MASS TRANSFER COEFFICIENT IN CYCLIC ADSORPTION AND DESORPTION

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Intraparticle distribution of adsorbate amount in cyclic adsorption and desorption is simulated by two methods: rigorous numerical solution of the particle-phase diffusion equation and the linear driving force (LDF) approximation. It becomes clear that the conventional value of $15 \frac{D_s}{R^2}$ as the intraparticle mass transfer coefficient, $k_{a_s}$, in the LDF method is not advisable for the simulation of transient adsorption and desorption. A mass transfer coefficient defined by including the cycle time is thus proposed. In this new conception, $k_{a_s}$ increases with decreasing cycle time and approaches $\pi^2 \frac{D_s}{R^2}$ with increasing cycle time. Simulations of cyclic mode by the LDF method using this new $k_{a_s}$ agree well in the steady state with that obtained by numerical solution of the diffusion equation. In unsteady-state operation, however, the two simulations do not coincide with each other because of overestimation of driving force for adsorption and underestimation for desorption in the LDF method.

Introduction

In the operation of adsorption in gas or liquid system and of desorption for the regeneration of adsorbent, the transport phenomenon of adsorbate in an adsorbent particle is expressed by the diffusion equation in an exact manner. As this equation cannot be solved analytically except for cases when the profile of the amount adsorbed is defined, it must be solved numerically in general, and the calculation is very complicated and tedious. Therefore the diffusion equation is often replaced by the linear driving force (LDF) method using intraparticle mass transfer coefficient.

In the LDF method, it is essential to determine the magnitude of the mass transfer parameter involved in the model. The parameter $k_{a_s}$, particle mass transfer coefficient, is usually related to the intraparticle diffusivity, $D_s$, and to the radius of an adsorbent particle, $R$, through the following equation:

$$k_{a_s} = 15 \frac{D_s}{R^2} \quad (1)$$

Equation (1) was derived for long-term adsorption/desorption from a uniform initial concentration distribution. In cases of rapid adsorption cycles, such as pressure swing adsorption, however, application of the particle mass transfer coefficient defined by Eq. (1) for analysis of reactor performance is dubious, since the cycle time is often much smaller than the time constant of diffusion inside the adsorbent particle and hence concentration distribution in the particle may show a complex change.

In this study, rapid cyclic adsorption and desorption in a spherical adsorbent particle is simulated by changing fluid-phase concentration stepwise by means of both numerical solution of the diffusion equation and the LDF method. Then the results of simulations by the two methods are compared. A new conception of particle mass transfer coefficient is proposed for describing rapid cycles correctly.

1. Basic Equations

1.1 Intraparticle diffusion model

When solid-phase or surface diffusion dominates the transport of adsorbate in a spherical adsorbent particle and the particle surface is in equilibrium with the external fluid whose concentration is constant, the basic diffusion equation for the amount adsorbed in the particle, $q$, is written as

$$\frac{\partial q}{\partial t} = D_s \left( \frac{\partial^2 q}{\partial r^2} \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (2)$$

with boundary conditions

$$r = R : \frac{\partial q}{\partial r} = 0 \quad (3)$$

$$r = 0 : \frac{\partial q}{\partial r} = 0 \quad (4)$$

and initial condition

$$q = f(r) \quad \text{for} \quad 0 \leq r \leq R \quad (5)$$

where $D_s$ is the effective diffusion coefficient, $q_o$ is the amount adsorbed in equilibrium with the concentration of outside fluid-phase and $f(r)$ is the initial distribution of $q$.

