Analytical Solution to an Axial Dispersion Model for the Fixed-Bed Adsorber

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An axial dispersion model for the operation of a fixed-bed adsorber with a linear adsorption isotherm was formulated and solved analytically using the separation of variables method. The asymptotic solution for a large Peclet number and/or a small operation time was also obtained using two limiting cases. The results can be used to correlate or to predict both the mass-transfer zones and the breakthrough curves of a fixed-bed adsorber. Influence of both the Peclet number and the retardation coefficient on the operation of a fixed-bed adsorber was also studied. As an example, the axial dispersion model was applied to the experimental data of the removal of phenol from the solution in the activated carbon and the Amberlite resin XAD-4 fixed-bed adsorbers.

Introduction

An adsorption process is often used at the end of a treatment sequence for pollution control due to the high degree of purification that can be achieved. Activated carbon is the most popular adsorbent used for the application of adsorption technology. For industrial applications in wastewater treatment, the most efficient arrangement for conducting adsorption operation is the fixed-bed adsorber. To evaluate the efficiency of a fixed-bed adsorber, a mathematical model is required for the design. A number of mathematical models have been developed to explain the kinetic behavior of a fixed-bed adsorber and to estimate the breakthrough curves. The mechanism of adsorption on an adsorbent includes external diffusion, internal diffusion, and the adsorption. Rosen (1954) analyzed the operation of a fixed-bed adsorber by the solid diffusion model. However, intraparticle diffusion may occur by ordinary or molecular diffusion, Knudsen diffusion, and the surface diffusion, depending on the pore size, the adsorbate concentration, and other conditions. Cooper and Liberman (1970) and Rasmuson (1981) described the diffusion in the pore network of the adsorbent with the pore diffusion model. Furusawa and Smith (1973), Neretnieks (1976), and Sheindorf (1983) use the surface diffusion model to interpret the mechanism of the migration of adsorbate through the pore space and pore walls. The combined diffusion models were developed to consider both the effects of pore diffusion and surface diffusion (Weber and Chakravorti, 1974; Merk et al., 1981).

In general, the analytical solutions of the modeling equations seem impossible to be obtained due to the complexity of the dynamic operation of a fixed-bed adsorber. Some numerical methods were applied to solve the modeling equations such as the Crank-Nicholson method (Garg and Ruthven, 1973; Hashimoto et al., 1977) and the orthogonal collocation method (Villadsen and Stewart, 1967; Finlayson, 1971). It was also shown that the orthogonal collocation method was better for solving fixed-bed models (Liapis and Rippin, 1978; Raghavan and Ruthven, 1983). Recently, Hsu and Dranoff (1987) and Chen and Hsu (1989) developed a numerical technique to solve fixed-bed problems by the direct application of the fast Fourier transform algorithm. To simplify the problem, it is highly desirable to have a simple and internally consistent model that contains the essential features of the fixed-bed adsorber. Zheng and Gu (1996) formulated a dynamic model of a fixed-bed reactor with first-order kinetics, axial dispersion, and film mass-transfer resistance, which is solved analytically using Laplace transform.

This work was undertaken to formulate a simple one-dimensional (1-D) flow model of a fixed-bed adsorber by an

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axial dispersion model with a linear adsorption isotherm. The objectives of this article are to obtain the analytical and the approximate solutions of the proposed model, and to examine experimentally the validity of this mathematical model. The adsorption data of phenol onto the activated carbon fixed-bed adsorber and onto the Amberlite XAD-4 fixed-bed adsorber (Noll et al., 1992) were used as practical examples.

Theoretical Considerations

Model approach and its analytical solution

The transport phenomena to porous media often involve dispersions, which include molecular diffusion and mechanical dispersion (Fried and Combarnous, 1971). The contaminant transport equation of the fixed-bed adsorber could be described by an axial dispersion model as follows

$$\frac{\partial(\epsilon C)}{\partial t} = -\underline{\nabla}\epsilon\left(C\underline{V} - \underline{D_m}\cdot\underline{\nabla}C - \underline{D_d}\cdot\underline{\nabla}C\right) - \bar{f} \qquad (1)$$

where $\bar{f}$ is the volume-averaged adsorption rate of adsorbate onto an adsorbent and can be written as

$$\bar{f} = (1-\epsilon)\rho_s\frac{\partial\bar{F}}{\partial t} \qquad (2)$$

In this study, the overhead sign indicates the volume average of any function. To obtain the relationship of $\bar{F}$ and C, the following assumptions are presumed in the analysis:

(1) The volume-averaged amount of adsorbate onto the adsorbent is proportional to the volume-averaged concentration of the fluid inside the porous adsorbent, that is, $\bar{F} = k\bar{C}_p$.

(2) The shape of the adsorbent is a sphere and the fluid concentration inside the adsorbent can be expressed as $C_p(Z,\zeta,t) = (1-\alpha_2+\alpha_2\zeta^2)C_{ps}(Z,1,t)$, where α_2 is a constant and $\zeta = r/R$.

(3) The film resistance between the external surface of adsorbent and the bulk fluid can be neglected, that is, $C_{ps} = C$.

Based on the preceding assumptions and along with the definition of $\bar{C}_p$, we obtain $\bar{C}_p = (1-\alpha_2/5)C$. So, the relationship of $\bar{F}$ and C can be expressed as $\bar{F} = K_dC$ where $K_d = k(1-\alpha_2/5)$. It is shown that the relationship of $\bar{F}$ and C is the same as the linear adsorption isotherm.

