Multicomponent Mass Transport Model for the Sorption of Metal Ions on Bone Char

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The sorption of binary mixtures of copper/cadmium and copper/zinc ions onto bone char was studied in fixed beds. The effects of solution flow rate, initial dye concentration, and bone char particle size range were investigated. A mass transport model based on film-surface diffusion and the IAS model for the equilibrium relationship was used to develop theoretical fixed-bed breakthrough curves. The model incorporates the Sips isotherm for the first time in fixed-bed predictions, since this isotherm gives an excellent correlation of the experimental equilibrium data. The model was used to determine the optimum surface diffusivities as 7.37×10^{-10} and 2.73×10^{-9} cm^2/s for copper and cadmium in the Cu/Cd system; and 1.61×10^{-9} and 2.43×10^{-9} cm^2/s for copper and zinc in the Cu/Zn system. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 2130–2141, 2004

Keywords: fixed bed; adsorption; copper; cadmium; zinc; surface diffusion

Introduction

Most single-component mass transport models can be extended to simulate the multicomponent mass transport by replacing the single-component isotherm with a multicomponent isotherm. Single-solute and bisolute adsorption of organic compounds on activated carbon in a fixed bed were studied by Crittenden and Weber (1978) using the homogeneous surface diffusion model with film resistance. The kinetic model accurately simulated the adsorption of the single solutes but was not as successful with the bisolute systems. Possible explanations given for the discrepancy in the simulated and experimental data were due to experimental data scatter, poor equilibrium description, and the breakdown of the assumption of independently diffusing species. Liapis and Rippin (1977) presented a model to describe the simultaneous adsorption of two components in a packed column. Two alcohols were studied with the fixed-bed model that accounted for film resistance, pore diffusion, and axial dispersion. The model predictions were good, although there was some difficulty in accurately predicting the overshoot of the weaker adsorbed species. The multicomponent isotherm gives accurate predictions of the adsorption equilibrium data; howeve, it requires considerable effort for the determination of the interrelated isotherm parameter based on the multicomponent isotherm experiments.

The IAS theory has been frequently applied to multicomponent fixed-bed adsorption systems. This theory was developed for the gas-phase multicomponent adsorption system by Myers and Prausnitz (1965) and was extended to liquid-phase adsorption by Radke and Prausnitz (1972). The major advantage of this theory is that it requires only single-component adsorption data in predicting the multicomponent adsorption equilibria. Crittenden et al. (1987) applied the equilibrium column model, which ignored the mass transfer resistance and used the IAS theory, to predict the competitive effects in multicomponent mixture of organics-activated carbon systems. The model can predict the elution order of the adsorbates, but it cannot accurately predict the breakthrough profiles because the mass transfer zone usually occupies a significant fraction of the bed. The use of IAS theory with different intraparticle mass transport models was applied to predict fixed-bed adsorber dynamics for many activated carbon adsorption systems (Fritz and Schlunder, 1981; Wang and Tien, 1982; Moon and Lee, 1986; Tien, 1994; Lo and Alok, 1996).

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In the present article, a multicomponent mass transport model was developed based on film-surface diffusion and applying the IAS model to describe the equilibrium relationship for the sorption of binary Cu/Cd and Cu/Zn systems on bone char in fixed beds.

Experimental Procedures

Materials, experimental setup, and procedures to carry out the fixed-bed experiments were described in detail in a previous paper (Ko et al., 1999). For the sake of completeness, they are briefly restated here. The metal ion salts to be contacted with the adsorbent were weighed out, added to the water tanks, and mixed well. The initial pH of the metal ion solution is fixed at 5.0. The metal ion solution could then be pumped vertically upward inside the column. Rotameters were calibrated to give the correct flow rate, which was maintained constant during each experiment. Periodic flow rate checks were carried out by physically collecting samples of solution at the outlet for a given time and weighing the amount collected. Sample points were located at 5-, 10-, 15-, 20-, and 25-cm height in the column, enabling a series of 10-cm^3 sample syringes to be used to withdraw samples from the center point of the bed for analysis. Samples were taken at time intervals ranging from 15 min to half an hour until the metal ion concentration was at the breakthrough point at the top of the bed. The metal ion concentrations were determined using inductively coupled plasma atomic emission spectrometry at wavelengths corresponding to the maximum sensitivity for each metal ion. This procedure enabled the breakthrough curves to be obtained. The experiment was repeated to ensure that the experimental data are reproducible.

Theory

Fixed-bed film-surface diffusion model

The film-surface diffusion model is based on the assumption that the adsorbate penetration rate is determined by the external film diffusion and the surface diffusion.

(1) Overall mass balance for the process dynamics:

Rate of solute in by flow - Rate of solute out by flow = Rate of accumulation of solute in the fluid phase and in the solid phase,

$$v\left[\frac{\partial C}{\partial Z}\right]_t + \left[\frac{\partial C}{\partial t}\right]_Z + \rho\left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{\partial \bar{q}}{\partial t}\right]_Z = 0. \tag{1}$$

(2) Mass transfer through the stagnant liquid film for a spherical particle:

The rate of accumulation of solute in the solid phase is equal to the rate of transfer of solute across the liquid film.

$$\rho\left[\frac{\partial \bar{q}}{\partial t}\right] = \frac{3k_f}{R}(C - C_s). \tag{2}$$

Put Eq. 2 into Eq. 1, and thus we obtain

$$v\left[\frac{\partial C}{\partial Z}\right]_t + \left[\frac{\partial C}{\partial t}\right]_Z + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{3k_f}{R}(C - C_s)\right] = 0. \tag{3}$$

(3) When the dominant effect is surface diffusion, the adsorption rate has the form

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[D_s r^2 \frac{\partial q}{\partial r}\right] \tag{4}$$

or

$$\frac{\partial q}{\partial t} = D_s\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}D_s\frac{\partial q}{\partial r}. \tag{5}$$

In this case, the surface diffusivity, D_s, is assumed to be constant and independent of surface loading inside the particle.

Boundary Condition 1 at the center of the particle is

$$\left.\frac{\partial q}{\partial r}\right|_{r=0} = 0. \tag{6}$$

Boundary Condition 2 at the surface of the particle is

$$\frac{k_f}{\rho}(C - C_s) = D_s\left.\frac{\partial q}{\partial r}\right|_{r=R}. \tag{7}$$

Initial conditions are

$$1.\ \ q = 0 \quad \text{for all } r \text{ at } t = 0 \tag{8}$$

$$2.\ \ C|_{Z=0} = C_0 \quad \text{at } t = 0. \tag{9}$$

In the multicomponent system, the flux is generally described in Fickian form as

$$-J_i = \sum_{j=1}^{n-1} D_{ij}\nabla q_j, \tag{10}$$

in which the D_{ij} are multicomponent diffusion coefficients. In a binary system, Eq. 10 will become

$$-J_1 = D_{11}\nabla q_1 + D_{12}\nabla q_2 \tag{11}$$

$$-J_2 = D_{22}\nabla q_2 + D_{21}\nabla q_1. \tag{12}$$

The cross-term Fickian diffusivities, D_{12} and D_{21}, are not equal and are generally less than 10% of the main-term diffusivities D_{11} and D_{22} (Cussler, 1976; Yang et al., 1991). Each cross term gives a measure of the flux of one solute that is provoked by the concentration gradient of a second solute.

