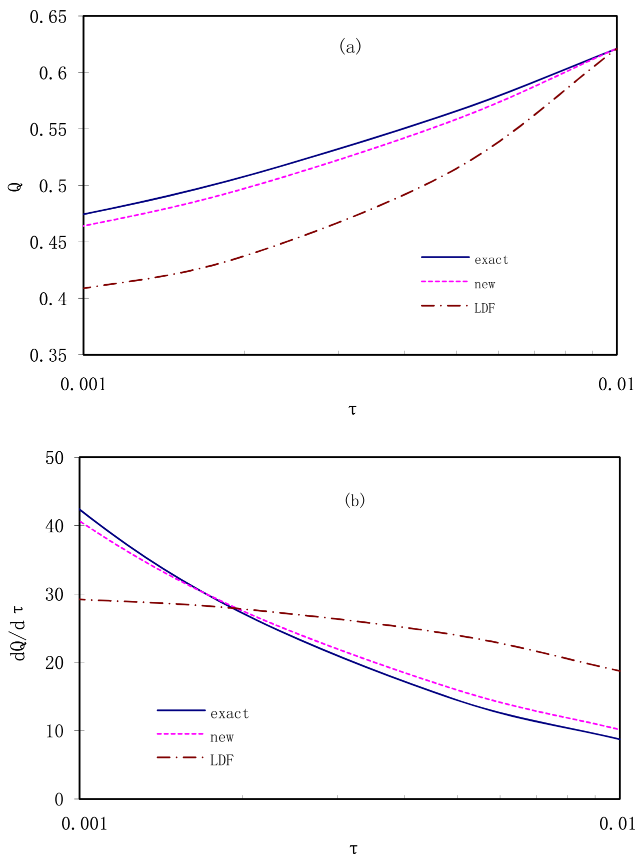


Fig. 2 Comparison of (**a**) Q and (**b**) $dQ/d\tau$ as a function of τ calculated by the new model with the exact solution and the LDF model ($K = 49.4$) for spherical adsorbents ($n = 3$) with $\tau_c = 0.01$

Then from Eq. (12) one has

$$\frac{d\bar{q}}{d\tau} = \frac{1.468n^2}{(1+0.8568n\sqrt{\tau_c})^2}\frac{(q_s-\bar{q}_0)^2}{\bar{q}-\bar{q}_0} \tag{16}$$

Equation (16) can be taken as a short time (when $\bar{q} \to \bar{q}_0$) approximation of the following adsorption rate expression

$$\frac{d\bar{q}}{d\tau} = \frac{1.468n^2}{(1+0.8568n\sqrt{\tau_c})^2}\frac{q_s-\bar{q}_0}{\bar{q}-\bar{q}_0}(q_s-\bar{q}) \tag{17}$$

For short cycle periods Eq. (17) can be simplified to

$$\frac{d\bar{q}}{d\tau} = 1.468n^2\frac{q_s-\bar{q}_0}{\bar{q}-\bar{q}_0}(q_s-\bar{q}) \tag{18}$$

which is the asymptotic adsorption rate for short cyclic periods.

From Eqs. (11) and (18) we construct a new adsorption rate model for cyclic adsorption and desorption in a slab, a cylinder or a sphere with arbitrary cycle periods

$$\frac{d\bar{q}}{d\tau} = n^2\left\{\frac{1.468}{(1+0.8568n\sqrt{\tau_c})^2}\right.$$

