Modeling the Sorption of Toxic Metals on Chelant-Impregnated Adsorbent

Varadarajan Ravindran, Mario R. Stevens, Badri N. Badriyha, and Massoud Pirbazari
Dept. of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA 90089

The application of a microporous adsorbent, such as activated carbon impregnated with 8-hydroxyquinoline (oxine), a chelating agent, to remove toxic metals from the aqueous phase is studied. A pore and surface diffusion model for predicting the dynamics of fixed-bed adsorbers using oxine-impregnated carbon is also discussed. The model incorporates adsorption equilibrium and kinetic parameters determined from independent isotherm tests and rate experiments, as well as adsorber column flow characteristics. Three modeling scenarios were employed with reference to intraparticle transport: (a) combined pore diffusion and surface diffusion; (b) pore diffusion alone, suppressing the effect of surface diffusion; and (c) surface diffusion alone, suppressing the effect of pore diffusion. Surface diffusion alone provided reasonably good predictions of the adsorber dynamics, as reflected by results from adsorber experiments. It is postulated that the sorption mechanism could be a combination of film transport of metal ions, followed by surface diffusion into adsorbent particles, and subsequent chelation of metal ions with the oxine molecules sorbed on carbon. The sorbed metals could be completely recovered under acidic conditions during the carbon regeneration process.

Introduction

The removal of toxic heavy metals such as cadmium, zinc, and lead has become an important concern to manufacturing industries with respect to water purification and wastewater treatment. Several physicochemical technologies have been used for this purpose, including adsorption, ion exchange, and membrane separation processes (Clifford et al., 1986). Adsorption and ion-exchange processes have been found less expensive than membrane processes for most industrial applications. Most resins have higher affinity for alkaline earth (calcium and magnesium) and alkali metals (sodium and potassium), and have poor selectivity for heavy metals. Improving resin selectivity by introducing new types of polymers into the matrix is a complex and expensive process. In comparison, an established technology that proves less expensive for the removal of trace metals, particularly radionuclides and heavy metals, is granular activated carbon (GAC) adsorption (Motojima et al., 1978, 1979a,b; Clifford et al., 1986).

Although GAC fixed-bed adsorbers are technologically feasible for the removal of heavy metals, they are not widely used due to their low adsorbent capacity and questionable regenerability (Clifford et al., 1986). On the other hand, impregnation or immobilization of a selective chelating agent such as 8-hydroxyquinoline (oxine) on activated carbon would provide a superior sorbent material for heavy metals (Stevens, 1987). The nonpolar oxine is well adsorbed on activated carbon, and such surface modified activated carbon (SMAC) would manifest higher adsorption capacity and easy regenerability for heavy metals (Vogt, 1948; Motojima et al., 1978). Among various chelating agents, oxine is highly selective for Cd, Zn, Pb and other heavy metals as compared to alkaline earth and alkali metals present in most waters and wastewaters (Stevens, 1987; Abollino et al., 1990). Additionally, oxine is relatively nontoxic as it has been widely used for medicinal and agricultural applications (Phillips, 1956). Thus, good selectivity for heavy metal ions, easy adsorbent regenerability, and low toxicity of oxine makes oxine-impregnated SMAC a suitable candidate for the removal of heavy metals. A few studies have been conducted on the application of oxine-impregnated activated carbon for the removal of radionuclides such as Co-58, Co-60, Mn-54, and Fe-57 from nuclear wastes by Motojima and coworkers (1978, 1979a,b). These re-

---

Correspondence concerning this article should be addressed to M. Pirbazari.

searchers observed that oxine-impregnated carbon was significantly more effective in the removal of these radioactive metal ions than pure activated carbon.

An important aspect in the use of oxine-impregnated SMAC is the consideration of mechanisms pertaining to the sorption of oxine on activated carbon, and subsequent chelation of metal ions on the adsorbent-impregnated oxine. It is important to note that the sorption of oxine on activated carbon can be attributed to chemisorption due to the characteristics of the functional groups on the carbon. The interactions between the functional groups of oxine and carbon and the binding of metal ions to specific functional sites on the oxine moiety are important considerations with respect to the sorbent capacity and regenerability.

The application of mathematical models has become an important aspect in the efficient and cost-effective process design by predicting or simulating the process dynamics under a variety of operating conditions. Modeling serves as an important tool for subsequent upscaling of processes from laboratory scale to pilot scale, and eventually to full-scale operation. The model parameters are determined from laboratory-scale adsorption equilibrium and adsorption rate experiments. Modeling is first employed to design laboratory-scale adsorber studies. Subsequently, model verification and/or model refinement is accomplished by comparing the results from adsorber experiments with those of the theoretical predictions. Therefore, this modeling technique constitutes a feedforward approach, wherein the laboratory-scale adsorber experiments are designed based on preliminary design by modeling, and a feedback approach, wherein the experimental results can be used for model verification and refinement. The model can then be employed for upscaling the laboratory-scale adsorber to pilot scale, and eventually to full scale by the theories of dimensional analysis and similitude.

