Characterization of adsorption uptake curves for both intraparticle diffusion and liquid film mass transfer controlling systems

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A B S T R A C T

In general, the adsorption uptake curve (AUC) can be easily determined in either intraparticle diffusion or liquid film mass transfer dominating systems. However, for both intraparticle diffusion and liquid film mass transfer controlling systems, the characterization of AUC is much more complicated, for example, when relatively small adsorbent particles are employed. In addition, there is no analytical solution available for both intraparticle diffusion and liquid film mass transfer controlling systems. Therefore, this paper is trying to characterize AUC for both intraparticle diffusion and liquid film mass transfer controlling adsorption systems using the shallow bed reactor technique.

Typical parameters influencing AUC include liquid film mass transfer coefficient (k_F), effective intraparticle diffusivity (D_S), influent concentration (c_0) and equilibrium parameters (such as Freundlich isotherm constants k and $1/n$). These parameters were investigated in this research and the simulated results indicated that the ratio of k_F/D_S and Freundlich constant $1/n$ had impact on AUC. Biot number (Bi) was used to replace the ratio of k_F/D_S in this study. Bi represents the ratio of the rate of transport across the liquid layer to the rate of intraparticle diffusion. Furthermore, Bi is much more significant than that of $1/n$ for AUC. Therefore, AUC can be characterized by Bi. In addition, the obtained Bi could be used to determine D_S and k_F simultaneously. Both parameters (D_S and k_F) are important for designing and operating fixed bed reactors.

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1. Introduction

Many techniques to determine the effective intraparticle diffusivity (D_S) and liquid film mass transfer coefficient (k_F) have been proposed [1–5], such as fixed bed breakthrough curves [1,4,6], Completely Mixed Batch Reactor (CMBR) method [2,3,5,7] and shallow bed technique [5,8]. One of the most commonly used techniques is the Mass Transfer Zone (MTZ) method [6]. The method estimated intraparticle diffusivity from the length of MTZ of experimental breakthrough curve. In general, the obtained diffusivity included experimental errors due to the fixed bed operation, such as channeling effect. An alternative method is the CMBR method [5,7]. However, it is difficult to neglect estimation error of the liquid film mass transfer when estimating D_S, because an empirical equation to evaluate mass transfer resistance within liquid film is not available.

The shallow bed reactor technique was developed to determine D_S for intraparticle diffusion controlling systems [5,8]. Satoh et al.

extended the technique to determine the intraparticle diffusivities for a ternary component system [9]. The technique has the following advantages: (1) the adsorption uptake curve (AUC) of the reactor has an analytical solution which could be used to determine the intraparticle diffusivity and (2) the equilibrium parameters are not required for the determination process [9].

When relatively small adsorbent particles are employed, contribution due to liquid film resistance to overall adsorption rate might be significant. In addition, there is no analytical solution available for intraparticle diffusion and liquid film mass transfer controlling systems using the shallow bed reactor technique. Therefore, this paper is trying to characterize AUC for both intraparticle diffusion and liquid film mass transfer controlling adsorption systems using the shallow bed reactor technique.

2. Fundamental equations and numerical simulation of adsorption curves

In a shallow bed reactor, since the bed length is very short, the adsorbate concentration at the effluent is the same as the concentration at the influent under high fluid velocity. Hence, the

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Nomenclature

a_P	surface area based on solid particle [$L^2 L^{-3}$]
Bi	Biot number based on surface diffusion
c_S	fluid concentration at interface [$M L^{-3}$]
c_t	final fluid concentration at any time (c_0 at time $t = 0$, i.e., initial concentration) [$M L^{-3}$]
d_p	adsorbate particle diameter [L]
D_S	effective intraparticle diffusivity (driving force is difference of local amount adsorbed within adsorbent between two points) [$L T^{-1}$]
k_F	liquid film mass transfer coefficient [$L^2 T^{-1}$]
q_0	amount adsorbed in equilibrium with fluid concentration c_S [$M L^{-3}$]
q_m	amount adsorbed at r [$M L^{-3}$]
Q_m	dimensionless amount adsorbed at $r = r$
q_S	amount adsorbed in equilibrium at interface with fluid concentration c_0 [$M L^{-3}$]
Q_t	dimensionless average amount adsorbed within a solid particles
q_t	average amount adsorbed within a solid particle [$M L^{-3}$]
R	dimensionless internal radial length (length from the solid center)
r	internal radial length (length from the solid center) [L]
r_P	particle radius [L]
t	adsorption time [L]
T	dimensionless adsorption time

Greek symbol

ρ_P	apparent adsorbent density [$M L^{-3}$]

adsorbate concentration at the interface between fluid and solid is the same as the concentration of the fluid running through spaces among particles. Therefore, a single particle adsorption concept can be applied [9].

Fundamental equations (Eqs. (1)–(4)) of the shallow bed reactor are based on the following assumptions: (a) constant temperature, (b) constant influent flow rate, (c) equal influent and effluent concentration and hence a single particle adsorption concept is applied in this study, (d) Freundlich-type isotherm, (e) local equilibrium established on the pore surface of adsorbent, (f) surface diffusion controlling, (g) constant effective intraparticle diffusivity and fluid film mass transfer coefficient, (h) two steps mass transfer concept applied (liquid film mass transfer and intraparticle diffusion). A typical experimental setup of the shallow bed reactor is illustrated in Fig. 1.

