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SHORT COMMUNICATION

A New Mass Transfer Model for Cyclic Adsorption and Desorption

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Abstract–This article presents a new mass transfer model which describes mass transfer rates in a spherical particle where cyclic adsorption and desorption occur. The parameters in the model equation were determined by matching the exact numerical solution to the prediction of this rate law over a range of cycle times. The maximum error was found to be 4.3 %. Since the parameters are independent of cycle time, this model equation can be generally used for cyclic adsorption and desorption process regardless of the cycle time and cycle configuration.

Key words : Mass Transfer Model, Adsorption, Desorption, Mass Transfer Coefficient, Cyclic Process, Pressure Swing Adsorption

INTRODUCTION

Fixed-bed adsorption processes often employ a cyclic operation involving adsorption and desorption. For mathematical simulation of the adsorption processes, a set of partial differential equations should be numerically solved with respect to time and spatial variables. Models and cycles of the cyclic adsorption processes are quite complex. Moreover, many cycles are often required to reach cyclic steady state and many repetitive computations should be performed. Since the intraparticle diffusion phenomenon is difficult to exactly describe in the cyclic adsorption process, approximate expressions are usually employed. LDF (linear driving force) model is widely used instead of pore diffusion model or solid diffusion model to simplify the computations.

The LDF approximation suggested by Glueckauf [1955], however, cannot be accurate for cyclic surface boundary conditions. Kim [1989] developed LDF approximations taking into account reaction as an extension of the work of Glueckauf. In order to apply the LDF approximation to the cyclic operation, Nakao and Suzuki [1983] established a graphical correlation between the mass transfer parameter in the LDF equation and the cycle time for stepwise changes in the surface concentration of a single particle. Raghavan et al. [1986] used the Nakao and Suzuki model to simulate a pressure swing adsorption process and compared the prediction results with the diffusion model. Buzanowski and Yang [1989] suggested a different type of extended LDF approximation based on a cubic intraparticle concentration profile, and showed that a time-dependent coefficient in the cubic term could lead to the exact solution. Later, Buzanowski and Yang [1991] proposed a better approximation using the adjustable parameter, which is a function of cycle time. Alpay and Scott [1992] used the same methodology as Nakao and Suzuki [1983] to express the mass transfer coefficient analytically, replacing the numerically derived results of Nakao and Suzuki. The same problem was solved by Carta [1993] using Laplace transforms. The solution matched the penetration theory approximation of Alpay and Scott [1992] and the numerical results of Nakao and Suzuki [1983] for short cycles, and the Fourier series expansion of Alpay and Scott [1992] and the numerical calculations of Buzanowski and Yang [1991] for longer cycles. For improvement of the LDF approximation for short cycle times, Kikkinides and Yang [1993] proposed an algorithm where the particle is divided into two zones, active or inactive for sorption, and then used one-point collocation in the active sorption zone whose length varies with time. The collocation points were approximately 0.88 during adsorption and 0.12 during desorption. In their algorithm, the two constants were in fact dependent upon the surface concentration. Recently, an analytical solution for the stepwise cyclic mass transfer problem has been obtained by Choong and Scott [1998] considering the effect of external fluid-film mass transfer. In their results, the external fluid resistance reduces the LDF mass transfer coefficient significantly at small cycle time. Fourier series approach was introduced by Kim [1996] to develop a simple linear formula that can be used for any cycle time. The coefficients in the formula were analytically derived using Fourier series and expressed as functions of the cycle time. High-order approximations were developed for adsorption and diffusion in a particle with a unimodal pore size distribution by Lee and Kim [1998]. Also, high-order approximations were used for noncyclic and cyclic adsorption in a biporous pellet [Kim and Lee, 1999].

The mass transfer models developed in earlier studies for cyclic operation mostly include parameters which are dependent upon cycle time. However, in an actual cyclic separation process, such as pressure swing adsorption, the whole cycle consists of several steps where adsorption and desorption occur in various modes and the step times are not always the same.