For 1-D plug flow, the mass balance equation for a fixed-bed tubular adsorber, Eq. 1 can be rewritten as

$$0 < Z < L,\ t > 0; \qquad R_d\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial Z} + D_e\frac{\partial^2 C}{\partial Z^2} \qquad (3)$$

where R_d and D_e are the retardation coefficient (dimensionless) and the effective dispersion coefficient (m^2/s) defined below, respectively,

$$R_d = 1 + \frac{\rho_s K_d(1-\epsilon)}{\epsilon}, \qquad D_e = D_m + D_d \qquad (4a,b)$$

For the operation of a fixed-bed adsorber, the initial and boundary conditions are

$$\text{at } 0 \leqq Z \leqq L,\ t = 0; \qquad C = C_i \qquad (5)$$

$$\text{at } Z = 0,\ t > 0; \qquad C(t,0) = C_o \qquad (6)$$

$$\text{at } Z = L,\ t > 0; \qquad \frac{\partial C}{\partial Z} = 0 \qquad (7)$$

Equation 3 can be solved by the method of separation of variables. To simplify the problem, new dimensionless variables are defined as

$$X = \frac{Z}{L} \qquad (8)$$

$$C^* = \frac{C - C_i}{C_o - C_i} \qquad (9)$$

$$\tau = \frac{Vt}{L} \qquad (10)$$

$$P_e = \frac{VL}{D_e} \qquad (11)$$

The dimensionless time τ corresponds physically to the number of displacements; that is, it is equal to the ratio of the total fluid volume introduced to the free volume of the bed. Then, Eq. 3 can be expressed as

$$0 < X < 1,\ \tau > 0; \qquad R_dP_e\frac{\partial C^*}{\partial\tau} = -P_e\frac{\partial C^*}{\partial X} + \frac{\partial^2 C^*}{\partial X^2} \qquad (12)$$

$$\text{at } 0 \leqq X \leqq 1,\ \tau = 0; \qquad C^* = 0 \qquad (13)$$

$$\text{at } X = 0,\ \tau > 0; \qquad C^* = 1 \qquad (14)$$

$$\text{at } X = 1,\ \tau > 0; \qquad \frac{\partial C^*}{\partial X} = 0 \qquad (15)$$

To solve this problem, we assume the separation of function $Y(X,\tau) = 1 - C^*$ into a dimensionless space-dependent and dimensionless time-dependent functions in the form $Y(X,\tau) = W(X)\Gamma(\tau)$. Substitution of $Y(X,\tau)$ into Eq. 12 yields

$$P_eR_d\frac{d\Gamma(\tau)/d\tau}{\Gamma(\tau)} = \frac{d^2W(X)/dX^2 - P_e dW(X)/dX}{W(X)} = -\beta^2 \qquad (16)$$

Then, the solution for the dimensionless time-variable function $\Gamma(\tau)$ is given as

$$\Gamma(\tau) = \exp\left(-\frac{\beta^2}{P_eR_d}\tau\right) \qquad (17)$$

and the dimensionless space-variable function $W(X)$ satisfy the following eigenvalue problem

$$0 < X < 1; \qquad \frac{d^2W(X)}{dX^2} - P_e\frac{dW(X)}{dX} + \beta^2W(X) = 0 \qquad (18)$$

$$\text{at } X = 0; \qquad W = 0 \qquad (19)$$

$$\text{at } X=1; \qquad \frac{dW}{dX}=0 \tag{20}$$

The eigenfunction $W_n(\delta_n, X)$ could be easily obtained as follows

$$W_n(\delta_n, X)=\sin(\delta_n X)\exp\left(\frac{P_e}{2}X\right) \tag{21}$$

where the δ_n $(n=1, 2, 3, \ldots)$ are the positive roots, taken in the order of increasing magnitude, of the following transcendental equation

$$\delta_n \cot(\delta_n)=-\frac{P_e}{2} \tag{22}$$

The first six roots of the transcendental equation at various Peclet numbers can be obtained from the tabulation in Carslaw and Jaeger (1959). If more roots are needed, they can be easily calculated by numerical methods such as Newton-Raphson method or the method of Regula Falsi. The solution of the problem (Eq. 12) is now constructed as

$$C^*=1-\sum_{n=1}^{\infty} b_n \sin(\delta_n X)\exp\left(\frac{P_e}{2}X-\frac{\beta_n^2}{R_d P_e}\tau\right) \tag{23}$$

where

$$\beta_n^2=\delta_n^2+\left(\frac{P_e}{2}\right)^2 \tag{24}$$

The application of the initial condition (Eq. 13) gives

$$\sum_{n=1}^{\infty} b_n \sin(\delta_n X)\exp\left(\frac{P_e}{2}X\right)=1 \tag{25}$$

Utilizing the orthogonality property of the eigenfunction, the coefficients b_n of Eq. 23 can be determined as

$$b_n=\frac{2\delta_n^2}{\beta_n^2(\delta_n-\sin\delta_n\cos\delta_n)} \tag{26}$$

Of particular interest is the exit concentration of adsorbate leaving the bed

$$C_L^*=1-\sum_{n=1}^{\infty} b_n \sin(\delta_n)\exp\left(\frac{P_e}{2}-\frac{\beta_n^2}{R_d P_e}\tau\right) \tag{27}$$

obtained by setting $X=1$ in Eq. 23.