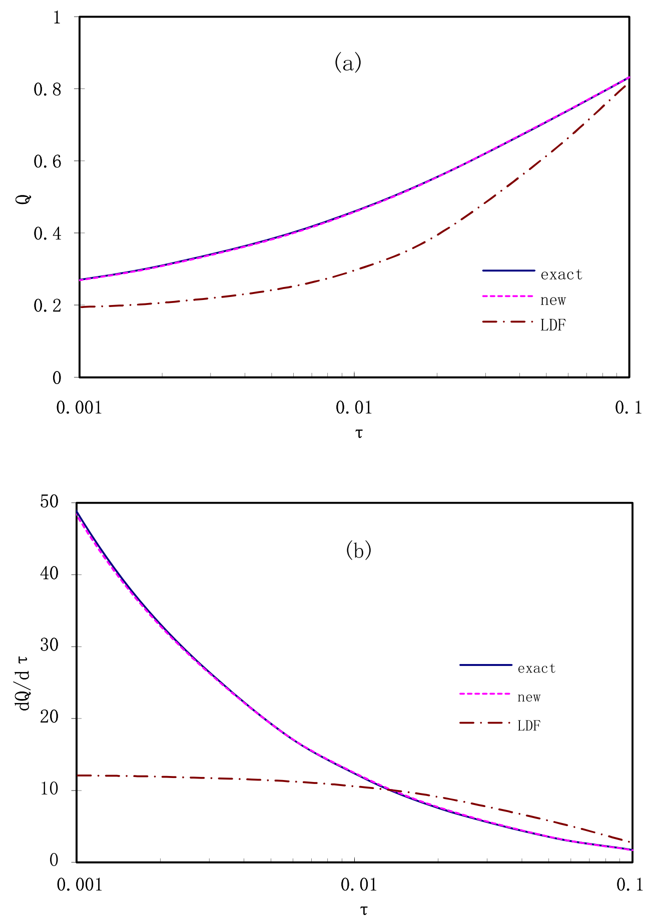


Fig. 3 Comparison of (**a**) Q and (**b**) $dQ/d\tau$ as a function of τ calculated by the new model with the exact solution and the LDF model ($K = 15$) for spherical adsorbents ($n = 3$) with $\tau_c = 0.1$

$$\left.+\frac{2}{\pi}\left[1-\frac{1}{(1+0.8568n\sqrt{\tau_c})^2}\right]\right\}\frac{q_s-\bar{q}_0}{\bar{q}-\bar{q}_0}(q_s-\bar{q})$$
$$= n^2\left[0.6366+\frac{0.8314}{(1+0.8568n\sqrt{\tau_c})^2}\right]\frac{q_s-\bar{q}_0}{\bar{q}-\bar{q}_0}(q_s-\bar{q}) \tag{19}$$

It is noted that $\bar{q}_0$ in Eq. (19) is the value of $\bar{q}$ at the start of an adsorption or desorption step.

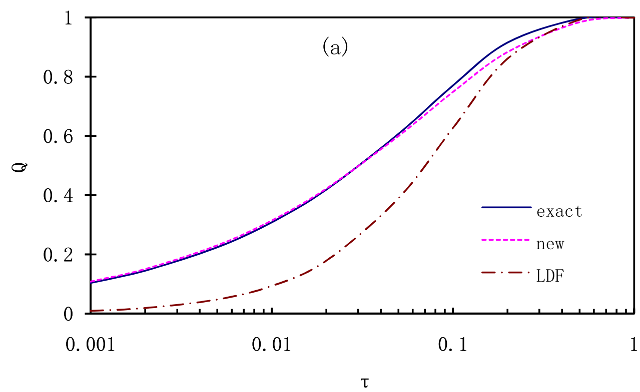
3 Comparison of the new model with the exact solution and the LDF model

For convenience we define a dimensionless variable y as

$$y = \frac{\bar{q}-\bar{q}_0}{q_s-\bar{q}_0} \tag{20}$$

Then Eq. (19) becomes

$$\frac{dy}{d\tau} = n^2\left[0.6366+\frac{0.8314}{(1+0.8568n\sqrt{\tau_c})^2}\right]\frac{1-y}{y} \tag{21}$$



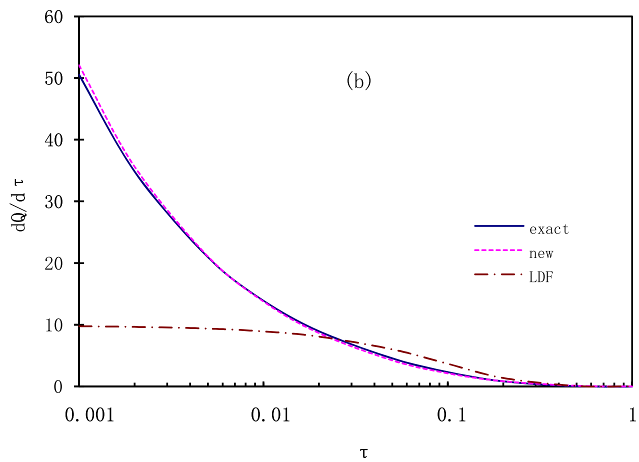
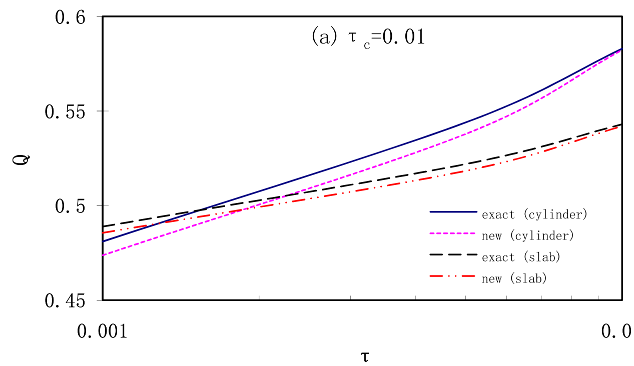


