

# Application of the concentration-dependent surface diffusion model on the multicomponent fixed-bed adsorption systems

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## Abstract

The ability of bone char to adsorb three metal ions, namely, cadmium, copper and zinc, from effluents in fixed beds has been studied. Two binary metal ion sorption systems, Cd + Cu and Cu + Zn, have been investigated. The variables studied include metal ion solution flowrate, initial metal ion concentration, and bone char particle size bed height. The experimental breakthrough curves for each binary system were measured at five bed heights.

A multicomponent film-surface diffusion model has been developed to predict the breakthrough curves by incorporating the IAS for both the Langmuir and the Sips equations, since they both correlate the single component equilibrium isotherm data well. A novel development is the modification of the solution methodology, previously restricted to a constant diffusivity, to incorporate a variable diffusivity correlated with adsorbent coverage by the constant self-diffusivity. The self-diffusivities for the metal ions have been evaluated.

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## 1. Introduction

Metal ions in wastewaters represent a significant environmental and health problem (Mido and Satake, 1995). Sorption by various mechanisms can produce a high-quality treated effluent containing little or no metal ions. Bone char has been shown to have significant sorption capacities for various metal ions (Raouf and Daifullah, 1997; Choy and McKay, 2005; Chen et al., 1997; Cheung et al., 2000) and on the strongly related hydroxyapatites (Da Rocha et al., 2002). The mechanism of sorption of metal ions on bone char and hydrous metal oxides has been discussed (Cheung et al., 2002; Trivedi and Axe, 2000) and appears to involve exchange, surface sorption and chelation. Other sorbents for metal ions also seem to have multimechanistic potential including peat and chitosan (Chen et al., 2001; Ngah et al., 2002; Cheung et al., 2002). Other evidence for this can be seen in equilibrium sorption studies in which heterogeneous

isotherms often provide a better correlation to equilibrium data than the ‘identical site’ Langmuir models (Cheung et al., 2003; Porter et al., 1999). Due to these difficulties, metal ion sorption systems are often modeled based on the rate controlling mechanisms. Consequently, film-pore diffusion (Spahn and Schlunder, 1975; Al Duri and McKay, 1992; Whitaker, 1988; McKay et al., 1997; Meshko et al., 2001) and film-surface diffusion (Mathews and Weber, 1976; Miyahara and Okazaki, 1993; Theis et al., 1992; Smith and Amini, 2000; Trivedi and Axe, 2000) mass transport diffusion models have been used for single component metal ion sorption. Very limited data is available for multicomponent metal ion sorption systems. The film-pore diffusion model, based on the shrinkage core theory (Yagi and Kunii, 1961; Levenspiel, 1962) has been extended to metal ion sorption on adsorbents (Arevalo et al., 1998; Ko et al., 2001) with limited success since the model requires a constant diffusivity. The film-surface diffusion model has been developed and extended to the batch sorption of zinc and cadmium onto bone char (Cheung et al., 2001) and copper and nickel from slag (Gupta, 1998) but the solution was restricted to a constant diffusivity.

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The present work concentrates on the development and application of a new film-variable surface diffusivity model to the adsorption of two binary metal ion systems onto bone char, cadmium+copper and copper+zinc for column adsorption. The IAS has been incorporated into the model and both the Langmuir and Sips single component isotherm data have been used to predict the fixed bed breakthrough curves by the variable diffusivity model. The system variables studied include initial metal ion concentration, solution flowrate, bone char particle size and adsorber bed height.

## 2. Theory

Most models developed using a concentration dependent surface diffusivity are based on the adsorption of gases and are predominantly single component systems (Hu and Do, 1994; Do and Rice, 1987; Do, 1996; Choi et al., 2001; Kapoor et al., 1989). A limited number of concentration dependent diffusion models have been developed and tested for liquid phase batch adsorption systems (Miyahara and Okazaki, 1992, 1993; Furuya et al., 1996; Nestle and Kimmich, 1996; Miyabe and Takeuchi, 1997). Previous work by the authors has demonstrated that the concentration-dependent diffusion model generates breakthrough curves which are closer matched to the experimental data than those using the constant diffusion model in single component systems (Ko et al., 2003). However, there are no tested applications for liquid-phase concentration-dependent diffusivity models in multicomponent fixed-bed metal ion adsorption systems.

The outline of the model can be considered by the flux in a multicomponent system is generally described in Fickian form as

$$-J_i = \sum_{j=1}^{n-1} D_{ij} \nabla q_j, \quad (1)$$

in which the  $D_{ij}$  are multicomponent diffusion coefficients. In a binary system, Eq. (1) will become

$$-J_1 = D_{11} \nabla q_1 + D_{12} \nabla q_2, \quad (2)$$

$$-J_2 = D_{22} \nabla q_2 + D_{21} \nabla q_1. \quad (3)$$

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). 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

$$\frac{\partial q_1}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{s,11} \frac{\partial q_1}{\partial r} + D_{s,12} \frac{\partial q_2}{\partial r} \right) \right], \quad (4)$$

$$\frac{\partial q_2}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{s,22} \frac{\partial q_2}{\partial r} + D_{s,21} \frac{\partial q_1}{\partial r} \right) \right]. \quad (5)$$

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

$$\frac{\partial q_1}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_{s,11} \frac{\partial q_1}{\partial r} \right], \quad (6)$$

$$\frac{\partial q_2}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_{s,22} \frac{\partial q_2}{\partial r} \right]. \quad (7)$$

Similar as in 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,

$$v \left[ \frac{\partial C_1}{\partial Z} \right]_t + \left[ \frac{\partial C_1}{\partial t} \right]_Z + \rho \left( \frac{1 - \varepsilon}{\varepsilon} \right) \left[ \frac{\partial q_1}{\partial t} \right]_Z = 0. \quad (8)$$

Since the rate of accumulation of solute in the solid 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

$$\rho \left[ \frac{\partial q_1}{\partial t} \right] = \frac{3k_{f1}}{R} (C_1 - C_{s1}). \quad (9)$$

Substitute Eq. (9) into Eq. (8), thus obtaining

$$v \left[ \frac{\partial C_1}{\partial Z} \right]_t + \left[ \frac{\partial C_1}{\partial t} \right]_Z + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \left[ \frac{3k_{f1}}{R} (C_1 - C_{s1}) \right] = 0. \quad (10)$$

Similarly, for component 2,

$$v \left[ \frac{\partial C_2}{\partial Z} \right]_t + \left[ \frac{\partial C_2}{\partial t} \right]_Z + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \left[ \frac{3k_{f2}}{R} (C_2 - C_{s2}) \right] = 0. \quad (11)$$

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 detailed procedures for solving the numerical solutions for the liquid and solid phase PDEs and applying the IAS theory are described in detail in the previous papers by the authors (Ko et al., 2003, 2004). With the use of the IAS theory, the effluent concentrations of metal ions in the column for multicomponent systems can be predicted.

For some cases such as diffusion in many zeolitic systems, the multicomponent surface diffusivities  $D_{s,ij}$  in Eqs. (4)

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