Thus, the objectives of the present study can be briefly summarized as follows: (1) Evaluate the application of adsorbers using oxine-impregnated SMAC for the removal of Cd, Zn, and Pb ions at trace levels, as well as their recovery, (2) propose mechanisms for the sorption of oxine on carbon based on the functional group characteristics of activated carbon, and the formation of metal chelates within the adsorbent; (3) develop as well as test mathematical models for predicting/simulating adsorber dynamics, and determine the suitability of models for describing sorption of heavy metals on oxine-impregnated SMAC.

Background and Theory

Characteristics of oxine and metal oxinates

Oxine (8-hydroxyquinoline or 8-quinolinol) is an amphiprotic substance with a minimum solubility of 500 mg/L (3.5×10^{-3} M at its isoelectric point of pH 7.4 at 25°C). Oxine forms stable chelates with most metals, and the intrinsic solubilities of most metal oxinates are in the range of 10^{-6} to 10^{-9} M. The number of oxine molecules required for the chelation of a metal ion is dependent on the valency of the metal ion. The metal oxinate is formed by the loss of a proton from oxine through an electrovalent bond with oxygen and a coordinate bond with nitrogen (Phillips, 1956; Dwyer and Mellor, 1964). The oxinate formation proceeds in a stepwise manner, depending on the valency of the metal ion in question. The metal M reacts with one oxine molecule to form MOx^{n-1} followed by reaction with another oxine molecule to form MOx_2^{n-2}, and so on, until a neutral compound is obtained (Motojima et al., 1978).

Table 1. Stability Constant for Metal Oxinates

Metal Ion	Stability Const., Log K	Equil. Const. of Ligands, pK_a
Ca(II)	3.27	3.27
Cd(II)	7.8	6.2
Cu(II)	12.1	10.9
Mg(II)	4.5	2.0
Mn(II)	6.8	5.8
Ni(II)	9.9	8.8
Pb(II)	9.02	7.0
Zn(II)	8.56	7.4

Two classes of divalent metal oxinates have been distinguished: those in which the metal ions react with the negatively charged oxygen as in the case of zinc, cadmium, and magnesium, and those in which the metal may react with covalent nitrogen as in the case of cobalt, copper, and nickel (Phillips, 1956). In the metal-oxine chelate, the bonding of the metal is predominantly ionic in the case of magnesium, zinc, and nickel compounds, since these chelates rapidly exchange their metal content with the corresponding ions. X-ray diffraction studies have shown that hydrated zinc oxinate has a transplanar arrangement of two oxinate groups about the central zinc atom. However, in the case of anyhydrous zinc oxinate, the structure appears to be tetrahedral around the zinc atom (Phillips, 1956). Oxinates of cadmium, lead, cobalt, copper, and nickel are isomorphous with hydrated zinc oxinate, and, therefore, have a transplanar structure.

The metal oxinates have relatively low solubility and high stability in aqueous systems. The solubility products of the oxinates of Cd(II), Zn(II), and Pd(II) ions (as pK values) are 21.96, 22.00, and 24.50, respectively (Phillips, 1956), and these demonstrate low aqueous solubility and a strong affinity for binding with polar adsorbents such as activated carbon. The high stability of metal oxinates is indicated by the high values of the stability constants, as shown in Table 1 (Abollino et al., 1990). The stability constants of the bivalent metal oxinates presented in Table 1 follow the Irving-Williams series. As can be seen in Table 1, the stability constants (as log K values) for Cd(II), Zn(II), and Pb(II) are 7.80, 8.56, and 9.02, respectively. Abollino and coworkers (1990) also observed that oxine exhibits a relatively low tendency to form oxinates with the alkaline earth metals metals, calcium, and magnesium. Its high selectivity for toxic metals, such as cadmium, lead, and zinc, to form metal oxinates is reflected by the stability constants presented in Table 1.

The selectivity of oxine for various metals is a significant factor in water and wastewater treatment applications. In water treatment applications, the concentration ranges of alkali metals such as sodium and potassium, and alkaline earth metals such as calcium and magnesium, are often in the few parts-per-million range, often exceeding the concentrations of heavy metals. The high selectivity for heavy metals, and insensitivity to alkaline earth and alkali metals at high concentrations, make oxine an ideal chelating agent. It is indeed important to note that oxinates formed with heavy metals are more stable than those formed with alkaline earth metals and alkali metals.