The set of equations (2) to (5) is expressed in a dimensionless manner, and can be transformed into simpler forms as

$$\frac{\partial z}{\partial \theta} = \frac{\partial^2 z}{\partial x^2} \quad (6)$$

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Three dimensionless numbers, \(x\), \(y\) and \(\theta\), are defined as
\[
x = \frac{r}{R}, \quad y = \frac{q}{q_0}, \quad \theta = \frac{D_{st}}{R^2}
\]
and the new variable, \(z\), is expressed as
\[
z = xy
\]
\(G(x)\) is the transformed initial distribution of \(q\). The analytical solution of Eqs. (6) to (9) is given as the following equation.2)
\[
z = x + 2 \sum_{n=1}^{\infty} \sin(n\pi x) \exp(-n^2\pi^2 \theta)
\]
\[
\times \int_0^1 \{G(x)-x\} \sin(n\pi x) dx
\]
When the distribution function, \(G(x)\), is known, the change in the profile of the amount adsorbed in an adsorbent particle can be obtained by Eq. (11). Since the function \(G(x)\) is generally unknown in cyclic adsorption and desorption, one cannot use Eq. (11) for the calculation of \(z\). A numerical solution must be employed.

For the numerical calculation, the Saul'yev two-point average method5,6) is used in this study.

### 1.2 Linear driving force method

By the linear driving force (LDF) method, the change of amount adsorbed with time is written as
\[
\frac{dq}{dt} = k_s a_s (q_o - q)
\]
where \(q_o\) is the value that is in equilibrium with the fluid-phase concentration outside the adsorbent particle. Equation (12) is integrated with the condition, \(t=0\): \(q=q_i\), and the result is expressed in the following dimensionless form:
\[
(y_o-y)/(y_o-y_i) = \exp(-K\theta)
\]
where
\[
K = k_s a_s R^2 / D_s
\]

### 1.3 Total amount adsorbed

Total amount of adsorbate adsorbed in a particle, \(Q\), is given as
\[
Q = \int_0^r q(r) \cdot (4\pi r^2) \rho_p dr
\]
\[
= \frac{3q_o W_p}{2} \int_0^1 xz dx
\]
where \(W_p\) is the weight of an adsorbent particle. Total amount adsorbed in equilibrium with outside fluid-phase, \(Q_o\), is equal to the product \(q_o W_p\), so the dimensionless total amount adsorbed is written as
\[
\frac{Q}{Q_o} = 3 \int_0^1 xz dx
\]
This integration is made by Simpson's three-point rule using the numerical solution of \(z\). For the LDF method, \(Q/Q_o\) is equal to \(y\).

### 1.4 Simulation of cyclic adsorption and desorption

The concentration of fluid phase outside the spherical particle of adsorbent changes stepwise between a certain constant value and zero in a cyclic manner. The cycle time is \(2\theta_c\), that is, a unit adsorption period of \(\theta_c\) and a unit desorption period of \(\theta_c\).

In the simulation based on the diffusion equation, Eq. (6), the distribution function \(G(x)\) is equal to zero at the start of calculation, then the first adsorption uptake is calculated till the time \(\theta_c\). Next, the calculated profile of the amount adsorbed at \(\theta_c\) is substituted into \(G(x)\), and the following desorption calculation with zero surface concentration is started. After the calculation for the desorption period, \(\theta_c\), the adsorption cycle is started by taking the final profile of the desorption step as \(G(x)\). The calculation is repeated till the dynamic steady state, in which the amount adsorbed and desorbed during one cycle becomes constant, is reached.

In the simulation by the LDF method, the value of \(y_o\) in Eq. (13) is held at unity for the adsorption period:
\[
y = 1 -(1-y_i) \exp(-K\theta) \quad (17)
\]
and held at zero for the desorption period:
\[
y = y_i \exp(-K\theta) \quad (18)
\]
The first adsorption step is started by Eq. (17) with the initial condition, \(y_i = 0\). The next desorption period is then obtained by Eq. (18) with the \(y\) value at the time \(\theta_c\) in Eq. (17) as the initial condition \(y_i\).