The analytical solutions, Eqs. 23 and 27, seem not to have been previously derived.

Approximate solutions

(a) For Large P_e and/or Small τ. The analytical solutions, Eqs. 23 and 27, converge too slowly to be of much use numerically when P_e is large and/or τ is small. Accordingly, it is necessary to develop an asymptotic solution for this situation. A rapidly converging solution of Eq. 3 can be obtained by the application of the Laplace transform. The result is as follows

$$\tilde{C}^*=\frac{\exp\left(\frac{P_e}{2}X\right)\left\{\cosh[\lambda L(1-X)]+\frac{P_e}{2\lambda L}\sinh[\lambda L(1-X)]\right\}}{s\left[\cosh(\lambda L)+\frac{P_e}{2\lambda L}\sinh(\lambda L)\right]} \tag{28}$$

where

$$\tilde{C}^*\equiv\int_0^{\infty} e^{-s\tau}C^*(X,\tau)\,d\tau \tag{29}$$

and λL is defined

$$\lambda L=\sqrt{\left(\frac{P_e}{2}\right)^2+R_d P_e s} \tag{30}$$

It seems impossible to get the direct inverse Laplace transform of Eq. 28. So, an asymptotic approximation technique may be used to conquer the problem. According to the definition of the hyperbolical functions, $\sinh(\lambda L)\cong\exp(\lambda L)/2$ and $\cosh(\lambda L)\cong\exp(\lambda L)/2$, while P_e is large and/or τ is small. Substituting the asymptotic approximation of the hyperbolical functions into Eq. 28 gives

$$\tilde{C}^*\cong\exp\left(\frac{P_e}{2}X\right)\frac{1}{s}\exp(-\lambda L X) \tag{31}$$

Now, the direct inverse Laplace transform of Eq. 31 can be easily obtained from the basic theorem of Laplace transform. After the inverse Laplace transform of Eq. 31, we get the asymptotic solution of the Eq. 12 for large P_e and/or small τ as follows

$$C^*=\frac{1}{2}\left[\operatorname{erfc}\left(\frac{X-\tau/R_d}{2\sqrt{\tau/R_d P_e}}\right)+\exp(P_e X)\operatorname{erfc}\left(\frac{X+\tau/R_d}{2\sqrt{\tau/R_d P_e}}\right)\right] \tag{32}$$

Equation 32 is identical to the result of Lapidus and Amundson (1952) for a column of infinite length. In this study, we also showed that Eq. 32 is valid for the case of large hydraulic loading and/or small effective dispersion coefficient.

(b) For Small P_e. For small value of P_e, a series expansion technique was used to solve the problem. At the adsorber exit, we have $X=1$. Thus, the second term of the numerator in Eq. 28 vanishes. Substituting the expansion series of the hyperbolical functions into Eq. 28 and rearranging, Eq. 28 becomes (Zheng and Gu, 1996)

$$\tilde{C}_L^*=\exp\left(\frac{P_e}{2}\right)\left[s\sum_{n=0}^{\infty}\left(\frac{1}{2n!}+\frac{P_e}{2}\frac{1}{(2n+1)!}\right)(\lambda L)^{2n}\right]^{-1} \tag{33}$$

By using the method of mathematical induction, Eq. 33 can be expressed as follows

$$\tilde{C}_L^* = \operatorname*{limit}_{n\to\infty} \exp\left(\frac{P_e}{2}\right)\frac{1}{a_n s}\sum_{m=1}^{n}\frac{A_m}{\Psi + B_m} \tag{34}$$

where

$$a_n = \frac{1}{2n!} + \frac{P_e}{2}\frac{1}{(2n+1)!} \tag{35}$$

$$\Psi = (\lambda L)^2 = q + P_e R_d s \tag{36}$$

$$q = \left(\frac{P_e}{2}\right)^2 \tag{37}$$

B_m was determined by the following equation

$$\sum_{m=0}^{n} a_m \Psi^m = a_n \prod_{m=0}^{n}(\Psi + B_m) \tag{38}$$

A_m could be determined by factoring the inverse of Eq. 38 into the form of Eq. 34.

Now, the direct inverse Laplace transform of Eq. 34 can be easily obtained by the basic theorem of Laplace transform. However, it is difficult to use since a general type of explicit expressions for the parameters A_m and B_m is not available. The approximate explicit expressions for A_m and B_m could be obtained if a limited number of terms of the infinite series are taken in Eq. 34. For example, if only the first three terms are considered ($n=2$), the approximate analytical solution can be expressed as follows

For $P_e \leq \sqrt{96} - 6$

$$C_L^* = \frac{\exp(P_e/2)}{\phi_2}\left\{1 - \frac{q+b_1}{b_1 - b_0}\exp\left(-\frac{q+b_0}{R_d P_e}\tau\right) + \frac{q+b_0}{b_1-b_0}\exp\left(-\frac{q+b_1}{R_d P_e}\tau\right)\right\} \tag{39}$$