Intraparticle diffusion

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

I.C.: $q_m = 0$ at $t = 0$; B.C.: $q_m = q_0$ at $r = r_P$

$$\left(\frac{\partial q_m}{\partial r}\right) = 0 \quad \text{at } r = 0$$

Transport in liquid film

$$\rho_S\left(\frac{\partial q_t}{\partial t}\right) = k_F a_P(c_0 - c_S) \tag{2}$$

Transport at interface

$$\left(\frac{\partial q_t}{\partial t}\right) = -D_S a_P \left(\frac{\partial q_m}{\partial r}\right)_{r=r_P} \tag{3}$$

Average amount adsorbed

$$q_t = \frac{\int_0^{r_P} 4\pi q_m r^2\,dr}{(4/3)\pi r_P^3} = \left(\frac{3}{r_P^3}\right)\int_0^{r_P} q_m r^2\,dr \tag{4}$$

Equilibrium relationship

$$q_S = k_F c_S^{1/n} \tag{5}$$

Since there is no analytical solution for average amount adsorbed (q_t) (Eq. (4)), finite difference equations were employed to evaluate simultaneous differential equations simultaneously. An iterative procedure, i.e. the successive over-relaxation method, was used to calculate the resulting finite difference equations of Eq. (1) with Eqs. (2) and (3), because this method accelerated the convergence of calculations. The computer program written with Borland C++ Builder for the numerical simulation in this research is referred as Adsorption of Shallow Bed Simulator (ASB simulator).

3. Results and discussion

3.1. Simulation methodology

3.1.1. Integration errors

In this paper, Simpson's procedure was employed to evaluate Eq. (4). Integration errors of the method were estimated by the comparison of simulated numerical values with the analytical solutions of q_t, assuming that q_t is a function of r, having the form of $q_t/q_0 = a (r/r_P)^2 + b$. a and b are constants. Assuming that the value of q_t/q_0 and r/r_P vary from zero to unity, the simulated distribution of q_t/q_0 is shown in Fig. 2 with various values of a and b. The optimum value of $(r_P/\Delta r)$ is evaluated by seeking the minimum integration errors. Δr is the increment length of radial length.
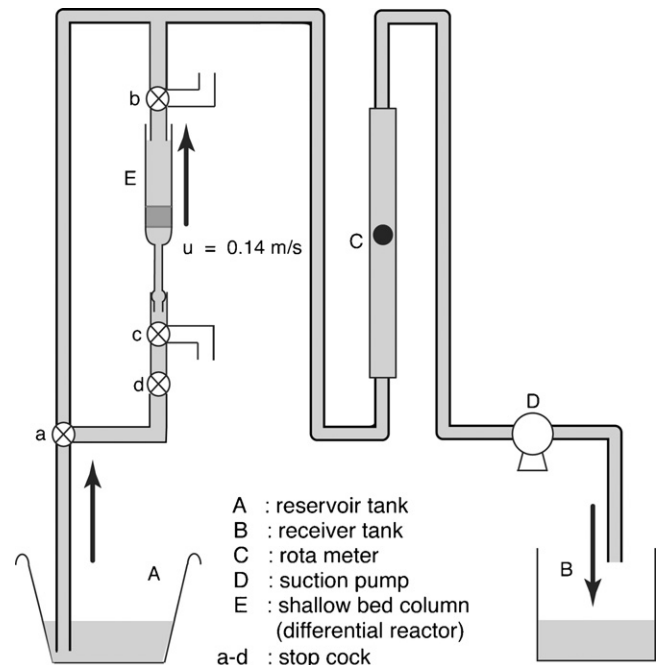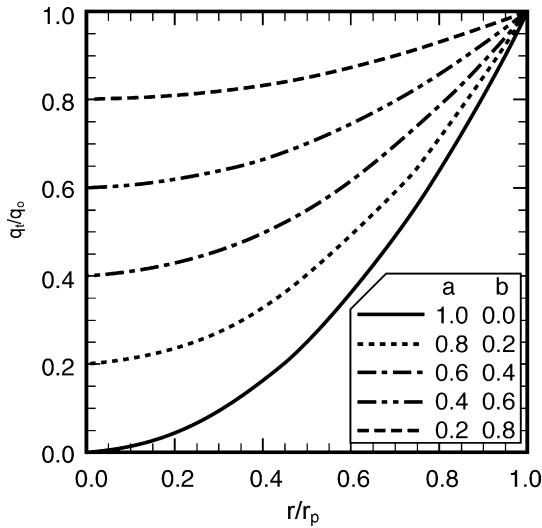

Fig. 1. Schematic of the shallow bed reactor.

Fig. 2. Simulated results of amount adsorbed by ASB simulator.

Table 1
Simulated conditions.

	Condition 1	Condition 2
Adsorbate	Phenol	Phenol
Adsorbent	Activated carbon	Activated carbon
Adsorbent particle diameter (cm)	0.06	0.06
Adsorbent apparent density (kg L^{-1})	396	396
Fluid concentration (mg L^{-1})	1000	1000
Freundlich parameter k (mmol g^{-1})	1.63	1.63
Freundlich parameter, n	4.32	4.32
D_S (cm^2 s^{-1})	8.0×10^{-8}	8.0×10^{-8}
k_F (cm s^{-1})	4.1×10^{-3}	4.1×10^{-3}

increment of $(r_P/\Delta r)$ is determined to be 30 for this research as shown in Fig. 5.

3.2. Dependency of AUC on k_F, D_S, c_0, k, and $1/n$

The fundamental equations of AUC are depending on liquid film mass transfer coefficient (k_F), effective intraparticle diffusivity (D_S), influent concentration (c_0) and equilibrium parameters (Freundlich isotherm constants k and $1/n$). Under the conditions listed

Relative errors of numerical simulation results with various ratios of $r_P/\Delta r$ are shown in Fig. 3. The integration errors performed with $r_P/\Delta r > 20$ are negligible (<10^{-4}% errors). Therefore, $r_P/\Delta r > 20$ is applied in this research. The above simulation verified the validity of the numerical simulation of AUC.