Fig. 4 Comparison of (**a**) Q and (**b**) $dQ/d\tau$ as a function of τ calculated by the new model with the exact solution and the LDF model ($K=\pi^2$) for spherical adsorbents ($n=3$) with $\tau_c=1$



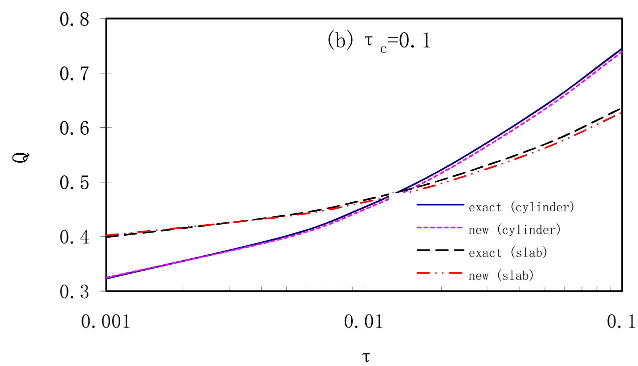


Fig. 5 Comparison of Q as a function of τ calculated by the new model with the exact solution for slab ($n=1$) and cylindrical ($n=2$) adsorbents with (**a**) $\tau_c=0.01$ and (**b**) $\tau_c=0.1$

which is integrated with $y=0$ at $\tau=0$ to give

$$y+\ln(1-y)+n^2\left[0.6366+\frac{0.8314}{(1+0.8568n\sqrt{\tau_c})^2}\right]\tau=0 \tag{22}$$

From Eqs. (5) and (20) one can show that the dimensionless instantaneous amount adsorbed Q may be expressed as

$$Q\equiv\frac{\bar{q}}{q_s}=\frac{1+y-y(\tau_c)}{2-y(\tau_c)} \tag{23}$$

Thus Q is readily calculated once y is determined from Eq. (22) and the dimensionless adsorption rate $dQ/d\tau$ can then be evaluated from Eq. (19).

For spherical adsorbents ($n=3$), values of Q and $dQ/d\tau$ as a function of τ are shown in Figs. 1, 2, 3 and 4, respectively, for $\tau_c=0.001, 0.01, 0.1, 1$ along with the exact solution by Alpay and Scott (1992)

$$Q=1-\frac{6}{\pi^2}\sum_{i=1}^{\infty}\frac{1}{i^2}\frac{1}{e^{i^2\pi^2\tau}+e^{i^2\pi^2(\tau-\tau_c)}}\quad\text{(sphere)} \tag{24}$$

as well as the LDF solution with the LDF coefficient K given by Nakao and Suzuki (1983). From Figs. 1, 2, 3 and 4 it is seen that the new model provides a very good approximation for the amount adsorbed as well as the adsorption rate (In some cases the new model and the exact solution are hardly distinguishable) and is much better than the LDF model.

For slab ($n=1$) and cylindrical ($n=2$) adsorbents, values of Q as a function of τ by the new model are shown in Fig. 5 for $\tau_c=0.01$ and 0.1 along with the exact solution by Scott (1994)

$$Q=1-\frac{2}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(i+\frac{1}{2})^2}\frac{1}{e^{(i+\frac{1}{2})^2\pi^2\tau}+e^{(i+\frac{1}{2})^2\pi^2(\tau-\tau_c)}}\quad\text{(slab)} \tag{25}$$

$$Q=1-4\sum_{i=1}^{\infty}\frac{1}{\alpha_i^2}\frac{1}{e^{\alpha_i^2\tau}+e^{\alpha_i^2(\tau-\tau_c)}}\quad\text{(cylinder)} \tag{26}$$

where α_i's are roots of $J_0(\alpha)=0$. It is again seen that the new model provides a very good approximation.

4 Conclusions

A new intraparticle mass transfer rate model for cyclic adsorption and desorption in a slab, cylinder or sphere, Eq. (19), is constructed on the basis of the asymptotic behaviors of the adsorption rate for short and long cycle periods. Through comparison with the exact solution and the linear driving force (LDF) model, the new model is shown to provide a very good approximation for the instantaneous amount adsorbed as well as the adsorption rate and is much better than the LDF model.

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