For $P_e > \sqrt{96} - 6$

$$C_L^* = \frac{\exp(P_e/2)}{\phi_2}\left\{1 - \exp(-a\tau)\left[\frac{a}{b}\sin(b\tau) + \cos(b\tau)\right]\right\} \tag{40}$$

where

$$\phi_2 = a_0 + a_1 q + a_2 q^2 \tag{41}$$

$$b_0 + b_1 = \frac{a_1}{a_2} \tag{42}$$

$$b_0 b_1 = \frac{a_0}{a_2} \tag{43}$$

$$a = \frac{q + a_1/2a_2}{R_d P_e} \tag{44}$$

$$b = \frac{\sqrt{4a_0 a_2 - a_1^2}}{2a_2 R_d P_e} \tag{45}$$

Limiting cases

Case I: Perfect Mixing; $P_e \to 0$ ($D_e \to \infty$). When the Peclet number approaches zero, each differential element of solution introduced into the bed is instantly mixed with the contents of bed, the axial dispersion effect in the bed can be neglected. Thus, the bed behaves like a perfect mixing chamber and the mass balance equation (Eq. 3), is reduced to

$$R_d\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial Z} \tag{46}$$

Combining the initial and boundary conditions, a step function can be obtained using Laplace transform

$$C^* = u(\tau - R_d X) = \begin{cases} 1 & \text{for } \tau > R_d X \\ 0 & \text{for } \tau \leq R_d X \end{cases} \tag{47}$$

Case II: Perfect Displacement; $P_e \to \infty$. The asymptotic solution (Eq. 32) can be used to discuss the conditions of the large *Pe* and/or small τ. The complimentary error function approaches either 0 or 2 accordingly as its argument approaches either positive or negative infinity. While $P_e \to \infty$, the second term in Eq. 32 will approach zero. Hence

$$C^* = \begin{cases} 1 & \text{for } \tau > R_d X \\ \dfrac{1}{2} & \text{for } \tau = R_d X \\ 0 & \text{for } \tau < R_d X \end{cases} \tag{48}$$

Discussion of the solutions

(a) Convergence and Accuracy Studies of the Analytical Solution. Before using the analytical solution (Eq. 23) to model a fixed-bed adsorber, it is desirable to evaluate how many terms were required to get accurate convergence. From Eqs. 22 and 26 it could be found that each eigenvalue δ_n is located in intervals $[(n-1)\pi,\ n\pi]$ and that the value of b_n is less than 1 for any value of n. So, the absolute value of $b_n \sin(\delta_n \cdot X)$ is also less than 1. Now we define a criterion $\Omega_k = \exp(P_e \cdot X/2 - \beta_k^2\tau/R_d P_e)$ to determine the convergence of the infinite summations in Eq. 23. When the value of Ω_k approaches zero (say, $\Omega_k \leqq 10^{-9}$), all the terms of infinite series in Eq. 23 could be neglected for $n > k$. As the result, the approximation of the infinite series in Eq. 23 is that all the terms with $n \leqq k$ need to be summed up. To provide a convenient criterion, k could be determined by the following equation

$$k = \frac{\sqrt{\left(\dfrac{P_e X}{2} + 21\right)\dfrac{R_d P_e}{\tau}}}{\pi} \tag{49}$$

Table 1. Effect of n Value Using Eq. 27 on the Exit Dimensionless Concentrations of Adsorber with $P_e = 20$ and $R_d = 2{,}000$

$\tau = 20$		$\tau = 1{,}000$		$\tau = 2{,}000$		$\tau = 3{,}000$	
n	C_L^*	n	C_L^*	n	C_L^*	n	C_L^*
10	342.4767972	3	−3.674723202	1	−0.313434590	2	0.952776670
25	−11.65689322	6	0.026222168	2	0.820867806	4	0.950266895
50	0.000557936	9	0.023954351	6	0.625967194	$6^\dagger$	0.950266818
$79^\dagger$	0.000000504	$11^\dagger$	0.023954364	$8^\dagger$	0.625896719	8	0.950266818
100	0.000000504	15	0.023954364	15	0.625896719	10	0.950266818

†Calculated from Eq. 49.

To determine whether the criterion proposed above is suitable for the calculation of the dimensionless concentration, the dimensionless concentrations at $X = 1$ with $P_e = 20$ and $R_d = 2{,}000$ for $\tau = 20 \sim 3{,}000$ were estimated and given in Table 1. Table 1 shows that the smaller value of τ is, the larger value of k is required. It is also confirmed that the values of C_L^* at a given τ for $n > k$ and $n = k$ are all the same for a wide range of τ. As a result, it is clear that sufficient accuracy could be obtained using Eq. 49 as a convergent criterion for the approximation of the infinite series in Eq. 23.