3.1.2. Optimum increment of time (Δt) and radial length (Δr)

Numerical results of the simulation were affected by simulation conditions, i.e. increment of time (Δt) and increment of radial length (Δr). Optimum values of Δt and Δr (or $r_P/\Delta r$ in this study) have to be determined before characterizing AUC. Using the conditions listed in Table 1-condition 1, AUC with Δt varied from 1 to 3 s is illustrated in Fig. 4. $\Delta t < 1.5$ s seems to be the optimum value, since there is no significant difference between 1 and 1.5 s. Therefore, $\Delta t = 1.5$ s is used in this study. Assuming the intraparticle diffusion controlling systems listed in Table 1-condition 2, the simulated AUC with various $r_P/\Delta r$ is shown in Fig. 5. The theoretical AUC (TUC) (solid line) is shown in the figure as well. The method for determining TUC can be found elsewhere [8–11]. By the comparison of numerical simulated results and the TUC, the optimum
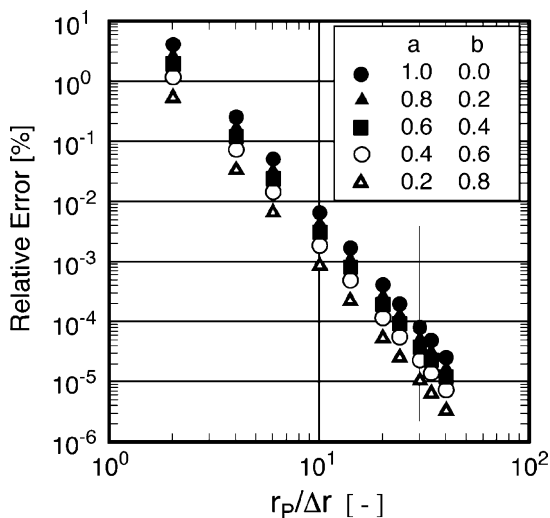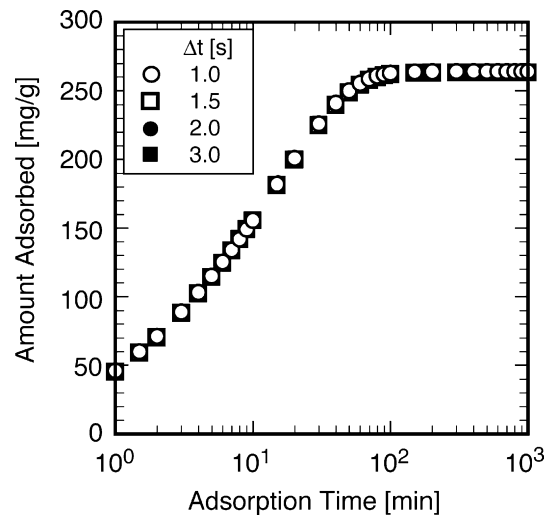

Fig. 4. Simulated results of AUC at various Δt.

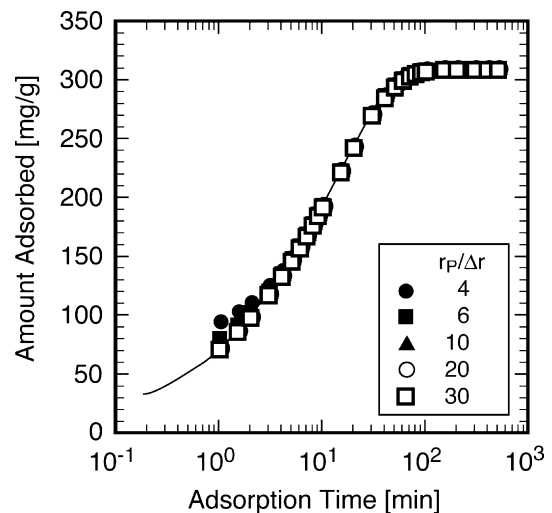**Fig. 3.** Relative errors at various $r_P/\Delta r$ simulated by ASB simulator.

Fig. 5. Simulated results of AUC at various $r_P/\Delta r$. The solid line is TUC.
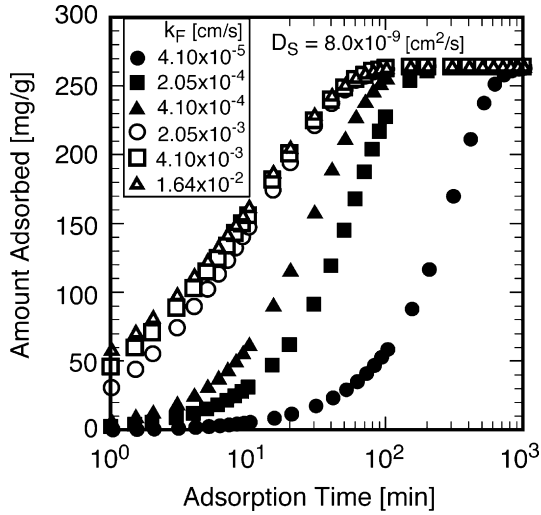
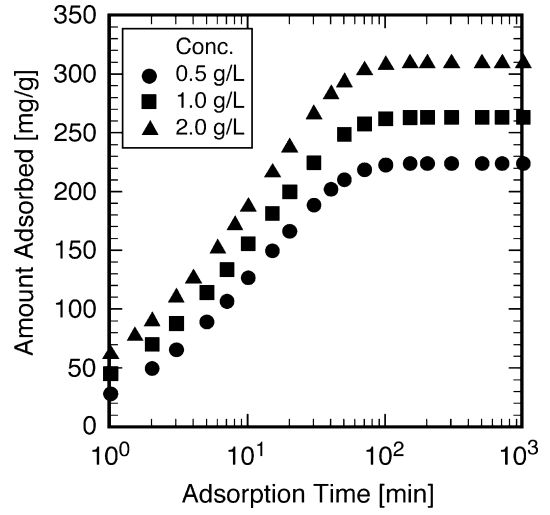**Fig. 6.** Simulated results of AUC at various k_F with constant D_S.

in Table 1-condition 1, simulated AUC with various k_F, D_S, c_0, and $(k, 1/n)$ are shown in Figs. 6–9, respectively. It is apparent that all these parameters have significant impacts on AUC. In addition, the AUC seems to be shifted upward by higher influent concentrations.