For spherical adsorbent particles using surface diffusion as the major intraparticle transport mechanism, the binary Fickian diffusion equations are

$$\frac{\partial q_1}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_{s,11}\frac{\partial q_1}{\partial r} + D_{s,12}\frac{\partial q_2}{\partial r}\right)\right] \tag{13}$$

Table 1. Parameters for Sensitivity Analysis on Binary Film Surface Diffusion Model

Volumetric flow rate	75 ml/min		
Mean particle diameter	605 μm		
Bed depth	25 cm		
Equilibrium isotherm equation	Sips isotherm equation		
Metal ion	Copper	Cadmium	Zinc
K_{LF}	3.153	1.655	1.464
a_{LF}	3.271	23.47	2.252
β_{LF}	0.442	0.404	0.374
Initial concentration, C_0	1.5 mmol/L	1.5 mmol/L	1.5 mmol/L
External mass transfer coefficient, k_f	6.06×10^{-4} cm/s	6.08×10^{-4} cm/s	5.99×10^{-4} cm/s
Surface diffusivity, D_s	2.46×10^{-9} cm^2/s	2.52×10^{-9} cm^2/s	4.79×10^{-9} cm^2/s

$$\frac{\partial q_2}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_{s,22}\frac{\partial q_2}{\partial r} + D_{s,21}\frac{\partial q_1}{\partial r}\right)\right]. \tag{14}$$

Assuming the effect of cross diffusion is small and the contributions of the cross diffusivities $D_{\mathrm{s},ij}$ to the overall diffusion are negligible, the above equations can be simplified to

$$\frac{\partial q_1}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_{s,11}\frac{\partial q_1}{\partial r}\right] \tag{15}$$

$$\frac{\partial q_2}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_{s,22}\frac{\partial q_2}{\partial r}\right]. \tag{16}$$

Boundary Condition 1 at the center of the particle is

$$\left.\frac{\partial q_i}{\partial r}\right|_{r=0} = 0. \tag{17}$$

Boundary Condition 2 at the surface of the particle is

$$\frac{k_{f,i}}{\rho}(C_i - C_{s,i}) = D_{s,ii}\left.\frac{\partial q_i}{\partial r}\right|_{r=R}. \tag{18}$$

Initial conditions are

$$1.\ \ q_i = 0 \quad \text{for all } r \text{ at } t = 0 \tag{19}$$

$$2.\ \ C_i|_{Z=0} = C_0 \quad \text{at } t = 0. \tag{20}$$

Similar to the single component system, the overall mass balance for each component in the column is Rate of solute in by flow - Rate of solute out by flow.

= Rate of accumulation of solute in the fluid phase and in the solid phase.

For component 1,

$$v\left[\frac{\partial C_1}{\partial Z}\right]_t + \left[\frac{\partial C_1}{\partial t}\right]_Z + \rho\left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{\partial \overline{q_1}}{\partial t}\right]_Z = 0. \tag{21}$$

Since the rate of accumulation of solute in the solid phase is equal to the rate of transfer of solute across the liquid film, the mass transfer through the stagnant liquid film for each component is

$$\rho\left[\frac{\partial \overline{q_1}}{\partial t}\right] = \frac{3k_{f1}}{R}(C_1 - C_{s1}). \tag{22}$$

Substitute Eq. 22 into Eq. 21, thus obtaining

$$v\left[\frac{\partial C_1}{\partial Z}\right]_t + \left[\frac{\partial C_1}{\partial t}\right]_Z + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{3k_{f1}}{R}(C_1 - C_{s1})\right] = 0. \tag{23}$$

Similarly for component 2,

$$v\left[\frac{\partial C_2}{\partial Z}\right]_t + \left[\frac{\partial C_2}{\partial t}\right]_Z + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{3k_{f2}}{R}(C_2 - C_{s2})\right] = 0. \tag{24}$$

The coupling equation between the solid and liquid concentration is the equilibrium isotherm. In multicomponent systems, the ideal adsorbed solution theory (IAST) can be used to predict the multicomponent adsorption data using only single-component isotherm relationships. The equilibrium isotherm studies of copper, cadmium, and zinc ions on bone char were reported by Ko and co-workers (2004). It was concluded that the best-fit model to describe the sorption of the two metal ions on bone char was the Sips isotherm equation (Sips, 1948)

$$q_e = \frac{K_{LF}C_e^{\beta_{LF}}}{1 + a_{LF}C_e^{\beta_{LF}}}. \tag{25}$$

The Sips isotherm constants (K_{LF}, $a_{\mathrm{LF},}$ and β_{LF}) for the three metal ion systems onto bone char are given in Table 1.

IAS theory

The thermodynamics of ideal dilute solutions were applied to develop a method for predicting multisolute adsorption, using only data for single-solute adsorption from dilute liquid solutions (Radke and Prausnitz, 1972). The procedure is illustrated below for two-solute equilibria.

(1) The spreading pressure for each single solute is evaluated by

$$\pi_i^0 = \frac{R_{gas}T}{A_{ads}}\int_0^{C_{ei}^0}\frac{q_{ei}^0}{C_{ei}^0}\,dC_{ei}^0. \tag{26}$$

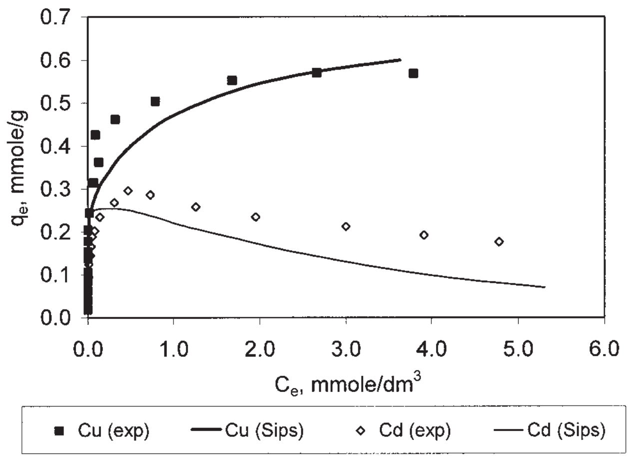

Figure 1. Experimental data and predictive curves for the sorption of Cd/Cu ions at equal molar ratio.

The experimental isotherm data are integrated according to the above equation giving the spreading pressure for each single solute

$$\pi_1 = f_1(C^0_{e1}); \quad \pi_2 = f_2(C^0_{e2}). \tag{27}$$

(2). The equilibrium relationships are written as

$$C^0_{ei} z_i = C_{eT} x_i \tag{28}$$

and

$$\sum_{i=1}^{n} x_i = 1 \tag{29}$$

$$\sum_{i=1}^{n} z_i = 1. \tag{30}$$

For a binary system, $C_{e1}{}^0\ z_1 = C_{eT}\ x_1$; $C_{e2}{}^0\ (1\text{-}z_1) = C_{eT}\ (1\text{-}x_1)$.