(b) Accuracy Studies of the Approximate Solutions. For the application of the approximate solutions (Eqs. 32, 39 and 40), it is desirable to determine the range of P_e in which the sufficient accuracy can be acquired. This is achieved by comparing the exact value of C_L^* obtained from Eq. 27 and its approximate value from Eqs. 32, 39 and 40. The results are illustrated in Figures 1 and 2. At a lower P_e value (such as

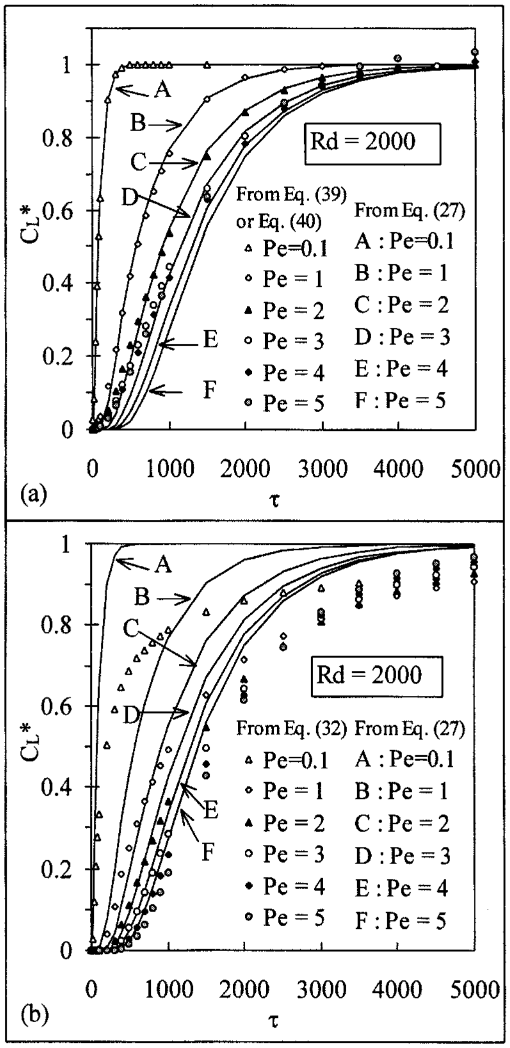

Figure 1. Exact vs. approximate values of C_L^* for small P_e.

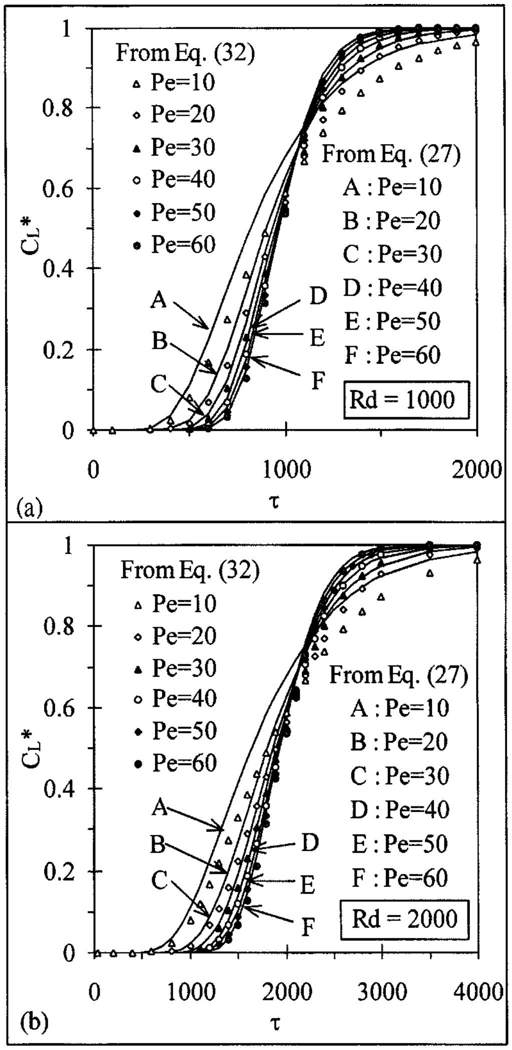

Figure 2. Exact vs. approximate values of C_L^* for large P_e.

$P_e < 4$), it is obvious that the approximate value of C_L^* obtained from Eqs. 39 or 40 is in good agreement with that obtained by the analytical solution. It is also found that for a large P_e value (such as $P_e \geqq 30$), the results obtained from the asymptotic solution (Eq. 32) will be almost the same as those obtained from the analytical solution. In general, the analytical solution or the approximate analytical solution can be employed at lower Peclet numbers, whereas the modified asymptotic solution is utilized at larger Peclet numbers. For $4 < P_e < 30$, the analytical solution is the better choice for calculation of C_L^*. According to Eq. 49 and the result of Table 1, it could be found that many terms of the analytical solution are required to sum up to obtain accurate result for small value of τ. From the result of Figure 1b, it is also found that the asymptotic solution is in good agreement with the analytical solution for small τ. So, the asymptotic solution can be used for $P_e < 30$ at small τ. To determine the ranges of utilization for asymptotic and analytical solutions, we suggest that the modified asymptotic solution will be used if more than 12 terms in Eqs. 23 or 27 are required for an accurate result. The proper range for each utilization is indicated in Figure 3.

(c) The Effects of P_e and R_d Values on the Operation of a Fixed-Bed Adsorber. Figures 4 and 5 illustrate the effects of the parameters P_e and R_d on the operation of a fixed-bed adsorber. According to Figure 3, both figures are calculated either from Eq. 23 or from Eq. 32. Figure 4 shows that when the value of P_e and τ are both kept constant and the value of R_d is increased, the curve of the mass-transfer zone (MTZ) levels off to $C^* = 0$ at a small value of X. It is therefore confirmed that the breakthrough appears earlier, and the wider MTZ will be acquired when the system has a weaker adsorptive capacity due to lower value of K_d. For constant R_d, decreasing the P_e value means an increase in the effective dispersion coefficient if the length of the adsorbent in the fixed-bed adsorber and the hydraulic loading of the fixed bed are both kept unchanged. From the result of Figure 4, it is clear that the lower the value of P_e is, the more mixing effect will be obtained. It is obvious that when R_d is a constant, the higher is the value of P_e, and the steeper MTZ will be obtained.