In this study, a new mass transfer model of a simple nonlinear form is developed for cyclic adsorption and desorption. The objective of this development is that the parameters in

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*Current address : Basic Technology Research Dept., Mabookri, Research Institute, Hyundai Heavy Industries Co., Yonginshi, Kyunggido, Korea the new model are independent of cycle time and the model equation can be generally used regardless of the cycle time and cycle configuration.

EARLIER MODELS

The new mass transfer model developed in this study is compared with the following earlier models in terms of the adsorbed amount in the particle that has cyclic change in the surface concentration.

1. Intraparticle Diffusion Model (Reference Model)

For spherical particles, the intraparticle diffusion equation is

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

where all the variables are made dimensionless. Dimensionless time θ and r are defined by tD_e/R^2 and r_a/R, respectively.

Boundary conditions for adsorption or desorption steps are

$$q=q_0(r) \quad \text{at the start of each step} \tag{2}$$

$$q=q_s \quad \text{at} \quad r=1 \tag{3}$$

$$\frac{\partial q}{\partial r}=0 \quad \text{at} \quad r=0 \tag{4}$$

where q_s is the surface concentration of adsorbate. This diffusion problem could be solved by numerical methods. In most PSA conditions, gas film mass transfer resistance around the particle is often negligible [Yang, 1987].

2. LDF Model with Parameter Changing with Cycle Time [Nakao and Suzuki, 1983]

The Nakao and Suzuki model employs a linear driving force equation with a mass transfer coefficient, K, which is dependent upon cycle time.

$$\frac{\partial \bar{q}}{\partial \theta}=K(q_s-\bar{q}) \tag{5}$$

where bar $\bar{q}$ is the adsorbed-phase concentration averaged over the entire pellet volume. This model is one of the typical LDF models that has parameter changing with cycle time. Nakao and Suzuki extracted the effective mass transfer coefficient K by comparing the solution of the intraparticle diffusion equation, Eq. (1), and that of the LDF equation, Eq. (5), for stepwise cyclic diffusion problem. The usefulness of the Nakao and Suzuki model was confirmed by other researchers using analytical mathematical techniques.

3. Kim Model [Kim, 1996]

Kim introduced the following equation to describe the change of adsorbed amount with time :

$$\frac{\partial \bar{q}}{\partial \theta}=\alpha(q_s-A_0)-\beta(\bar{q}-A_0) \tag{6}$$

where A_0 is the time-average concentration of q_s. The parameters in Eq. (7) are given as

$$\alpha=\omega^2\phi_1+\frac{\psi_1^2}{\phi_1} \qquad \beta=\frac{\psi_1}{\phi^1} \tag{7}$$

$$\phi_1=\sum_{n=1}^{\infty}\frac{6}{n^4\pi^4+\omega^2} \qquad \psi_1=\sum_{n=1}^{\infty}\frac{6n^2\pi^2}{n^4\pi^4+\omega^2} \tag{8}$$

where ω is the cycle speed which is 2π divided by the cycle time. As shown above, the parameters α and β in Kim model depend upon cycle time. This formula was demonstrated to provide an excellent representation of the mass change rate in a cyclic adsorption system.

NEW MODEL (THIS STUDY)

In this study, the following model equation was suggested for cyclic adsorption and desorption :

$$\frac{d\bar{q}}{d\theta}=A(q_s-\bar{q})+B\frac{(q_s-\bar{q})^2}{(\bar{q}-\bar{q}_0)} \tag{9}$$

where $\bar{q}_0$ is the initial adsorbed-phase concentration in the adsorption step or desorption step. Therefore, $\bar{q}_0$ at the start of the adsorption step or desorption step is the same as the end of the previous step. We aimed to obtain the coefficient for the linear term and the coefficient for the nonlinear term so that the error between the simulation results using the new model and those using the diffusion model could be minimized for cyclic adsorption and desorption.