(3). Since single-solute concentrations $C_{ei}{}^0$ are defined at the same spreading pressure as that of the mixture,

$$\pi_i = \pi. \tag{31}$$

(4). For a given value of C_{eT} and x_1, the above equations determine the remaining five variables π_1, π_2, z_1, $C_{e1}{}^0$, and $C_{e2}{}^0$.

(5). The total invariant adsorption can now be calculated using the single-solute isotherm data and the equation

$$\frac{1}{q_{eT}} = \sum_{i=1}^{n} \frac{z_i}{q^0_{ei}}. \tag{32}$$

The invariant adsorption of each solute species in mixture follows by mass balance

$$q_{ei} = q_{eT} z_i. \tag{33}$$

The above procedure, which involves a trial-and-error calculation of π_i, can be evaluated conveniently using a computer program. Once the iteration converges, the multicomponent equilibrium data can be obtained and the effluent concentrations of metal ions in the column for multicomponent systems can be predicted. The SSE values are calculated based on the sum of the difference between the theoretical results and all the experimental data from the five-bed height at 5, 10, 15, 20, and 25 cm for each experiment, that is

$$\text{SSE} = \sum_{i=1}^{n} \left(\frac{C_{ti,\text{exp}} - C_{ti,\text{theoretical}}}{C_{0i,\text{exp}} - C_{0i,\text{theoretical}}} \right)^2. \tag{34}$$

Results and Discussion

Multicomponent equilibrium studies

The IAST has been used to predict multicomponent adsorption isotherms using single-component equilibrium data. Figures 1 and 2 show the sorption of Cu/Cd and Cu/Zn systems onto bone char, respectively. The sorption capacities for the copper ions are always higher than that of the cadmium and zinc ions. The possible reason may be due to the selectivity of ion exchange in multicomponent systems. The selectivity of metal ions onto bone char follows the order $Cu^{2+} > Cd^{2+} > Zn^{2+}$, which matches with the reversed order of hydrated ionic radii Cu^{2+} (4.19 Å) $> Cd^{2+}$ (4.26 Å) $> Zn^{2+}$ (4.30 Å). This may be due to the fact that the smaller the ionic radius and the greater the valence, the more closely and strongly is the ion adsorbed. On the other hand, the greater the ion's hydration, the farther it is from the adsorbing surface and the weaker its adsorption (Ko et al., 2004).

Sensitivity analysis

The two model parameters for each metal ion in the film-surface diffusion model were the surface diffusivity, D_s, and the external mass-transfer coefficient, k_f. The impact of varying

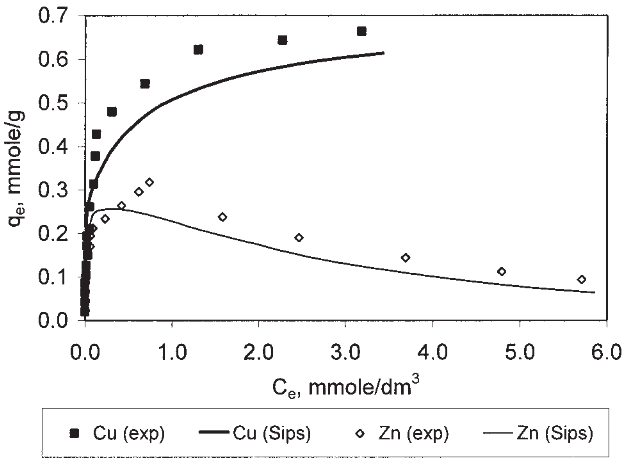

Figure 2. Experimental data and predictive curves for the sorption of Cu/Zn ions at equal molar ratio.

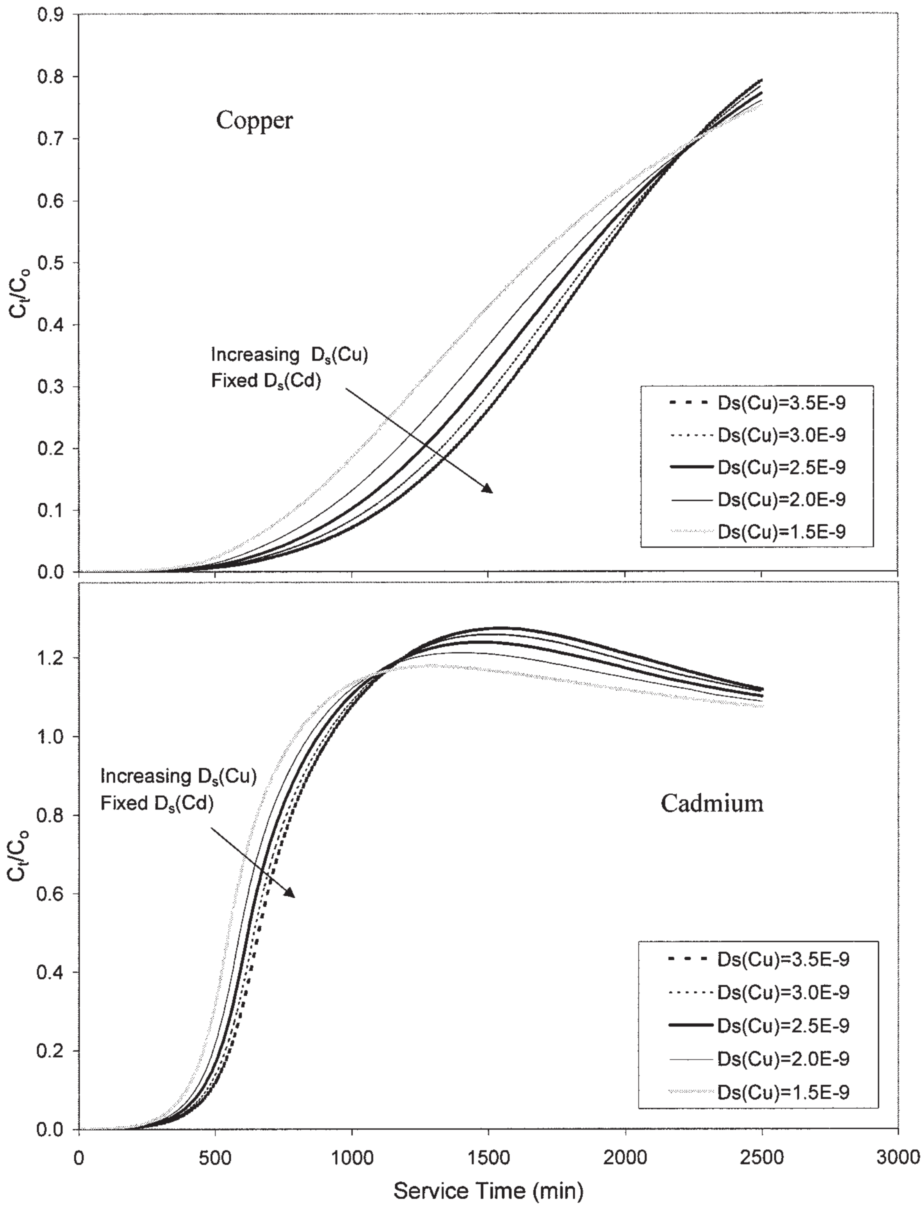

Figure 3. Effect of varying D_s(Cu) on copper (upper graph) and cadmium (lower graph) in the Cu/Cd binary system (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 1.5 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm, bed depth = 25 cm).

mass-transfer parameters on model predictions in the multicomponent system was also examined in a sensitivity analysis.