3.3. Dependency of dimensionless AUC on dimensionless variables

For intraparticle diffusion and liquid film mass transfer controlling systems, as mentioned above, several parameters affect AUC. Dimensionless variables are introduced in this research to minimize the number of parameters. For example, Biot number (Bi) was used to replace k_F and D_S. Bi represents the ratio of the rate of transport across the liquid layer to the rate of intraparticle diffusion within the particle [3,4]. The dimensionless variables are listed below.

Fig. 7. Simulated results of AUC at various D_S with constant k_F.

Dimensionless variables:

$$T = \left(\frac{D_S}{r_P^2}\right) t, \qquad R = \frac{r}{r_P}, \qquad Q_m = \frac{q_m}{q_0}, \qquad Q_t = \frac{q_t}{q_0},$$

$$\mathrm{Bi} = \frac{k_F r_P c_0}{D_s \rho_p q_0} \qquad (6)$$

Dimensionless Eqs. (7)–(10) were derived from Eqs. (1)–(5) by use of dimensionless variables listed above. Eq. (8) was obtained from Eqs. (2) and (3) as shown in Appendix A. Freundlich isotherm was employed at the interface of the adsorbent as shown in Eq. (10).

Intraparticle diffusion

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left(\frac{1}{R^2}\right) \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q_m}{\partial R}\right) \qquad (7)$$

I.C.: $Q_m = 0$ at $T = 0$; B.C.: $Q_m = 1$ at $R = 1$

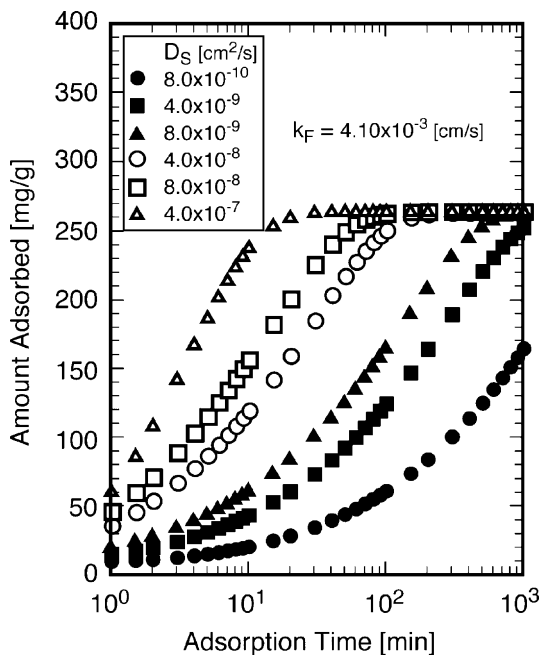$$\left(\frac{\partial Q_m}{\partial R}\right) = 0 \quad \text{at } R = 0$$

Fig. 8. Simulated results of AUC at various c_0.
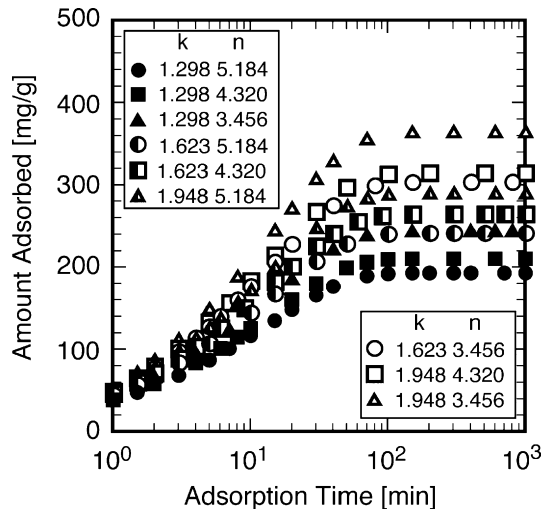

Fig. 9. Simulated results of AUC at various equilibrium parameters (k, n).
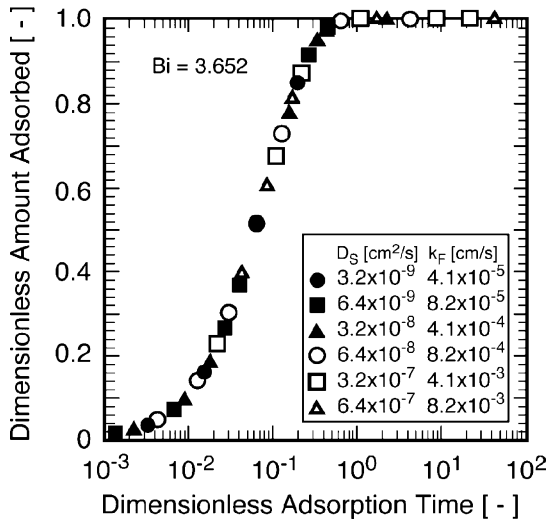
Fig. 10. Simulated results of AUC at Bi = 3.652 with different values of k_F and D_S.