If one solves Eq. (9) with the initial condition of $\bar{q}_0=0$ at $\theta=0$, the analytical solution is

$$\left[1+\left(\frac{A}{B}-1\right)\left(\frac{\bar{q}-\bar{q}_0}{q_s-\bar{q}_0}\right)\right]^{\left[\frac{B}{A-B}\right]}\left[1-\frac{(\bar{q}-\bar{q}_0)}{(q_s-q_0)}\right]=\exp[-A\theta] \tag{10}$$

For stepwise change in the surface concentration, cyclic boundary conditions are

$$q_s=q^* \qquad \text{for adsorption step} \tag{11}$$

$$q_s=0 \qquad \text{for desorption step} \tag{12}$$

The dimensionless adsorbed-phase concentration Q is defined by

$$Q=\frac{\bar{q}}{q^*} \tag{13}$$

Eq. (10) is used to calculate the adsorbed-phase concentration Q_1 at the end of the first adsorption step :

$$\left[1+\left(\frac{A}{B}-1\right)Q_1\right]^{\left(\frac{B}{A-B}\right)}[1-Q_1]=\exp[-A\theta_c] \tag{14}$$

where θ_c is a half-cycle time corresponding to adsorption period or desorption period. Applying cyclic boundary conditions described by Eqs. (11) and (12), we get the adsorbed-phase concentration Q_{2n-1} at the end of nth adsorption step :

$$Q_{2n-1}=\sum_{i=1}^{n}Q_1(1-Q_1)^{2i-2} \quad \text{at} \quad \theta=(2n-1)\theta_c \tag{15}$$

The adsorbed-phase concentration Q_{2n} at the end of nth desorption step is similarly obtained :

$$Q_{2n}=\sum_{i=1}^{n}Q_1(1-Q_1)^{2i-1} \quad \text{at} \quad \theta=2n\theta_c \tag{16}$$

As adsorption and desorption steps repeat infinitely, the adsorbed amount reaches cyclic steady state. The adsorbed amount at the end of adsorption step and that at the end of desorption step at cyclic steady state are, respectively,

$$Q_{ads}=\lim_{n\to\infty}Q_{2n-1}=\frac{1}{2-Q_1} \tag{17}$$

$$Q_{des}=\lim_{n\to\infty}Q_{2n}=\frac{1-Q_1}{2-Q_1} \tag{18}$$

It is noted from Eqs. (17) and (18) that the sum of Q_{ads} and Q_{des} is 1 and the average of Q_{ads} and Q_{des} is 0.5 at cyclic steady state.

The mass balance, Eq. (1), describing the intraparticle diffusion problem, has been numerically solved to get Q_{ads} and Q_{des} for stepwise change in the surface concentration until the solution reaches cyclic steady state. The average dimensionless adsorbed amount in the diffusion model was calculated by

$$Q=\left[3\int_0^1 q(r)r^2dr\right]/q^* \tag{19}$$

The solution obtained from the diffusion model and that obtained from the new model were compared at cyclic steady state for various cycle time θ_c. We optimized the two parameters in the new model so that the error between the solutions of the diffusion model and new model was minimized. As the result, parameters A and B were found to be 5.381 and 12.41, respectively. Therefore, the final mass transfer equation can be written as

$$\frac{d\bar{q}}{d\theta}=5.381(q_s-\bar{q})+12.41\frac{(q_s-\bar{q})^2}{(\bar{q}-q_0)} \tag{20}$$