The copper/cadmium binary system was taken as an example to perform the sensitivity analysis on the mass transfer parameters D_s and k_f. The process conditions used to study this system are shown in Table 1. The initial D_s values were obtained based on the best-fit D_s values from their single-component sorption systems, and the k_f values were calculated from the external mass transfer correlation (Ko et al., 2003)

$$Sh = 0.325/\varepsilon \, Re^{0.36} Sc^{1/3}. \tag{35}$$

The impact of varying the surface diffusivity of copper ion on the model prediction for the copper and cadmium ions is presented in Figure 3. The surface diffusivity was varied by ±20 and ±40% of the reference value, and everything else was kept constant. For a smaller D_s value, an earlier breakthrough is observed in both cases. The curves in Figure 4, which show the impact of the surface diffusivity of cadmium ion on model prediction for the cadmium and copper ions, reveal the same trend as was observed in Figure 1. In both cases, the trend shows that the smaller the surface diffusivity, the larger the intraparticle diffusion resistance within the sorbent particle, thus resulting in a less steep breakthrough curve and earlier breakthrough.

The results shown in Figures 3 and 4 demonstrate that the cadmium ion concentration has exceeded its initial feed concentration (that is, C_t/C_0 is larger than unity). This is a common feature of multicomponent adsorption systems (Liapis and Rippin, 1977; Crittenden and Weber, 1978) and is sometimes

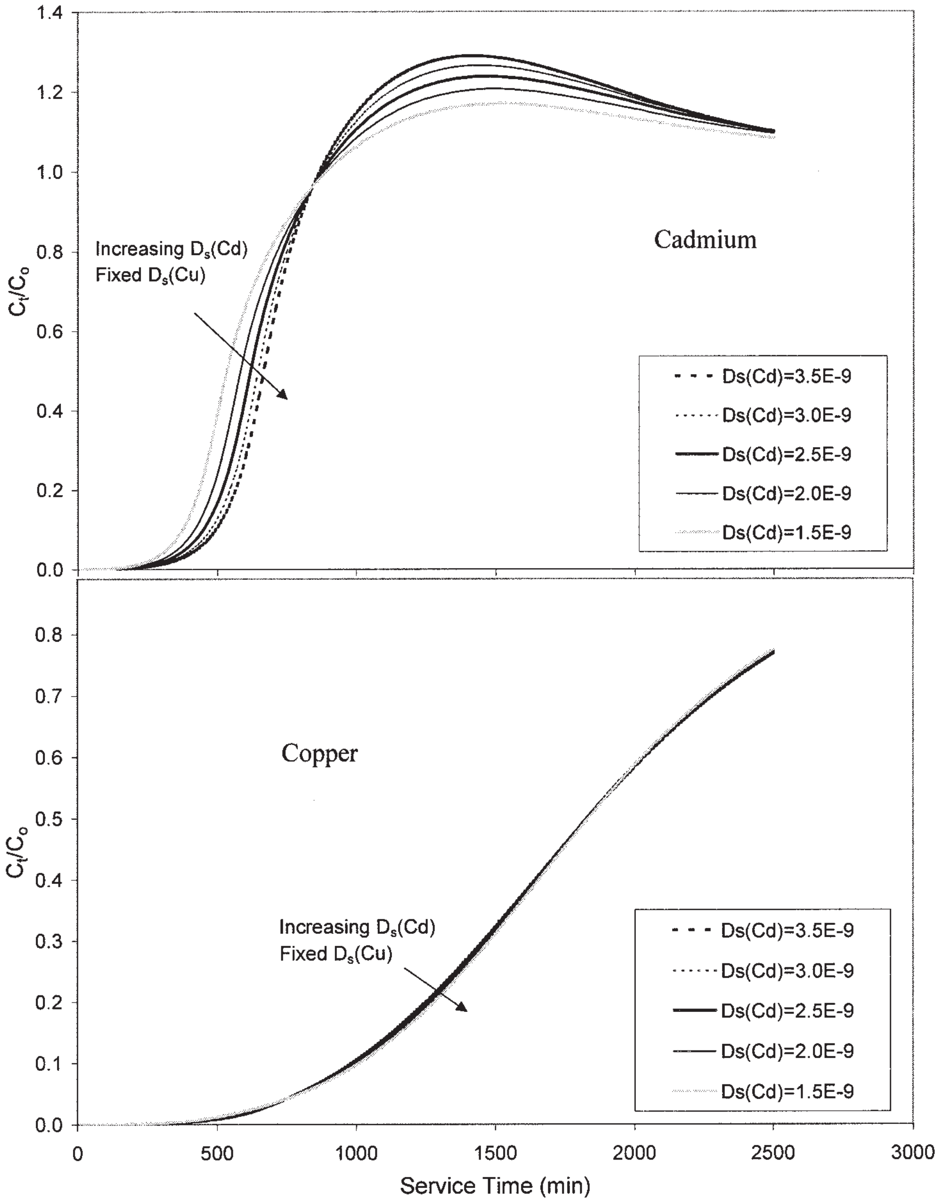

Figure 4. Effect of varying D_s(Cd) on cadmium (upper graph) and copper (lower graph) in the Cu/Cd binary system (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 1.5 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm, bed depth = 25 cm).

referred to as roll-up (Ruthven, 1984). The effect is due to the displacement of the less strongly adsorbed species by the slower-moving more strongly adsorbed component. Based on the equilibrium studies, copper has a larger sorption equilibrium capacity than cadmium and zinc, which would imply that copper is a more strongly adsorbed component than cadmium or zinc. Therefore, in this case, the cadmium ion is the less strongly adsorbed component, and it will be displaced by the slower-moving more strongly adsorbed copper ion, thus resulting in a cadmium solution concentration higher than the initial feed concentration.

As shown in Figure 3, the D_s value of the copper ion is increased, which means it diffuses faster, a later breakthrough of copper results. More cadmium will be displaced and a larger cadmium overshoot is observed. On the other hand, as shown in Figure 4, if the D_s value of the cadmium ion is smaller, the displacement of cadmium ions by copper ions will be relatively slower, and a later and a smaller overshoot of the cadmium breakthrough curves results. However, the effect of changing surface diffusivity of cadmium on copper ion is relatively small, since the diffusion of the slower diffusing copper ion is not much affected by the diffusion of the fast diffusing cadmium ion. In other words, the change of surface diffusivity of the slower diffusing species (that is, copper in this case) will affect the breakthrough curves for both the faster and the slower diffusing species; however, the change of the surface diffusivity of the faster diffusing species (that is, cadmium in this case) will only affect the breakthrough curves for the faster diffusing species.