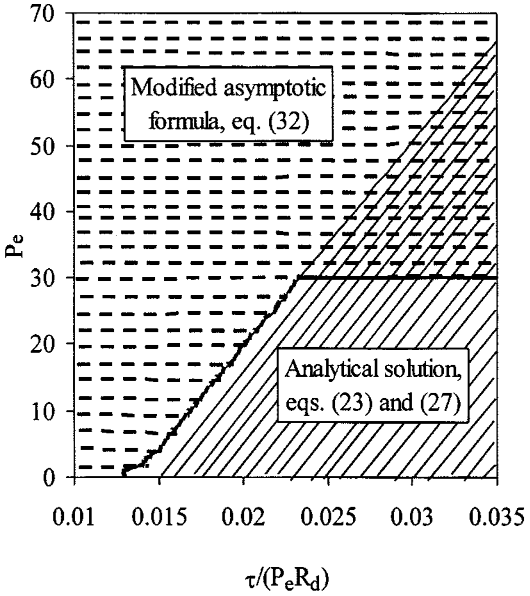

Figure 3. Ranges of applicability of formulae for calculation of C^*.

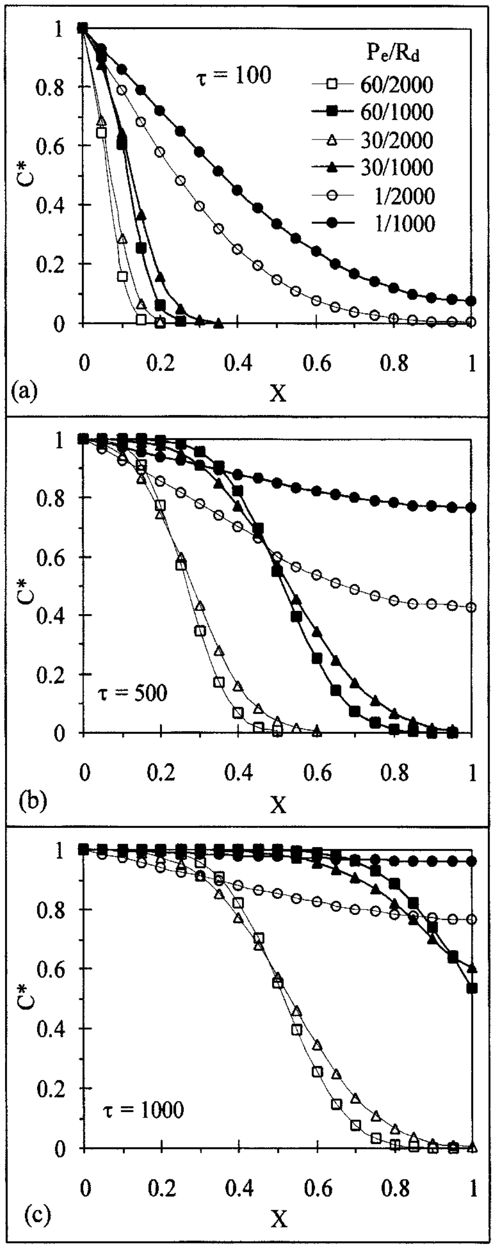

Figure 4. Effects of P_e and R_d on the mass-transfer zone for fixed-bed adsorber operation at different value of τ.

The effects of the parameters P_e and R_d on the breakthrough curves of a fixed-bed adsorber are given in Figure 5. Figure 5 shows that when the value of P_e is kept constant and the value of R_d is increased, the breakthrough curves level up more slowly to $C_L^* = 1$ and larger breakthrough time is required. According to the result of Figure 5b, for large P_e, the effluent concentration of adsorbate will quickly reach the

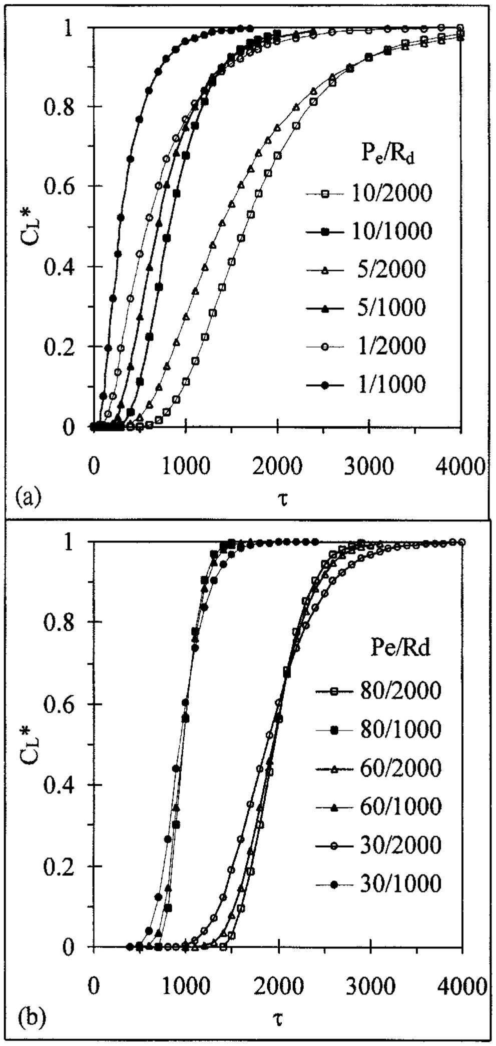

Figure 5. Effects of P_e and R_d on the breakthrough curve for fixed-bed adsorber operation.