RESULTS AND DISCUSSION

The adsorbed-phase concentration calculated using the new model was compared with the results of the Kim model, the Nakao and Suzuki model, and the diffusion model to test the validity of the new model. Fig. 1 illustrates the case where the spherical adsorbent is subject to cyclic stepwise concentration change. In the Nakao and Suzuki model, K is 15 when half-cycle time is 0.1. Generally, the results obtained from three approximate models show good agreement with the exact solution from the diffusion model. At cyclic steady state, the adsorbed amount in the Nakao and Suzuki model increases more slowly with time in the adsorption step and decreases more slowly in the desorption step than the diffusion model. On the contrary, in the Kim model, the adsorbed amount at the end of the adsorption step is smaller than the diffusion model and gives the smallest value among the three approximate models. Also, the adsorbed amount in Kim model at the end of desorption model gives the largest value among the three approximate models. The error in the Kim model was caused by neglecting nonlinear terms in the approximation. In terms of the transient behavior during each step and the error of the adsorbed amount at the end of each step, the new model shows excellent agreement with the diffusion model.

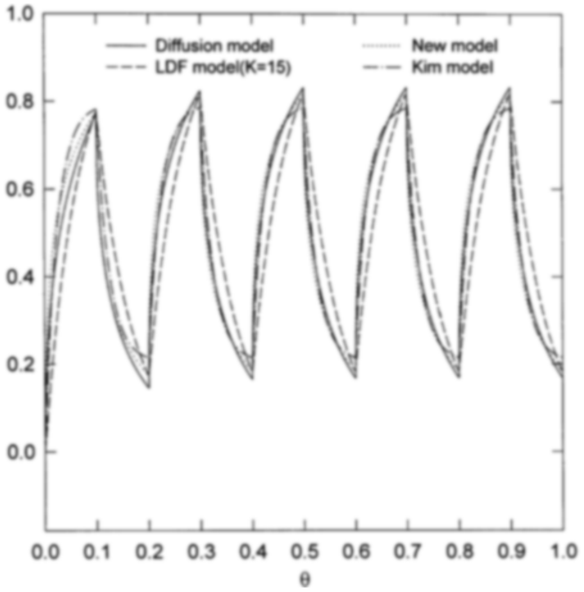

Fig. 1. Comparison of different models in calculation of adsorbed-phase concentration for cyclic stepwise surface concentration change with θ_c=0.1.

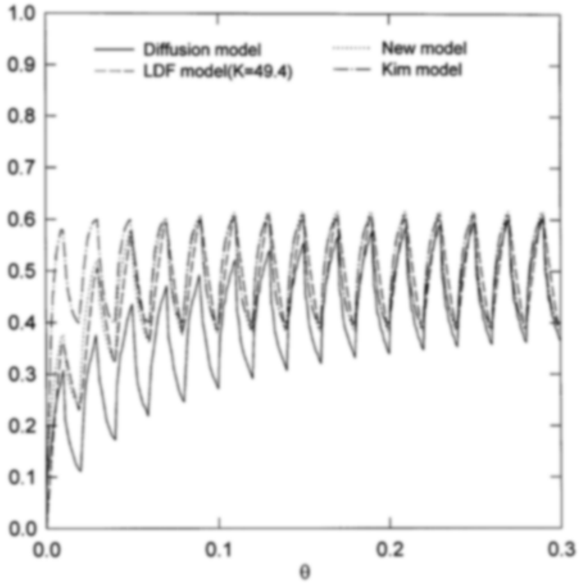

Fig. 2. Comparison of different models in calculation of adsorbed-phase concentration for cyclic stepwise surface concentration change with θ_c=0.01.

If half-cycle time is 0.01, K is 49.4 in the Nakao and Suzuki model. As cycle time becomes shorter, Fig. 2 shows that the result from the Kim model approaches cyclic steady state much more rapidly than the diffusion model. Accordingly, there exists a large error between the Kim model and the diffusion model in the transient state. The new model and the Nakao and Suzuki model in the transient state also show larger error in the cycle where half-cycle time is 0.01 than in the cycle where half-cycle time is 0.1. All the approximate models fail to represent transient behavior for the first few cycles just after the cyclic operation starts. Nevertheless, all the models are in good agreement at cyclic steady state. Comparison between the three approximate models at cyclic steady state in Fig. 2 is similar to the case of larger cycle time in Fig. 1.