The curves in Figures 5 and 6 illustrate the impact of varying the external mass-transfer coefficient of copper and cadmium ion on the model prediction in the binary system, while keeping

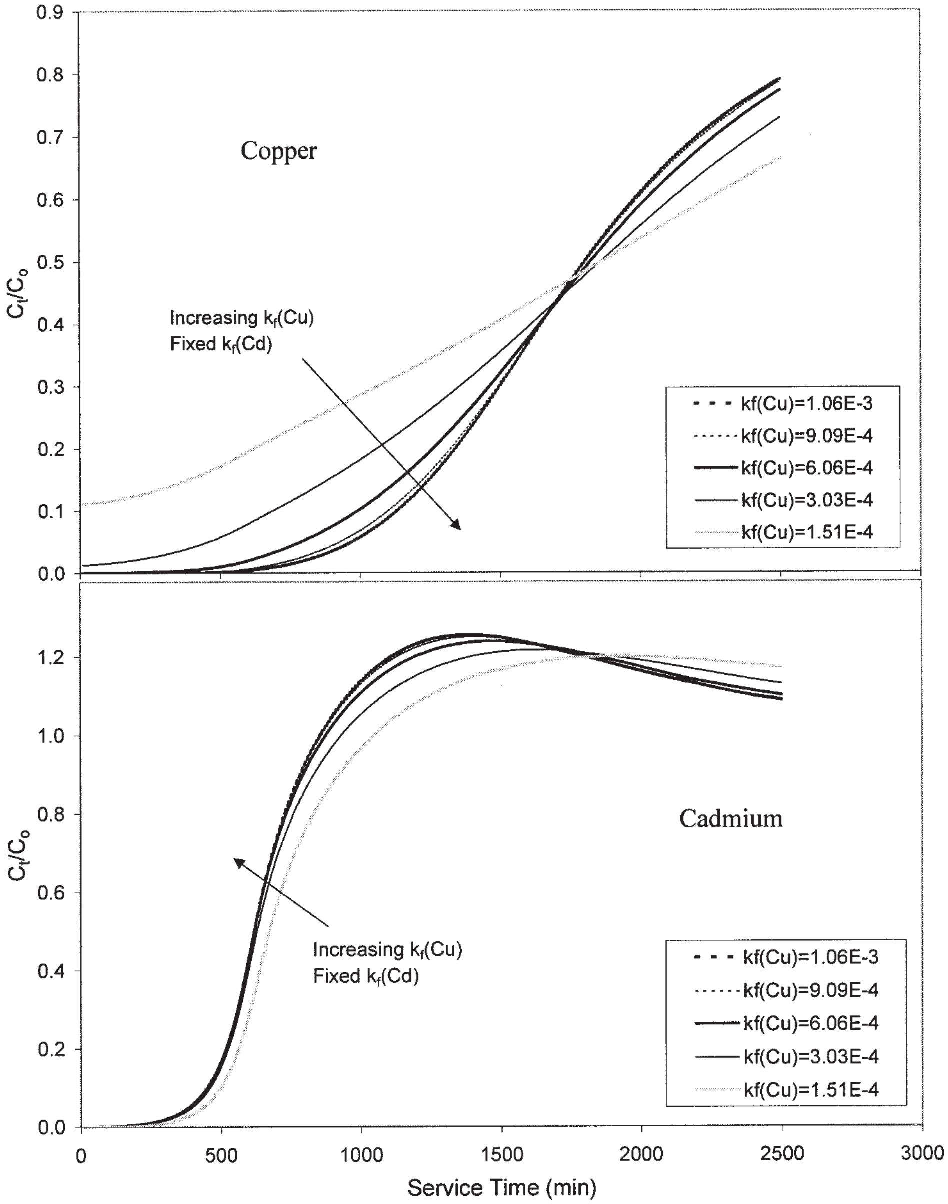

Figure 5. Effect of varying k_f(Cu) on copper (upper graph) and cadmium (lower graph) in the Cu/Cd binary system (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 1.5 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm, bed depth = 25 cm).

the other parameters constant. The external mass-transfer coefficients, k_f, were varied by ±50 and ±75% of the reference values. The effect of the external mass-transfer coefficient is less compared with the effect of surface diffusion on the breakthrough curves. For smaller k_f values, an earlier breakthrough is observed. As the value of k_f increases, the breakthrough curve will become more and more steep, but the effect on the breakthrough curve is less prominent for a higher k_f. This suggests that, for a given intraparticle diffusion rate, there is a limiting value of the external mass-transfer coefficient beyond which the model is relatively insensitive to the additional increase in the external mass-transfer coefficient. Similar to the analysis on the effect of surface diffusion, the change of the external mass-transfer coefficient of the slower diffusing species will affect the breakthrough curves for both the faster and the slower diffusing species; however, the change of the external mass-transfer coefficient of the faster diffusing species will only affect the breakthrough curves for the faster diffusing species.

Effects of changing system variables

The mass-transfer model program is supplied with the experimental data obtained from five different bed heights (5, 10, 15, 20, and 25cm) for each column, and the effects of changing the system variables on the film surface diffusion model are summarized in Table 2. In the initial surface diffusion model, the surface diffusivity is assumed independent of particle size, flow rate, and concentration. Thus, a mean D_s value is taken from the optimized D_s values under different system condi-