influent concentration, but the breakthrough time is larger, while the value of R_d is kept constant and the value of P_e is increased. From the result of Figure 5a, for constant R_d and small P_e, the effect of P_e on the breakthrough curve is similar to that of R_d. As the result of Figure 5, it could be found that the intersection of the breakthrough curves is coincident for large P_e only (such as $P_e \geqq 30$). It also illustrates that when the P_e is larger, the intersection approaches more to a center position.

Practical Example

In order to examine the developed solutions of the proposed model in this study, the removal of phenol from wastewater in an activated carbon fixed-bed adsorber was studied. According to the results of equilibrium adsorption test, the adsorption isotherm could be described by linear isotherm. Therefore, the system can be used to examine the analytical solution. To clarify our method is valid for other cases. We also compared the results obtained from this work to those from the solid diffusion model and the combined diffusion model (Noll et al., 1992).

Experimental Studies

Materials

The activated carbon used in this study was supplied from Merck Chemical Co. The carbon was first sieved (the fraction between Mesh 14 and Mesh 16 was used) and washed repeatedly with extra pure water and then dried in the oven at 105°C for 24 h. Solvents and reagents for preparing standard solutions and analysis of COD of phenol solution are of the reagent grade, which were used as received.

Adsorption test and analysis

The equilibrium adsorption data were carried out in an experimental batch adsorber. Isotherm experiments were conducted in the adsorber by contacting a given amount of activated carbon (1.0 g) with 500 cm^3 of a phenol solution of a different initial concentration at 25°C. For the fixed-bed experiments, a pyrex glass column with an inside diameter of 2.5 cm and a length of 18.0 cm was used as an adsorber. The void fraction of the activated carbon bed was found to be 0.35. The influent concentration of phenol solution was kept constant ($C_o = 0.85$ kgCOD/m^3) and the operation temperature was kept at 25 ± 2°C. The operation conditions and the corresponding values of the parameters P_e and R_d are given in Table 2. The samples were analyzed using the APHA (1981) standard COD method at determined time intervals. The amount of phenol adsorbed was determined by mass balance.

Results and Discussion

Equilibrium adsorption test

The result of the equilibrium adsorption test is shown in Table 3. The linear adsorption isotherm was utilized to fit the experimental data based on the least-square technique. The fitting result shows that the adsorption result could be described reasonably by the following equation (relative mean error = 8.8%, $R^2 = 0.9771$)

$$\bar{F} = 1.803C \tag{50}$$

From the result of Table 5.2 in Noll et al. (1992), the following linear isotherm of phenol/XAD-4 for $Ce < 0.1$ kg phenol/m^3 can be obtained by the least-square technique

$$\bar{F} = 0.387C \tag{51}$$

Table 2. Experimental Parameters of Activated Carbon and Amberlite Resin XAD-4 Fixed-Bed Adsorbers

Run No.	Intersitital Velocity, m/s	Hgt. of Carbon Bed, m	D_e m^2/s	P_e	R_d
(1)	1.746×10^{-3}	0.08	3.91×10^{-5}	3.577	1842.3
(2)	5.238×10^{-3}	0.08	5.65×10^{-5}	7.421	1842.3
(3)	5.238×10^{-3}	0.04	4.21×10^{-5}	4.982	1842.3
(4)	5.238×10^{-3}	0.02	4.41×10^{-5}	2.375	1842.3
(A1)	1.010×10^{-2}	0.18	7.90×10^{-4}	2.301	455.4
(A3)	1.350×10^{-2}	0.18	5.90×10^{-4}	4.119	598.0
(A4)	1.720×10^{-2}	0.29	2.30×10^{-3}	2.169	455.4

Notes: (a) The value of D_e was correlated from experimental data using Eq. 27.
(b) The experimental parameters of A1, A3, and A4 are obtained from the tabulation in Noll et al. (1992).

Table 3. Equilibrium Adsorption of Phenol onto Activated Carbon at 25°C

Init. Conc. Co, kg COD/m^3	Equilib. Conc. Ce, kg COD/m^3	Equilib. Ads. Fe, kg COD/kg
0.249	0.042	0.104
0.465	0.103	0.181
0.540	0.127	0.207
0.854	0.176	0.339
1.013	0.215	0.399
1.166	0.260	0.453

Fixed-bed adsorber test

The experimental data on the operation of activated carbon fixed-bed adsorber for removal of phenol from wastewater is shown in Figure 6a. For the application of the analytical and the approximate solutions derived in this study, the values of D_e and R_d should be determined first. The R_d value can be easily calculated from the adsorption properties of adsorbent. In the determination of D_e, Wakao and Funazkri (1967) had proposed the correlation equation for the estimation of the effective dispersion coefficient in packed beds. Their result is not suitable for our case since the model proposed in this study is different from other workers. So, we compare the breakthrough curve from experimental data with that from Eq. 27 for a given value of D_e. The optimal value of D_e is the one where the result is in the best agreement with experimental data. Figure 6a shows that the predicted curves using Eq. 27 are in good agreement with the experimental data. With an increase in the hydraulic loading for the constant height of activated carbon, P_e will increase and the breakthrough curve will become steeper.