The amount adsorbed after repeating this calculation \(2n\) times, that is, \(n\) cycles of adsorption and desorption, is given as
\[
y_{2n} = (1 - T) \sum_{k=1}^{n} T^{2k-1} \quad (19)
\]
where
\[
T = \exp(-K\theta) \quad (20)
\]
Equation (19) expresses the amount adsorbed at the end of the desorption period, and the value at the end of the adsorption period is given by Eq. (18) as
\[
y_{2n-1} = y_{2n}/T \quad (21)
\]
The amounts adsorbed at the end of the adsorption step and that of the desorption step in the dynamic steady state, \(y_{ads}\) and \(y_{des}\), are obtained by putting \(n=\infty\) in Eqs. (19) and (21).
\[
y_{ads} = 1/(1 + T) \quad (22)
\]
\[
y_{des} = T/(1 + T) \quad (23)
\]
Fig. 1. Changes of profiles of amount adsorbed in an adsorbent particle with time at unsteady state. \( \theta_c = 0.01 \); numbers express repetition times.

On the basis of these considerations, it is clear that by the LDF method the amount adsorbed and its change with time in the dynamic steady state can be simulated with Eqs. (17), (18), (22) and (23), if the half-cycle time, \( \theta_c \), and particle mass transfer coefficient \( k_s a_e \) are given.

2. Results and Discussion

2.1 Simulation by the diffusion equation

A typical change of profiles of the amount adsorbed in a particle at the end of the adsorption or desorption period with time is shown in Fig. 1. In the dynamic steady state, the dimensionless amount adsorbed is found to be almost 0.5 near the center of a particle in the cases when nondimensional half cycle time, \( \theta_c = D_s t / R^2 \), is smaller than 0.1.

Changes in the profile of the amount adsorbed in a particle during steady-state cycles are illustrated for three \( \theta_c \) values, 0.1, 0.01 and 0.001, in Figs. 2(a) to (c). As shown in these figures, the small part near the surface of an adsorbent particle is utilized when \( \theta_c \) is small. Therefore, for cyclic operation of adsorption and desorption it is significant for the effective utilization of adsorbent to choose an appropriate size of particles on the basis of cycle time.

Changes in total amount adsorbed in a particle in the transient cycles are shown in Figs. 3(a) and (b) for the two cases, \( \theta_c = 0.1 \) and 0.01. The number of repetitions to reach the steady mode increases with decreasing \( \theta_c \), but the total time necessary to reach steady state is almost constant at about 0.5 independent of \( \theta_c \) value.

The total amount adsorbed in a particle at the end of the adsorption step and that at the end of the desorption step in the dynamic steady state are shown against half-cycle time \( \theta_c \) in Fig. 4. As is clear from this figure, the adsorption and desorption equilibria are reached alternately in the operation when a larger half-cycle time than 0.5 is employed.
2.2 Simulation by the LDF method

As mentioned before, the value of $15D/R^2$ is conventionally used as the particle mass transfer coefficient in the LDF method. Thus, this relation is first adopted for the simulation of cyclic adsorption and desorption. Results of the change in amount adsorbed are shown in Figs. 3(a) and (b), respectively, for $\theta_c=0.1$ and 0.01. Apparently, the result by the LDF method agrees well with that by numerical solution of the diffusion equation for $\theta_c=0.1$. However, for the case of smaller $\theta_c$ (Fig. 3(b)), the two results show a big discrepancy, and the total amount adsorbed or desorbed in one cycle calculated by the LDF method becomes far smaller than that calculated from the diffusion equation.

Therefore, one can conclude that Eq. (1) cannot be employed for the simulation of cyclic operations such as pressure swing adsorption except in the case when $\theta_c$ is almost equal to 0.1. Hence the particle mass transfer coefficient must be modified in order that the amount adsorbed/desorbed in cyclic operation can be properly estimated by the LDF method.