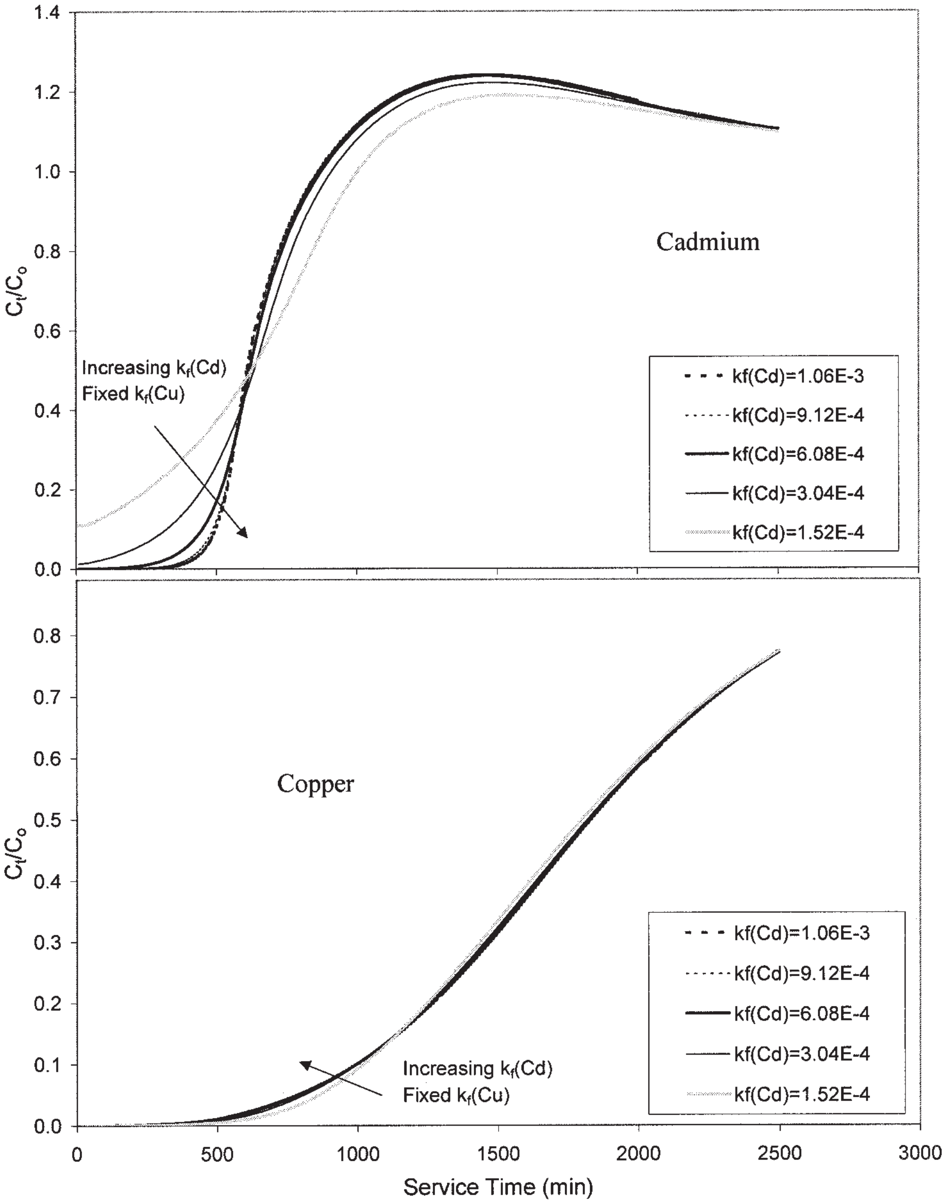

Figure 6. Effect of varying k_f(Cd) on cadmium (upper graph) and copper (lower graph) in the Cu/Cd binary system (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 1.5 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm, bed depth = 25 cm).

tions. In the Cu/Cd system, the mean D_s values for copper and cadmium are 7.37×10^{-10} and 2.73×10^{-9} cm^2/s, respectively; while in the Cu/Zn system, the mean D_s values for copper and zinc are 1.61×10^{-9} and 2.43×10^{-9} cm^2/s, respectively.

The effect of a change in flow rate was tested on both the Cu/Cd system and the Cu/Zn system. It can be seen that the change of flow rate does not significantly affect the D_s values, as the flow rate should affect the film thickness—and thus the external mass-transfer coefficient—but not the intraparticle diffusivity. The change of the molar ratio of the feed concentrations does not result in any noteworthy change in the D_s value. This again demonstrates the applicability of the surface diffusion model on the metal ion bone char sorption system. For fixed feed concentrations, the change of d_p and flow rate does not considerably alter the surface diffusivity, as would be expected. A summary of results obtained using the mean D_s value is shown in Table 3.

For the binary system, by visual inspection, an SSE value less than 1.0 provides a qualitatively good fit for the model to the experimental data; an SSE between 1.0 and 2.0 indicates a satisfactory and acceptable fit by the model; an SSE between 2.0 and 3.0 suggests the model provides general agreement with the experimental data; and an SSE larger than 3.0 indicates that the model cannot truly predict the experimental data. Figures 7 and 8 demonstrate a good fit by the model and Figure 9 shows an acceptable fit by the model with the experimental data.

The surface diffusivities of the copper, the cadmium, and the zinc ion obtained from the single component film-surface diffusion model analysis are 2.46×10^{-9}, $2.52 \times$

Table 2. Results Summary for Changes in Flow Rate, d_p, and C_0 on Film Surface Diffusion Model with Constant Diffusivity for Binary Cu/Cd and Cu/Zn Bone Char Sorption Systems

Flow Rate (ml/min)	Mean d_p (μm)	Comp. 1	Conc. 1 (mmol/L)	Optimized D_s (1) (cm^2/s)	SSE (1)	Comp. 2	Conc. 2 (mmol/L)	Optimized D_s (2) (cm^2/s)	SSE (2)	SSE (1 + 2)
25	604	Cu	1.5	9.9×10^{-10}	2.160	Cd	1.5	2.08×10^{-9}	2.307	4.468
50	605	Cu	1.5	7.97×10^{-10}	1.130	Cd	1.5	2.20×10^{-9}	0.845	1.976
75	605	Cu	1.5	7.19×10^{-10}	1.077	Cd	1.5	2.67×10^{-9}	0.273	1.350
100	605	Cu	1.5	8.75×10^{-10}	0.675	Cd	1.5	2.13×10^{-9}	0.309	0.983
50	605	Cu	1.5	7.97×10^{-10}	1.130	Cd	1.5	2.20×10^{-9}	0.845	1.976
50	605	Cu	1.5	7.05×10^{-10}	0.804	Cd	2	3.38×10^{-9}	0.311	1.115
50	605	Cu	2	7.99×10^{-10}	1.466	Cd	1.5	3.52×10^{-9}	1.559	3.025
75	605	Cu	1.5	6.92×10^{-10}	0.730	Cd	2	3.14×10^{-9}	0.224	0.954
50	605	Cu	1.5	7.05×10^{-10}	0.804	Cd	2	3.38×10^{-9}	0.311	1.115
50	427	Cu	1.5	3.91×10^{-10}	1.636	Cd	2	2.74×10^{-9}	0.470	2.105
			Mean D_s (1)	7.37×10^{-10}			Mean D_s (2)	2.73×10^{-9}		
50	605	Cu	1.5	1.57×10^{-9}	0.526	Zn	1.5	2.70×10^{-9}	0.659	1.184
75	605	Cu	1.5	1.46×10^{-9}	0.438	Zn	1.5	2.08×10^{-9}	0.238	0.676
100	605	Cu	1.5	1.80×10^{-9}	0.548	Zn	1.5	2.50×10^{-9}	0.389	0.937
			Mean D_s (1)	1.61×10^{-9}			Mean D_s (2)	2.43×10^{-9}		