Fluid-to-solid transport

$$-\left(\frac{\partial Q_m}{\partial R}\right)_{R=1} = \text{Bi}(C_t - C_S) \tag{8}$$

Average amount adsorbed

$$Q_t = 3 \int_0^1 Q_m R^2 \, dR \tag{9}$$

Equilibrium relationship

$$Q_S = c_S^{1/n} \tag{10}$$

Major steps of numerical calculations are shown in Appendix B. As shown in Eqs. (7)–(10), only Bi and $1/n$ would affect the dimensionless AUC. These results indicated that the ratio of k_F to D_S has significant impact on the dimensionless AUC. This concept is further verified in Fig. 10. Under condition of Bi = 3.65 with various values of k_F and D_S, all these AUCs overlap with each other.

The dependency of dimensionless AUC on equilibrium parameter, n, was studied as well. Fig. 11 shows AUC estimated at various values of $1/n$ at Bi = 3.65 and 12.5, respectively. The dependency
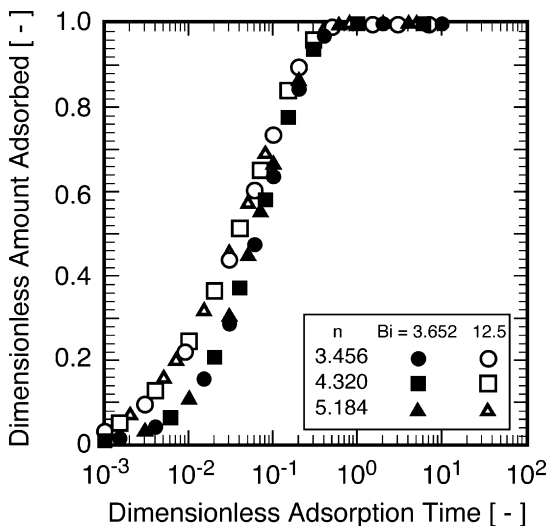

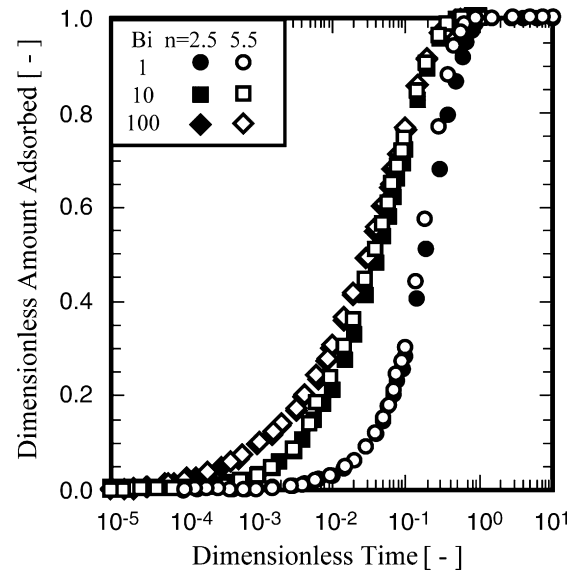**Fig. 11.** Simulated results of AUC at various n. Bi = 3.652 and 12.5, respectively.

Fig. 12. Sensitivity check of simulation results for Bi (1, 10 and 100) and n (2.5 and 5.5).

of dimensionless AUC on equilibrium parameter $(1/n)$ is not significant. Furthermore, sensitivity analysis for Bi (1, 10 and 100) and n (2.5 and 5.5) is shown in Fig. 12. In general, AUC shifted to the right with smaller value of Bi. In other word, a smaller Bi has longer dimensionless breakthrough time. Therefore, based on these observations, AUC can be characterized by Bi.

4. Conclusions

AUC were estimated numerically under various experimental and numerical conditions in this study. The optimum simulation conditions are $\Delta t < 1.5$ s and $r_P/\Delta r > 30$.

With the assistance of the dimensionless variable conversion, the simulated results of this research indicated that the ratios of k_F/D_S and Freundlich isotherm constant $(1/n)$ have impact on AUC. In addition, the ratio of k_F/D_S is much more significant than that of $1/n$ for AUC. The ratio of k_F/D_S can be further represented by Biot number, since Bi represents the ratio of the rate of transport across the liquid layer to the rate of intraparticle diffusion.

Therefore, based on these results, AUC can be characterized by Bi for both intraparticle diffusion and liquid film mass transfer controlling adsorption systems using the shallow bed reactor technique. As a result, the obtained Bi might be used to determine D_S and k_F, simultaneously. Both parameters (D_S and k_F) are important for designing and operating a fixed bed reactor.

Appendix A

A.1. Fundamental equations

1. Intraparticle diffusion

$$\left(\frac{\partial q_m}{\partial t}\right) = \left(\frac{D_S}{r^2}\right) \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_m}{\partial r}\right) \tag{1-1}$$

I.C.: $q_m = 0$ at $t = 0$; B.C.: $q_m = k(c_S)^{1/n}$ at $r = r_P$

$$\left(\frac{\partial q_m}{\partial r}\right) = 0 \quad \text{at } r = 0$$

2. Fluid-to-solid film transport

$$\rho_S \left(\frac{\partial q_t}{\partial t}\right) = k_F a_P (c_t - c_S), \quad c_t \text{ is constant} \tag{1-2}$$

3. Interface transport

$$\left(\frac{\partial q_t}{\partial t}\right) = -D_S a_P \left(\frac{\partial q_m}{\partial r}\right)_{r=r_P} \tag{1-3}$$