2.3 Particle mass transfer coefficient as a function of cycle time

Desorption processes after the cyclic operation for various $\theta_c$ values reaches dynamic steady state are calculated by the diffusion equation, and results are shown in Fig. 5, where $Q_t$ expresses the total amount adsorbed at the end of the adsorption period, which is the starting point of desorption in the dynamic steady state. As illustrated in Fig. 5, the $Q/Q_t$ value decreases rapidly in the first stage, and then decreases with the constant slope of $\pi^2$. The value of $\pi^2$ can be derived theoretically. (See appendix.) It is obvious from this figure that there is little difference in desorption rate in spite of the big difference of $\theta_c$ value, that is, $Q_t$ value, and that the final slopes become $\pi^2$.

On the basis of the LDF method, this desorption process is calculated by Eq. (18), and this equation can be rewritten as

$$\ln \left( \frac{Q}{Q_t} \right) = -K\theta$$

(24)

If values of $\ln \left( \frac{Q}{Q_t} \right)$ are plotted against dimensionless time $\theta$, the result exhibits a linear line through unity on an ordinate, and its slope has the value of $K$. In the case of $\tau_c=0.2$, for example, if one draws the line of Eq. (24) between unity on an ordinate and the end-point of the desorption curve for $\theta_c=0.2$, which is shown by the thin solid line in Fig. 5, the slope of this line gives the value of $K$ for $\theta_c=0.2$. Values of $y_{ads}$ and $y_{des}$ can be calculated from Eqs. (22) and (23) using this $K$ value, and agree with those calculated from the diffusion equation. Thus, the particle mass transfer
The mass transfer coefficient is considered as a function of the cycle time of $\theta_c$, cyclic operations.

The relationship between $K$ determined by the above method and $\theta_c$ is shown in Fig. 6. This relationship becomes linear for $\theta_c$ values less than about 0.1, and $K$ approaches asymptotically to $\pi^2$ for large $\tau_c$. The value of $k$ at $\theta_c = 0.1$ falls near 15, so the results of simulation by the two methods agree spontaneously, as illustrated in Fig. 3(a).

Results of the simulation of cyclic adsorption and desorption by the LDF method using the mass transfer coefficient obtained in Fig. 6 are shown in Figs. 7(a) and (b) for $\theta_c = 0.01$ and 0.001 together with the simulations from the diffusion equation. As illustrated in these figures, both results agree very well in the dynamic steady state, but show different speeds of approach to steady state. This disagreement becomes large for small $\theta_c$ values. In the early stage of cyclic operations, the total amount adsorbed for one adsorption period calculated by the LDF method is larger than that from the diffusion equation, and the total amount desorbed during one desorption period by the former method is smaller. Therefore, simulation by the LDF method approaches more rapidly to steady state.

For the adsorption period in the transient state, the amount adsorbed decreases continuously from the surface of a particle, where $y$ is unity, as illustrated in Fig. 1. But a uniform profile of the amount adsorbed is assumed in the LDF method, and thus the driving force between the surface and the inside of a particle is overestimated. On the other hand, desorption begins from the surface of a particle which is almost in equilibrium, that is, $y \approx 1$. But a much smaller amount of desorption is derived from the LDF method, because the driving force is underestimated. These are the reasons for disagreement in transient behavior from the startup of the cyclic adsorption process as illustrated in Figs. 7(a) and (b).

On the basis of the above results, it is concluded that cyclic operation in dynamic steady state can be simulated very well by the LDF method using the particle mass transfer coefficient defined in Fig. 6. However, transient behavior cannot be simulated well, particularly when the operation is carried out with a small cycle time.

Conclusion

Simulations of cyclic adsorption and desorption in a spherical adsorbent particle were performed by using two methods, the LDF method and the diffusion equation method, and the following results were obtained.

1) The conventional value of $15D_1/R^2$ as the particle mass transfer coefficient is not advisable for the estimation of the steady-state performance of cyclic adsorption and desorption processes, such as pressure swing adsorption.

2) Mass transfer coefficient determined by taking into account the cycle time of the process is proposed from a comparison of the LDF method and the rigorous numerical solution of the diffusion equation.