10^{-9}, and 4.79×10^{-9} cm^2/s, respectively (Ko et al., 2003). In the binary Cu/Cd system, the mean optimized surface diffusivities, D_s, for copper and cadmium are 7.37×10^{-10} and 2.73×10^{-9} cm^2/s, respectively, while in the Cu/Zn system, the mean optimized surface diffusivities for copper and zinc are 1.61×10^{-9} and 2.43×10^{-9} cm^2/s, respectively. The result from the Cu/Cd system shows that the diffusivity of cadmium is almost unaffected by the presence of the copper ion, but the diffusivity of copper will become smaller in the presence of the cadmium ion. The cadmium ions, being the faster diffusing species, will be displaced by the slower-moving more strongly adsorbed copper ions. Thus, the concentration front of cadmium will move faster than the concentration front of copper, and, so, at the concentration front, the cadmium ions will behave like a single component. As a result, the surface diffusivity of cadmium obtained is similar to the one obtained from the single-component analysis. The copper ion, which is affected by the displacement of the cadmium ion moving in an opposite direction, will have a smaller diffusivity since it will be moving more slowly than the condition in the single-component system. The possible small deviation of diffusivity of cadmium in the single- and multicomponent systems would be due to the fact that these diffusivities are obtained based on the optimization of different sets of experimental data. In the Cu/Zn system, copper will be the more strongly adsorbed species and it will displace the zinc ion. The zinc ions, showing a similar effect as the cadmium ions in the Cu/Cd system, will move faster than the copper ions and they will diffuse in a manner similar to their behavior in the single-component system. The surface diffusivity of the zinc ion obtained from the multicomponent analysis should be similar to the value in the single-component analysis. The difference between the surface diffusivity of the zinc ion obtained from the single- and multicomponent analysis may be due the fact that the surface diffusivity is taken as a constant which is a time-averaged surface diffusivity and does not take the change of surface diffusivity with surface loading into account, or the surface diffusivity of zinc ion obtained in the single component analysis is not accurate. Thus, in some cases, the surface diffusivity obtained from the multicomponent analysis may not be directly comparable to the D_s obtained from the single-component system.

Since, in some cases, the model predictions based on the

Table 3. Results Summary for Changes in Flow Rate, d_p, and C_0 on Film Surface Diffusion Model with Constant Mean Diffusivity for Binary Cu/Cd and Cu/Zn Bone Char Sorption Systems

Flow Rate (ml/min)	Mean d_p (μm)	Comp 1	Conc. 1 (mmol/L)	k_f (1) (cm/s)	D_s (1) (cm^2/s)	SSE (1)	Comp 2	Conc. 2 (mmol/L)	k_f (2) (cm/s)	D_s (2) (cm^2/s)	SSE (2)	SSE (1 + 2)
25	605	Cu	1.5	4.06×10^{-4}	7.37×10^{-10}	1.747	Cd	1.5	4.08×10^{-4}	2.73×10^{-9}	2.987	4.733
50	605	Cu	1.5	5.23×10^{-4}	7.37×10^{-10}	1.328	Cd	1.5	5.25×10^{-4}	2.73×10^{-9}	0.654	1.982
75	605	Cu	1.5	6.06×10^{-4}	7.37×10^{-10}	1.083	Cd	1.5	6.08×10^{-4}	2.73×10^{-9}	0.279	1.362
100	605	Cu	1.5	6.72×10^{-4}	7.37×10^{-10}	2.102	Cd	1.5	6.76×10^{-4}	2.73×10^{-9}	1.036	3.137
50	605	Cu	1.5	5.23×10^{-4}	7.37×10^{-10}	1.328	Cd	1.5	5.25×10^{-4}	2.73×10^{-9}	0.654	1.982
50	605	Cu	1.5	5.23×10^{-4}	7.37×10^{-10}	1.011	Cd	2	5.25×10^{-4}	2.73×10^{-9}	0.338	1.349
50	605	Cu	2	5.23×10^{-4}	7.37×10^{-10}	3.202	Cd	1.5	5.25×10^{-4}	2.73×10^{-9}	1.845	3.224
75	605	Cu	1.5	6.06×10^{-4}	7.37×10^{-10}	0.740	Cd	2	6.08×10^{-4}	2.73×10^{-9}	0.228	0.968
50	605	Cu	1.5	5.23×10^{-4}	7.37×10^{-10}	1.011	Cd	2	5.25×10^{-4}	2.73×10^{-9}	0.338	1.349
50	427	Cu	1.5	6.64×10^{-4}	7.37×10^{-10}	3.202	Cd	2	6.67×10^{-4}	2.73×10^{-9}	2.719	5.917
50	605	Cu	1.5	5.23×10^{-4}	1.61×10^{-9}	0.692	Zn	1.5	5.17×10^{-4}	2.43×10^{-9}	0.579	1.271
75	605	Cu	1.5	6.06×10^{-4}	1.61×10^{-9}	0.488	Zn	1.5	5.99×10^{-4}	2.43×10^{-9}	0.280	0.768
100	605	Cu	1.5	6.72×10^{-4}	1.61×10^{-9}	0.510	Zn	1.5	6.65×10^{-4}	2.43×10^{-9}	0.487	0.997
											Total SSE	25.709

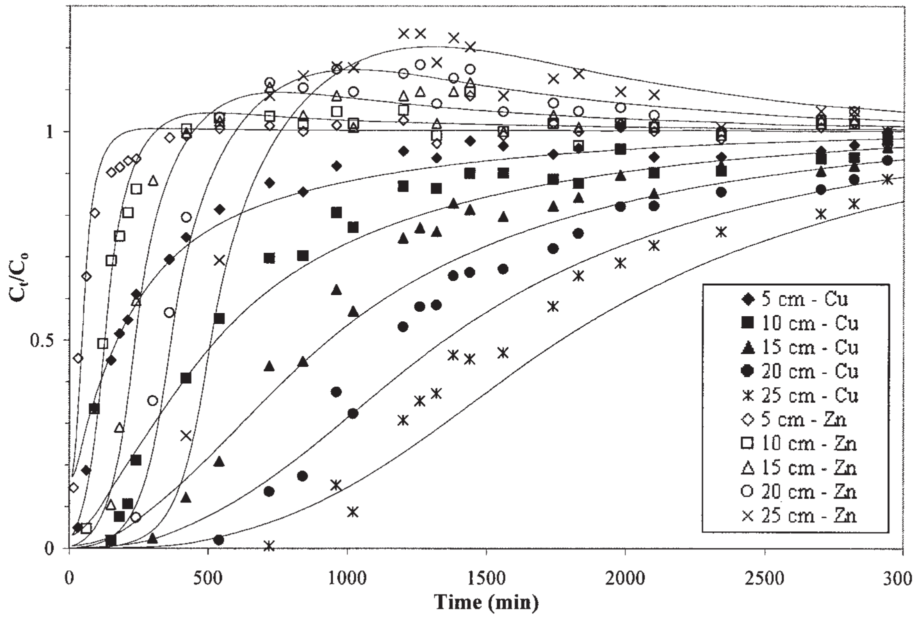

Figure 7. Model prediction for a Cu/Zn binary system based on a mean constant surface diffusivity model and experimentally correlated k_f (C_0(Cu) = 1.5 mmol/L, C_0(Zn) = 1.5 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm).

multicomponent diffusion model with constant surface diffusivity cannot accurately describe the column performance, modifications to the model could be made with a view to achieving a better fit to the experimental data from the pilot-plant studies. Possible modifications would be the use of concentration-dependent diffusivities or the incorporation of the cross diffusivity terms to describe the mass transport behavior within the adsorbent, which would require further investigation and modeling studies.