4. Average amount adsorbed

$$q_t = \frac{\int_0^{r_P} 4\pi q_m r^2 \, dr}{4/3\pi r_P^3} = \left(\frac{3}{r_P^3}\right) \int_0^{r_P} q_m r^2 \, dr \tag{1-4}$$

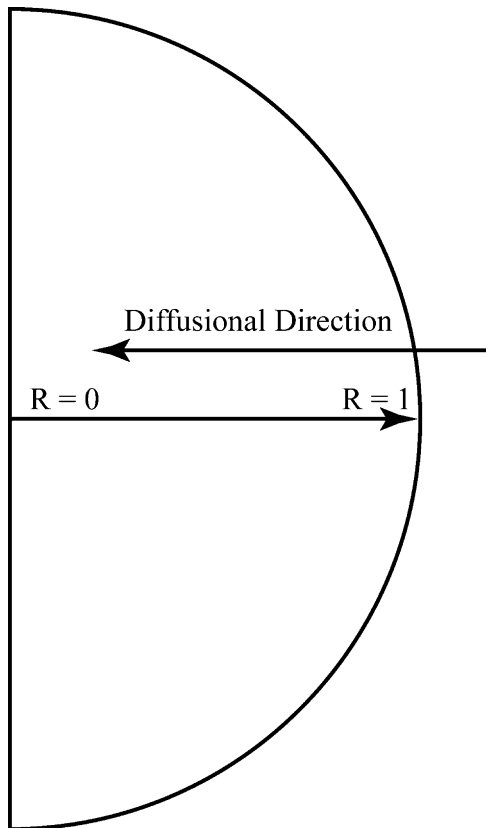Direction of diffusion and particle radius is shown in Fig. A1.

Fig. A1. Directions of diffusion and particle radius for numerical calculations.

A.2. Dimensionless variables

$$T = \left(\frac{D_S}{r_P^2}\right) t, \qquad \left(\frac{\partial T}{\partial t}\right) = \left(\frac{D_S}{r_P^2}\right)$$

$$R = \left(\frac{r}{r_P}\right), \qquad \left(\frac{\partial R}{\partial r}\right) = \left(\frac{1}{r_P}\right)$$

$$C_t = \left(\frac{c_t}{c_0}\right), \qquad \left(\frac{\partial c_t}{\partial C_t}\right) = c_0$$

$$Q_t = \left(\frac{q_t}{q_0}\right), \qquad \left(\frac{\partial q_t}{\partial Q_t}\right) = q_0$$

$$Q_m = \left(\frac{q_m}{q_0}\right), \qquad \left(\frac{\partial q_m}{\partial Q_m}\right) = q_0$$

A.3. Dimensionless equations

1. Intraparticle diffusion

$$\left(\frac{\partial q_m}{\partial t}\right) = \left(\frac{D_S}{r^2}\right) \frac{\partial}{\partial r}\left(r^2 \frac{\partial q_m}{\partial r}\right)$$

$$\left(\frac{\partial q_m}{\partial Q_m} \frac{\partial T}{\partial t} \frac{\partial Q_m}{\partial T}\right) = \left(\frac{D_S}{r^2}\right)\left(\frac{\partial R}{\partial r} \frac{\partial}{\partial R}\right)\left(r^2 \frac{\partial q_m}{\partial Q_m} \frac{\partial R}{\partial r} \frac{\partial Q_m}{\partial R}\right)$$

$$\left(q_0 \frac{D_S}{r_P^2} \frac{\partial Q_m}{\partial T}\right) = \left(\frac{D_S}{R^2 r_P^2}\right)\left(\frac{1}{r_P} \frac{\partial}{\partial R}\right)\left(R^2 r_P^2 q_0 \frac{1}{r_P} \frac{\partial Q_m}{\partial R}\right)$$

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left(\frac{1}{R^2}\right) \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q_m}{\partial R}\right)$$

I.C.: $q_m = 0$ at $t = 0$; $Q_m = 0$ at $T = 0$; B.C.: $q_m = k(c_S)^{1/n}$ at $r = r_P$

$$\frac{q_m}{q_0} = \frac{k(c_S)^{1/n}}{k(c_0)^{1/n}}$$

$$Q_m = \left(\frac{c_S}{c_0}\right)^{1/n} = (C_S)^{1/n} \quad \text{at } R = 1$$

$$\left(\frac{\partial q_m}{\partial r}\right) = 0 \quad \text{at } r = 0$$

$$\left(\frac{\partial q_m}{\partial Q_m} \frac{\partial R}{\partial r} \frac{\partial Q_m}{\partial R}\right) = \left(\frac{q_0}{r_P} \frac{\partial Q_m}{\partial R}\right) = 0$$

$$\left(\frac{\partial Q_m}{\partial R}\right) = 0 \quad \text{at } R = 0$$

2. Fluid-to-solid film transport

$$\rho_S \left(\frac{\partial q_t}{\partial t}\right) = k_{F,i} a_P (c_t - c_S)$$

$$\rho_S \left(\frac{\partial q_t}{\partial Q_t} \frac{\partial T}{\partial t} \frac{\partial Q_t}{\partial T}\right) = k_F \left(\frac{3}{r_P}\right) c_0 (C_t - C_S),$$

$$a_P = \frac{4\pi r_P^2}{(4/3)\pi r_P^3} = \left(\frac{3}{r_P}\right)$$

$$\rho_S \left(q_0 \frac{D_S}{r_P^2} \frac{\partial Q_t}{\partial T}\right) = k_F \left(\frac{3}{r_P}\right) c_0 (C_t - C_S)$$

$$\left(\frac{\partial Q_t}{\partial T}\right) = 3\left(\frac{k_F}{r_P}\right)\left(\frac{r_P^2}{D_S \rho_S}\right)\left(\frac{c_0}{q_0}\right)(C_t - C_S)$$

$$\left(\frac{\partial Q_t}{\partial T}\right) = 3\left(\frac{k_F}{r_P}\right)\left(\frac{r_P^2}{D_S \beta \rho_S}\right)(C_t - C_S), \qquad \beta = \left(\frac{q_0}{c_0}\right)$$

$$\left(\frac{\partial Q_t}{\partial T}\right) = 3\left(\frac{k_F r_P}{D_S \beta \rho_S}\right)(C_t - C_S)$$

$$\left(\frac{\partial Q_t}{\partial T}\right) = 3\mathrm{Bi}(C_t - C_S), \qquad\qquad \mathrm{Bi} = \left(\frac{k_F r_P}{D_S \beta \rho_S}\right)$$