3) This new definition of mass transfer coefficient could simulate cyclic adsorption and desorption very well in the steady state, but not satisfactorily in the transient processes from startup, particularly for the small cycle time operation.

Appendix

For the desorption process, the analytical solution of the basic diffusion equation defined by Eq. (11) is rewritten as
\[ z = \sum_{n=1}^{\infty} I_n \sin(n\pi x) \exp(-n^2\pi^2\theta) \]  
\[ Q = \sum_{n=1}^{\infty} I_n \exp(-n^2\pi^2\theta) \int_0^{\frac{1}{1}} G(x) \sin(n\pi x) \, dx \]

The dimensionless total amount adsorbed is written in the following form by substituting Eq. (A-1) into Eq. (16).

\[ \frac{Q}{Q_0} = 6 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} I_n \exp(-n^2\pi^2\theta) \]  
\[ \text{The dimensionless total amount adsorbed at the start of desorption is given as} \]

\[ \frac{Q}{Q_i} = 3 \int_0^{\frac{1}{1}} xG(x) \, dx = 3I_i \]  
\[ \text{Then one can obtain the following equation from Eqs. (A-2) and (A-3).} \]

\[ \frac{Q}{Q_i} = \frac{2}{\pi I_i} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} I_n \exp(-n^2\pi^2\theta) \]  
\[ \text{For infinite time, } \theta \to \infty, \text{ Eq(A-4) is expressed by the first-term approximation as} \]

\[ \frac{Q}{Q_i} = \frac{2I_i}{\pi I_i} \exp(-\pi^2\theta) \]  
\[ \text{Therefore, the desorption curves in Fig. 5 approach linear lines having a constant slope of } \pi^2. \]

\[ y = 1, \text{ that is, } G(x) = x \]

Then Eq. (A-5) is expressed as

\[ \frac{Q}{Q_i} = \frac{6}{\pi^2} \exp(-\pi^2\theta) \]  
\[ \text{The line given by Eq. (A-7) agrees with the linear part of the curve of } \theta_i = 1.0 \text{ in Fig. 5.} \]

**Nomenclature**

- \( D_s \) = effective surface diffusion coefficient [m²/s]
- \( f(r) \) = distribution function of absorbate amount [mol/kg]
- \( G(x) \) = distribution function of \( z \) [-]
- \( K \) = quantity defined by Eq. (14) [-]
- \( k_{ads} \) = particle mass transfer coefficient [l/s]
- \( Q \) = total amount adsorbed in an adsorbent particle [mol]
- \( Q_i \) = total amount adsorbed at end of adsorption period in steady state [mol]
- \( Q_0 \) = total amount adsorbed in equilibrium with outside fluid phase [mol]
- \( q \) = amount adsorbed [mol/kg]
- \( q_i \) = initial amount adsorbed [mol/kg]
- \( q_{ads} \) = amount adsorbed in equilibrium with outside fluid-phase [mol/kg]
- \( R \) = radius of a spherical adsorbent particle [m]
- \( r \) = distance from center of an adsorbent particle [m]
- \( T \) = quantity defined by Eq. (20) [-]
- \( t \) = time [-]
- \( W_p \) = weight of an adsorbent particle [kg]
- \( x \) = dimensionless distance defined by \( r/R \) [-]
- \( \gamma \) = dimensionless amount adsorbed defined by \( q/q_0 \) [-]
- \( \gamma_{ads}, \gamma_{des} \) = dimensionless amount adsorbed at end of adsorption and desorption period in steady state, respectively [-]
- \( \gamma_i \) = dimensionless initial amount adsorbed [-]
- \( \gamma_{ads} \) = dimensionless amount adsorbed at surface of an adsorbent particle [-]
- \( z \) = quantity defined by Eq. (10) [-]
- \( \theta \) = dimensionless time defined by \( D_s t/R^2 \) [s]
- \( \theta_i \) = dimensionless half-cycle time [-]
- \( \rho_p \) = adsorbent particle density [kg/m³]

**Literature Cited**