In an actual industrial cyclic adsorption and desorption process, such as the pressure swing adsorption process, surface concentration around adsorbent particles does not exactly follow stepwise change. Thus, we consider sinusoidal surface concentration in the following equation.

$$q_s = 0.5\ q^*\ [\sin(\omega\theta) + 1] \tag{21}$$

Figs. 3. and 4 represent the results where half-cycle time is 0.1 and 0.01, respectively. Similar trends are observed for sinusoidal surface concentration as the case of square wave surface concentration. All the models are still in good agreement with the exact solution of the diffusion model, especially at the cyclic steady state.

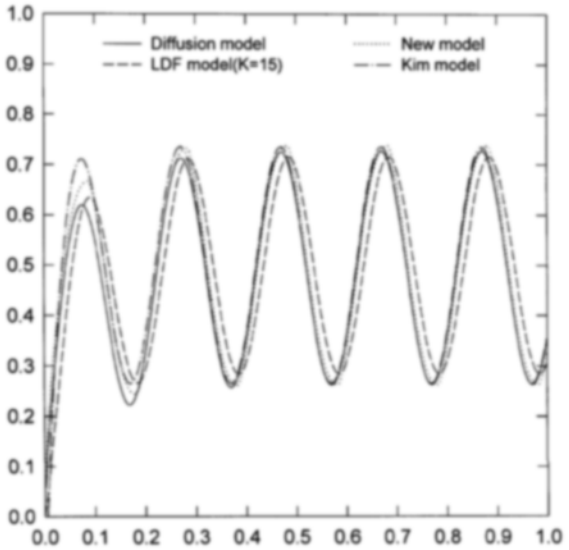

Fig. 3. Comparison of different models in calculation of adsorbed-phase concentration for sinusoidal surface concentration change with θ_c=0.1.

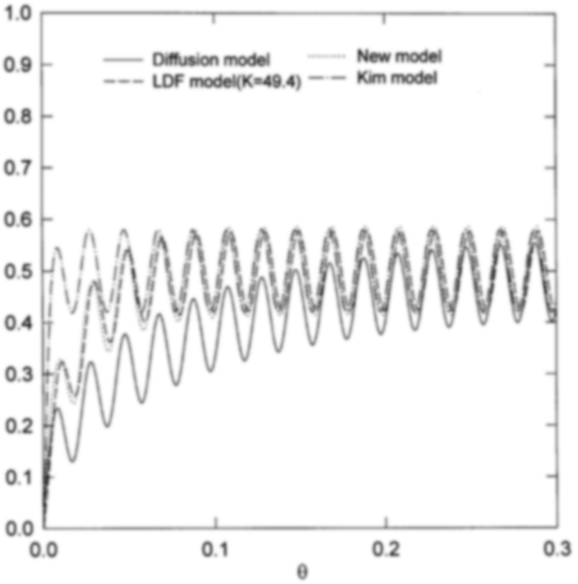

Fig. 4. Comparison of different models in calculation of adsorbed-phase concentration for sinusoidal surface concentration change with θ_c=0.01.