Adsorption of oxine on activated carbon

The sorption of oxine on carbon is an important factor for consideration in the preparation of a surface modified activated carbon adsorbent for metal removal. The research of Vogt (1948) clearly established that oxine was strongly adsorbed on activated carbon in the aqueous phase, as compared to other adsorbents including medicinal carbon, bone charcoal, granulated coal, and gas-mask carbon, as well as two other types of commercial carbons. Vogt further observed that the extent of oxine adsorption was dependent on the pH. The study showed that there was an insignificant reduction in oxine adsorption when the pH was lowered from 5.4 to 1.0, an important consideration regarding the regenerability of oxine-impregnated carbon. At an acidic pH of 3, the metal-oxine chelates have low stability, and the oxine-complex decomposes to liberate free metal ions. Under such circumstances, it is important that the oxine molecules do not leach out of the activated carbon particles. These results seem to indicate that oxine is irreversibly adsorbed on the activated carbon. Subsequent studies by Vanderborght and Van Grieken (1977) highlighted the irreversibility of oxine adsorption on activated carbon. These researchers showed that the adsorption of oxine by activated carbon was essentially constant in the pH range of 3 to 10. They suggested that the N and OH groups of the oxine molecule did not act as adsorption centers, and that adsorption was merely attributable to the pi-orbital overlap interaction of the two aromatic centers of oxine with the carbon surface. They further observed that, as the N and OH groups appeared not to be responsible for the interactions with the carbon surface, an analogous pH dependence could be expected for the adsorption of the metal oxinates as well.

It is also reported that activated carbon surfaces manifest the behavior of diprotic acids after the hydration of the surface functional groups of the type $> CO_x$ (Jevtitch and Bhattacharya, 1983; Stumm and Morgan, 1996). The oxine adsorption on activated carbon could be significantly influenced by the presence of certain surface functional groups on carbon including the carbonyl, hydroxyl, phenolic hydroxyl, lactones, quinones, carboxyl, acid anhydrides, and cyclic peroxides (Boehm, 1994). The type of functional groups present depends on the carbon source, and the activation process, although most activated carbons have similar functional groups contributing to surface interactions. The sorption of oxine on activated carbon can be considered as an electron-donor-acceptor interaction. While reversible physical sorption could arise merely through van der Waals forces without any contribution from functional groups, irreversible chemisorption could be attributed to interactions between the hydroxyl group of oxine and the phenolic and carboxylic groups of activated carbon. The interactive mechanism between carbon surface and oxine moiety would be the formation of hydrogen bonds. It appears that oxine adsorption on activated carbon is irreversible, and could possibly depend on factors such as charge distribution on the carbon surface, pH of the system, and the surface functional group of the carbon.

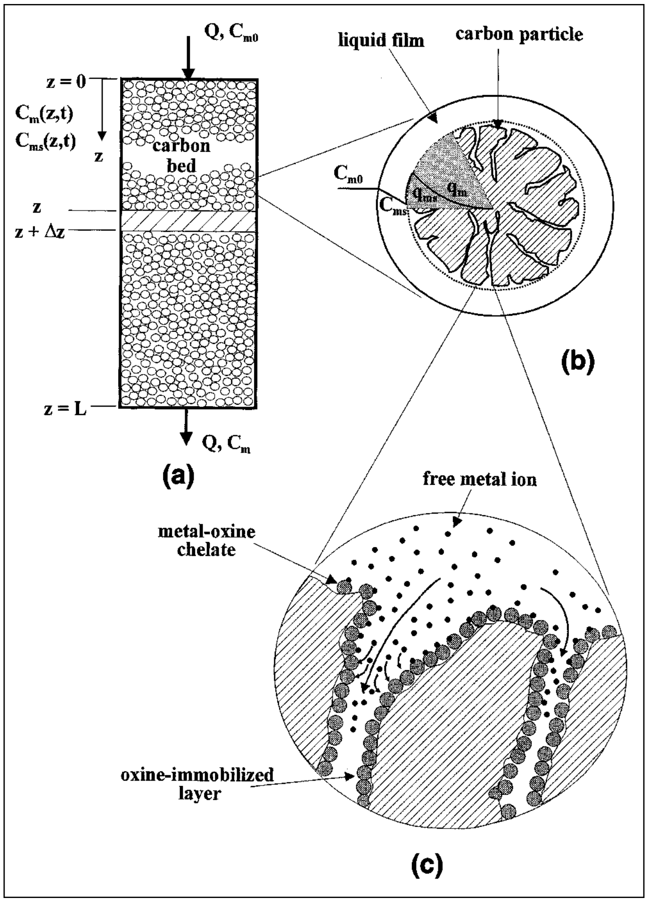

Figure 1. Adsorption of metal ions on oxine-immobilized carbon.