3. Interface transport

$$\left(\frac{\partial q_t}{\partial t}\right) = -D_S a_P \left(\frac{\partial q_m}{\partial r}\right)_{r=r_P}$$

$$\left(\frac{\partial q_t}{\partial Q_t}\frac{\partial T}{\partial t}\frac{\partial Q_t}{\partial T}\right) = -D_S\left(\frac{3}{r_P}\right)\left(\frac{\partial q_t}{\partial Q_t}\frac{\partial R}{\partial r}\frac{\partial q_m}{\partial R}\right)_{r/r_P=r_P/r_P}$$

$$\left(q_0\frac{D_S}{r_P^2}\frac{\partial Q_t}{\partial T}\right) = -D_S\left(\frac{3}{r_P}\right)\left(q_0\frac{1}{r_P}\frac{\partial Q_m}{\partial R}\right)_{R=1}$$

$$\left(\frac{\partial Q_t}{\partial T}\right) = -3\left(\frac{\partial Q_m}{\partial R}\right)_{R=1}$$

4. Average amount adsorbed

$$q_t = \left(\frac{3}{r_P^3}\right)\int_0^{r_P} q_m r^2\,dr$$

$$q_0 Q_t = \left(\frac{3}{r_P^3}\right)\int_0^1 q_0 Q_m (r_P R)^2 \left(\frac{dr}{dR}\right)dR$$

$$q_0 Q_{t,i} = \left(\frac{3}{r_P^3}\right)\int_0^1 q_0 Q_m (r_P R)^2 (r_P)\,dR$$

$$Q_t = \left(\frac{3}{r_P^3}\right)\left(\frac{q_0 r_P^3}{q_0}\right)\int_0^1 Q_m R^2\,dR$$

$$Q_t = 3\int_0^1 Q_m R^2\,dR$$

Appendix B. Major steps of numerical calculations

B.1. Dimensionless fundamental equations

1. Intraparticle diffusion

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left(\frac{1}{R^2}\right)\frac{\partial}{\partial R}\left(R^2\frac{\partial Q_m}{\partial R}\right) \tag{2-1}$$

I.C.: $Q_m = 0$ at $T = 0$; B.C.: $Q_m = (c_S)^{1/n}$ at $R = 1$

$$\left(\frac{\partial Q_m}{\partial R}\right) = 0 \quad \text{at } R = 0$$

2. Fluid-to-solid film transport

$$\left(\frac{\partial Q_t}{\partial T}\right) = 3\,\mathrm{Bi}(c_t - c_S), \quad c_{t,i} = 1 \tag{2-2}$$

$$\mathrm{Bi} = \left(\frac{k_F r_P}{D_S \beta \rho_S}\right), \quad \beta = \left(\frac{q_0}{c_0}\right)$$

3. Interface transport

$$\left(\frac{\partial Q_t}{\partial T}\right) = -3\left(\frac{\partial Q_m}{\partial R}\right)_{R=1} \tag{2-3}$$

4. Average amount adsorbed

$$Q_t = 3\int_0^1 Q_m R^2\,dR \tag{2-4}$$

B.2. Intraparticle diffusion

Eq. (2-1) can be derived as follows

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left(\frac{1}{R^2}\right)\frac{\partial}{\partial R}\left(R^2\frac{\partial Q_m}{\partial R}\right)$$

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left(\frac{1}{R^2}\right)\left\{R^2\left(\frac{\partial^2 Q_m}{\partial R^2}\right) + 2R\left(\frac{\partial Q_m}{\partial R}\right)\right\}$$

$$\left(\frac{\partial Q_m}{\partial T}\right) = \left\{\left(\frac{\partial^2 Q_m}{\partial R^2}\right) + \frac{2}{R}\left(\frac{\partial Q_m}{\partial R}\right)\right\}$$

$$\frac{(Q_m)_{T=T+\Delta T} - (Q_m)_{T=T}}{\Delta T} = \frac{1}{2}\left[\left\{\left(\frac{\partial^2 Q_m}{\partial R^2}\right) + \frac{2}{R}\left(\frac{\partial Q_m}{\partial R}\right)\right\}_{T=T+\Delta T}\right.$$

$$\left. + \left\{\left(\frac{\partial^2 Q_m}{\partial R^2}\right) + \frac{2}{R}\left(\frac{\partial Q_m}{\partial R}\right)\right\}_{T=T}\right]$$

$$\frac{(Q_{m,j})_{T=T+\Delta T} - (Q_{m,j})_{T=T}}{\Delta T}$$

$$= \frac{1}{2}\left\{\frac{Q_{m,j+1} - 2Q_{m,j} + Q_{m,j-1}}{(\Delta R)^2} + \frac{2}{j(\Delta R)}\frac{Q_{m,i,j+1} - Q_{m,j-1}}{2(\Delta R)}\right\}_{T=T+\Delta T}$$