Conclusions

Based on film-surface diffusion and applying the IAS model, a multicomponent mass transport model was developed and

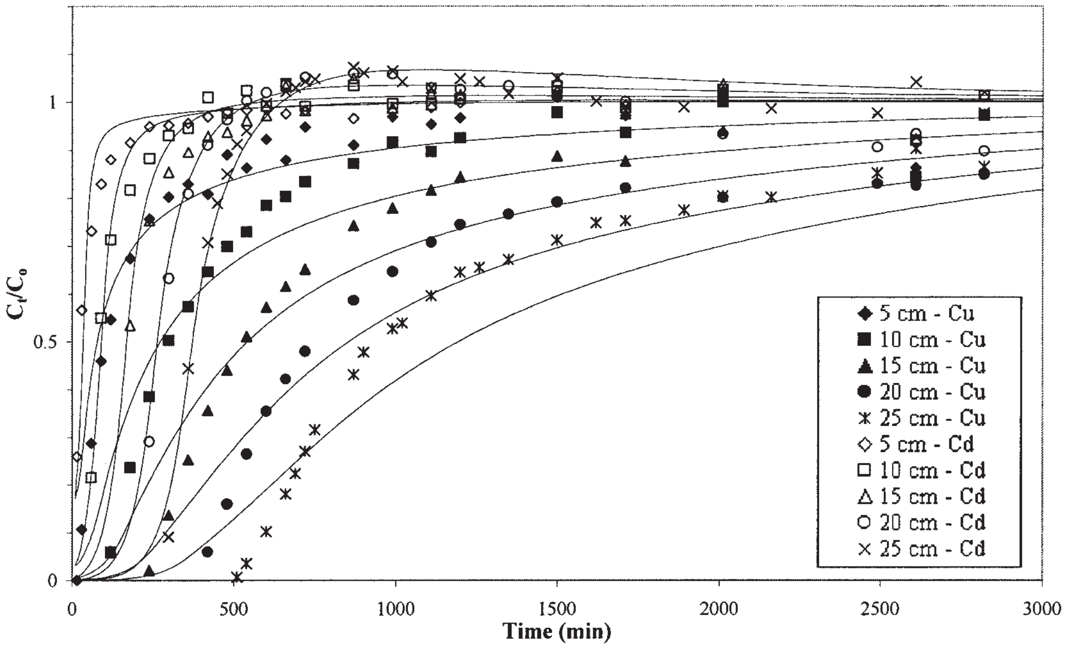

Figure 8. Model prediction for a Cu/Cd binary system based on a mean constant surface diffusivity model and experimentally correlated k_f (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 2.0 mmol/L, flow rate = 75 ml/min, mean d_p = 605 μm).

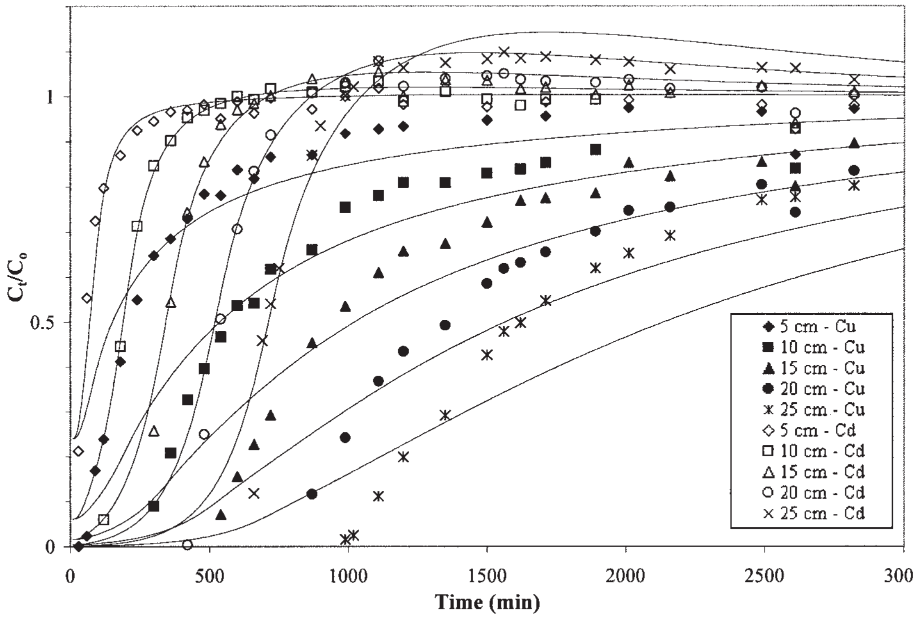

Figure 9. Model prediction for a Cu/Cd binary system based on a mean constant surface diffusivity model and experimentally correlated k_f (C_0(Cu) = 1.5 mmol/L, C_0(Cd) = 2.0 mmol/L, flow rate = 50 ml/min, mean d_p = 605 μm).

applied to describe the equilibrium relationship for the sorption of binary Cu/Cd and Cu/Zn systems on bone char in fixed beds. It is found that the diffusivity of Cu will be affected by the presence of Cd or Zn in the binary systems. These may be due to the fact that the fast-moving cadmium or zinc ions will be displaced by the slower-moving more strongly adsorbed copper ions. Therefore, the copper ion will be affected by the displacement of the cadmium ion moving in an opposite direction, thus having a smaller diffusivity than the condition in the single-component system. The cadmium or zinc ion, on the other hand, is moving faster than the copper ion, and therefore at the concentration front the cadmium or zinc ion will behave like a single component. Further work could be done to improve the model results by incorporating a concentration-dependent diffusivity or cross diffusivity terms into the mass transport model.

Notation

ε = void fraction of the bed (dimensionless)
π = spreading pressure (N/m)
β_{LF} = sips isotherm constant (dimensionless)
ρ = particle density of adsorbent (g/m^3)
μ = viscosity of solution (Nsm^{-2})
A_{abs} = surface area of adsorbent (m^2)
α_{LF} = sips isotherm constant ((m^3/mol)$^{\beta LF}$)
C = concentration of solute (mol/m^3)
C_t = concentration of solute at time t (mol/m^3)
C_e = equilibrium fluid phase concentration (mol/m^3)
C_{eT} = the total concentration of all solutes in the liquid phase (mol/m^3)
C_o = initial solute concentration (mol/m^3)
C_s = liquid concentration at fluid/solid interface (mol/m^3)
D_s = surface diffusion coefficient (m^2/s)
J_d = mass-transfer coefficient flux (mol/ms)
k_f = external mass-transfer coefficient (m/s)
K_{LF} = sips isotherm constant ((m^3)$^{\beta LF}$(mol)$^{1-\beta LF}$/g)
$\overline{q}$ = local solid phase concentration (mol/g)
q = overall solid phase concentration in the particle (mol/g)
q_e = equilibrium solid phase concentration (mol/g)
r = radial distance within the adsorbent particle (m)
R = radius of adsorbent particle (m)
Re = Reynolds number (dimensionless)
R_{gas} = gas constant (8.314kJ/mol K)
Sc = schmidt number (dimensionless)
Sh = sherwood number (dimensionless)
SSE = sum of squares errors, Σ(Experimental Data –Simulated Data)^2
t = service time/operating time of the bed (s)
v = volumetric flowrate (m^3/s)
x_i = liquid phase solvent-free mole fraction of solute i (dimensionless)
Z = bed depth (m)
z_i = adsorbed-phase mole fraction of solute i (dimensionless)

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