To check whether the proposed model is valid for other cases, the experimental data of removal of phenol from wastewater by the Amberlite resin XAD-4 fixed-bed adsorber were examined (Noll et al., 1992). The results are illustrated in Figures 6b–6d. The experimental data and the results of solid diffusion and combined diffusion models for A1, A3, and A4 were estimated from the figures in Noll et al. (1992). The results of the solid diffusion model were not compared with the results of this work in Figures 6c and 6d, since they were not given in the original figures of Noll et al. (1992). According to the results of Figures 6b–6d, it proves that the axial dispersion model is somewhat better than the solid diffusion and combined diffusion models that do not take into account the dispersion effect. It is also shown that our method is valid for the case of removal of phenol from the Amberlite XAD-4 fixed-bed adsorber.

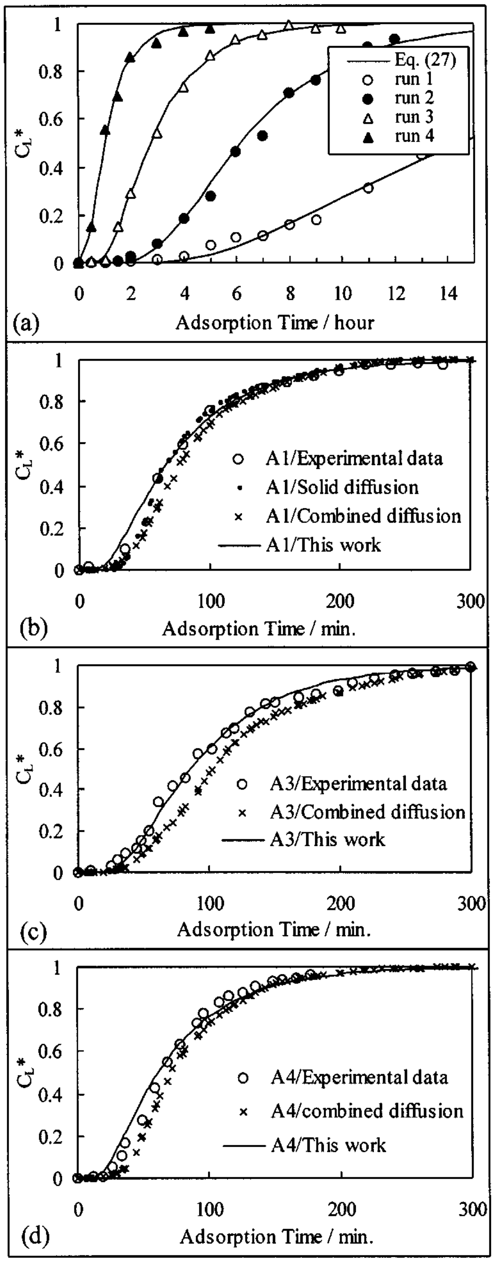

Figure 6. Validity of this work for phenol removal from activated carbon and XAD-4 resin fixed-bed adsorbers.

Conclusions

An analytical solution for the dynamic behavior of a fixed-bed adsorber with linear adsorption isotherm, and an axial dispersion model was obtained by the method of separation of variables. As the result, a convenient criterion was proposed to determine the approximation of the infinite series in the analytical solution. For a large P_e and/or small τ, the analytical solution is inconvenient to use since many terms of infinite summations in the analytical solution are required to get accurate converging result. A rapid converging solution was obtained by using the Laplace transform. The ranges of application of the analytical and asymptotic solutions are also determined. The solutions are capable of predicting the dynamic operation of a fixed-bed adsorber. It could also be used to estimate the effective dispersion coefficient. A practical example using an activated carbon fixed-bed adsorber to remove phenol from wastewater successfully demonstrated that the analytical solution provides a satisfactory fit of the experimental data. By comparing our method with the solid diffusion model and the combined diffusion model, it is also found that our method is valid for the case of removal of phenol from the Amberlite resin XAD-4 fixed-bed adsorber.

Notation

C = concentration of adsorbate in solution, kg COD/m^3 or kg phenol/m^3

C_p = concentration of adsorbate inside the adsorbent, kg COD/m^3

C_{ps} = concentration of adsorbate at the external surface of adsorbent, kg COD/m^3

C^* = dimensionless concentration defined in Eq. 9

D_d = mechanical dispersion coefficient, m^2/s

D_m = effective diffusivity, m^2/s

F = amount of adsorbate adsorbed onto adsorbent, kg COD/kg or kg phenol/kg

K_d = parameter of linear adsorption isotherm

L = length of the fixed-bed column, m

r = distance from center of adsorbent, m

R = radius of adsorbent, m

t = operation time, s

V = interstitial velocity, m/s

X = dimensionless space-variable defined in Eq. 8

Z = column length axis starting from the inlet of the fixed-bed adsorber, m

ϵ = void fraction of the fixed-bed, dimensionless

ρ_s = bulk density of adsorbent, kg/m^3

Subscripts

o = adsorber inlet

i = initial condition of adsorber

L = adsorber exit

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