$$+ \frac{1}{2}\left\{\frac{Q_{m,j+1} - 2Q_{m,j} + Q_{m,j-1}}{(\Delta R)^2} + \frac{2}{j(\Delta R)}\frac{Q_{m,j+1} - Q_{m,j-1}}{2(\Delta R)}\right\}_{T=T}$$

$$\frac{(Q_{m,j})_{T=T+\Delta T} - (Q_{m,j})_{T=T}}{\Delta T}$$

$$= \frac{1}{2}\left\{\frac{(j+1)Q_{m,j+1} - 2jQ_{m,j} + (j-1)Q_{m,j-1}}{j(\Delta R)^2}\right\}_{T=T+\Delta T}$$

$$+ \frac{1}{2}\left\{\frac{(j+1)Q_{m,j+1} - 2jQ_{m,j} + (j-1)Q_{m,j-1}}{j(\Delta R)^2}\right\}_{T=T} \tag{2-5}$$

where subscript j: position number at $r = j\,\Delta r$.

To solve the above equation (Eq. (2-5)), two critical radial points have to be considered.

(1) Center point of the particle ($j = 0$). At $j = 0$, calculation is not required, because value at right-hand-side is zero. (intraparticle amount adsorbed Q_m is symmetry with respect to the center of the particle, therefore, $Q_{m,-1} = Q_{m,1}$).

(2) Geometric surface of particle ($j = S$). As shown in Eq. (2-5), values of amount adsorbed at $j = S + 1$ ($Q_{m,S+1}$) have to be obtained. The values can be derived from Eqs. (2-2) and (2-3).

Combine Eqs. (2-2) and (2-3).

$$3\,\mathrm{Bi}(C_t - C_S) = -3\left(\frac{\partial Q_m}{\partial R}\right)_{R=1}$$

$$\left(\frac{\partial Q_m}{\partial R}\right)_{R=1} = -\mathrm{Bi}(C_t - C_S)$$

$$\frac{Q_{m,S-1} - Q_{m,S+1}}{2(\Delta R)} = -\mathrm{Bi}(C_t - C_S)$$

$$Q_{m,S+1} = Q_{m,S-1} + 2(\Delta R)\mathrm{Bi}(C_t - C_S)$$

B.3. Average amount adsorbed

Eq. (2-4) can be calculated by the following equations (Simpson's rule).

$$Q_t = 3\int_0^1 Q_m R^2 \, \mathrm{d}R$$

$$Q_t = 3\left(\frac{\Delta R}{3}\right)\{(0\,\Delta R)^2(Q_{m,0}) + 4(1\,\Delta R)^2(Q_{m,1}) + 2(2\,\Delta R)^2(Q_{m,2})$$

$$+4(3\,\Delta R)^2(Q_{m,3})\cdots\cdots\}\quad R = j\,\Delta R$$

$$Q_t = (\Delta R)^3\{4(Q_{m,1}) + 2(2)^2(Q_{m,2}) + 4(3)^2(Q_{m,3})\cdots\}$$

$$Q_t = \left\{\frac{1}{S^3}\right\}\left\{4(1)^2(Q_{m,1}) + 2(2)^2(Q_{m,2}) + 4(3)^2(Q_{m,3}) + \cdots\right.$$

$$\left.+(S)^2(Q_{m,S})\right\}\quad \because \Delta R = \frac{1}{S}$$

The derivation mentioned above is similar to Carter's paper [12].

References

[1] Y. Takeuchi, E. Furuya, A simple method to estimate effective surface diffusivity for Freundlich isotherm systems from breakthrough curves based on numerical results, J. Chem. Eng. Jpn. 13 (1980) 500.

[2] U.K. Traegner, M.T. Suidan, Evaluation of surface and Film diffusion coefficients for carbon adsorption, Water Res. 23 (3) (1989) 267–273.

[3] U.K. Traegner, M.T. Suidan, Parameter evaluation for carbon adsorption, J. Environ. Eng. 115 (1) (1989) 109–128.

[4] D.O. Cooney, Determining external film mass transfer coefficients for adsorption columns, AIChE J. 37 (8) (1991) 1270–1274.

[5] E.G. Furuya, H.T. Chang, Y. Miura, H. Yokomura, S. Tajima, S. Yamashita, K.E. Noll, Intraparticle mass transport mechanism in a activated carbon adsorption of phenols, J. Environ. Eng. 122 (10) (1996) 909–916.

[6] K. Hashimoto, K. Miura, A simplified method to design fixed-bed adsorbers for the Freundlich isotherm, J. Chem. Eng. Jpn. 9 (1976) 388.

[7] D. Roy, G. Wang, D.D. Adrian, A simplified solution technique for carbon adsorption model, Water Res. 27 (6) (1993) 1033–1040.

[8] A.A. Aguwa, J.W. Patterson, C.N. Haas, K.E. Noll, Estimation of effective intraparticle diffusion coefficients with differential reactor columns, J. WPCF 56 (1984) 442–448.

[9] K. Satoh, H.J. Fan, H. Hattori, K. Tajima, E. Furuya, Simultaneous determination of intraparticle diffusivities from ternary component uptake curves using the shallow bed technique, J. Hazard. Mater. 155 (2008) 397–402.

[10] J. Crank, The Mathematics of Diffusion, 2nd ed., Clarendon Press, Oxford, 1975.

[11] K.E. Noll, V. Gounaris, W.S. Hou, Adsorption Technology for Air and Water Pollution Control, Lewis Publishers Inc., Michigan, USA, 1991.

[12] J.W. Carter, H. Husain, Trans. Inst. Chem. Eng. 50 (1972) 69.