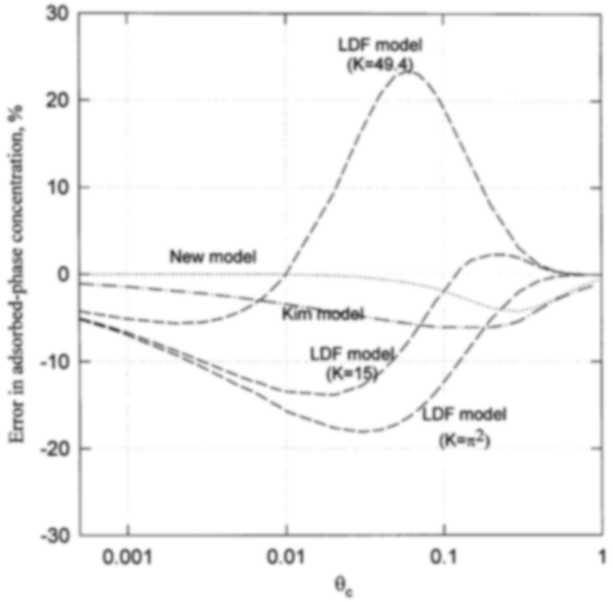

Fig. 5. Comparison of errors between approximate models and diffusion model in terms of the maximum adsorbed-phase concentration at cyclic steady state for cyclic stepwise surface concentration change.

In Fig. 5, errors between approximate models and the diffusion model are compared in terms of the maximum adsorbed amount at the end of the adsorption step at cyclic steady state for cyclic stepwise surface concentration change. The errors were presented for various half-cycle times. It can be seen in Fig. 5 that simulation results of LDF model are in agreement with the diffusion model at only one cycle time if the K value in the LDF equation is fixed. In the Nakao and Suzuki model, the optimum K value in the LDF equation was chosen varying with cycle time to match the results of the LDF equation and those of the diffusion equation. As cycle time increases, K approaches asymptotically to π^2. The relationship between K and cycle time was graphically presented in Nakao and Suzuki [1983]. The Kim model also employs parameters that change with cycle time. The parameters in the Kim model were obtained by analysis using Fourier series and the results were firmly based on theoretical background. The relationship between cycle time and the two parameters was presented in Kim [1996]. Both α and β in Eq. (6) approach 15 as cycle time decreases.

The new model in this study employs a nonlinear term added to the linear driving force term in the mass transfer equation, and the parameters in the new equation are independent of cycle time. As illustrated in Fig. 5, the simulation results from the new model show excellent agreement with the exact solution from the diffusion model regardless of cycle time. The error in the new model is less than that in the Kim model in most regions of cycle time. Also, the maximum error in the whole range of cycle time in the new model is less than that in the Kim model. The maximum error was found to be 4.3 % for the half-cycle time between 0.1 and 1.

CONCLUSIONS

A new and simple mass transfer model, Eq. (20), has been developed to simulate cyclic adsorption and desorption. The simulation results from the new model show excellent agreement with the diffusion model in the whole range of cycle times. The new model includes parameters which are unchanged with cycle time. Thus, this equation could be used regardless of adsorption and desorption step times and applied to the simulation of pressure swing adsorption processes.

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NOMENCLATURE

A : parameter in Eq. (10), dimensionless
A_0 : time-average concentration of q_s in Eq. (7), dimensionless
B : parameter in Eq. (10), dimensionless
De : effective intraparticle diffusion coefficient [cm^2/s]
K : effective mass transfer coefficient in Eq. (5), dimensionless
Q : defined by Eq. (13) ($=\bar{q}/q^*$), dimensionless
q : adsorbed-phase concentration in particle, dimensionless
q_o : initial adsorbed-phase concentration in particle, dimensionless
q_s : surface concentration of adsorbate, dimensionless
q^* : maximum surface concentration of adsorbate, dimensionless
$\bar{q}$: average adsorbed concentration over the entire particle, dimensionless
$\bar{q}_o$: initial average adsorbed concentration in each step, dimensionless
R : radius of particle [cm]
r : dimensionless radial position in particle [$=r_a/R$]
r_a : radial position in particle [cm]
t : time [s]

Greek Letters

α : parameter defined in Eq. (8), dimensionless
β : parameter defined in Eq. (8), dimensionless
θ : dimensionless time [$=tD_e/R^2$]
θ_c : half-cycle time, dimensionless
ψ_1 : parameter defined in Eq. (9), dimensionless
ϕ_1 : parameter defined in Eq. (9), dimensionless
ω : cycle speed [$=\pi/\theta_c$]

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