(a) Fixed-bed adsorption; (b) film and intraparticle diffusion of metal ions; (c) chelation of metal ions.

Sorption of divalent metal ions on oxine-impregnated carbon

The sorption of metal ions on oxine-impregnated carbon essentially consists of the following steps as shown in Figure 1: (1) transport of metal ions from the bulk solution to the carbon surface through a liquid film; (2) intra-particle diffusion of metal ions into the oxine-impregnated carbon; and (3) chelation of metal ions with the oxine moiety adsorbed on the carbon surface.

The first step involves the mass transfer of the metal ions from the bulk fluid to the liquid film surrounding the adsorbent particle. This phenomenon is dependent on the free liquid diffusivity of the metal ions, and the fluid dynamic regime in the vicinity of the particle. The second step involves the penetration of the metal ions through the pores of the adsorbent seeking sites for attachment, most likely the functional groups on the oxine moiety that can result in the formation of a ligand or complex between the chelating agent and the metal ion. Some important interactions might occur in this stage during the ligand formation. The sorption of the oxine molecules on the activated carbon sites is dependent on the pH and the surface functional groups of the activated carbon that can bind with those of the oxine moiety. The intraparticle diffusion of the metal ions could be a combination of the pore diffusion and surface diffusion mechanisms (Crittenden et al., 1986; Hutzler et al., 1986; Hand et al., 1997). It is important to determine whether pore diffusion or surface diffusion or both mechanisms are important in describing the intraparticle transport. It is quite possible that the metal ions diffuse through the pores or diffuse along the surface of the macropores and then micropores of the carbon particle as shown in Figure 1. It is hypothesized at this stage that as the free metal ions enter the pores, they are attracted by the oxine species to form an organo-metallic bond. This is the third step in the entire process, and the oxine-metal chelate formation is an instantaneous reaction. After this chelant-metal complex is formed and site on the sorbed oxine moiety is occupied, the next metal ion would further diffuse into the pores by a combination of surface diffusion and pore diffusion mechanisms, and eventually occupy the next available oxine site. This process could continue until all the oxine sites within the macropores and micropores of the carbon are exhausted. It must be noted that the second and third steps often occur simultaneously as the oxine-metal chelate is formed on the adsorbent surface. It is important to note that sorption of metal ions on the chelant-impregnated adsorbent is not regarded as the sorption of the charged metal ion on a charged adsorbent surface, but conceptually viewed as the binding of the metal ions with the functional groups of the chelating agent presorbed on the adsorbent. Thus, the movement of the metal ions into the adsorbent surface prior to chelation is essentially a mass-transfer process, and not a physical phenomenon.

Modeling of Fixed-Bed Adsorbers

Modeling sorption of metal ions on a chelant-impregnated sorbent

The model formulation is based on the concept that the sorption process is the chelation of the metal ion with oxine preadsorbed on activated carbon particles. The adsorption on SMAC can be viewed as a chelation of metal ions with a chelating agent immobilized on an adsorbent. The sorption is not viewed as an ion adsorption on a charged surface, but is considered as the bonding of the metal to the functional groups of the chelating agent presorbed on the adsorbent. Therefore, the stability of the metal-oxine chelate or the oxinate is important with regard to the overall uptake of the metal. A fundamental assumption is that the metal-oxine chelate is stable, and most of the metal exists in the chelated form.

The metal uptake involves mass transfer of the metal ions from the liquid phase into adsorbent phase through the liquid film surrounding the adsorbent particle, followed by diffusion of the metal ions through the pore fluid and the SMAC surface, and chelation of the metal ion with the sorbed oxine moiety, as discussed in the previous section. Thus, in this dual resistance, model pore diffusion and surface diffusion might be operative in the sorption of the metal-chelate complex in the pores of adsorbent particles. Pore diffusion is dominated by the free liquid diffusivity of the species as it occurs due to the movement of the molecules or ions through the pore liquid of the adsorbent. Surface diffusion, on the other hand, is controlled by the availability of surface area within the pores of the adsorbent. It is a general notion that surface diffusion occurs by the hopping of molecules or ionic species (as in this case) between adsorption sites. In the sorption of metal ions on a surface-modified adsorbent, it would be appropriate to observe whether pore diffusion or surface diffusion would be more important. It is quite possible that either film diffusion transport or adsorbent particle diffusion transport of the metal ions will be the rate-limiting step, as chelation reactions between the metal ion and the oxine moiety generally exhibit relatively fast kinetics.

Pore and surface diffusion model

The pore-surface diffusion model for the sorption of metal ions on chelant-impregnated adsorbent is conceptualized based on the following assumptions:

- The uptake of the metal ions by the surface-modified adsorbent is controlled by a two-step mass-transport mechanism: external liquid-film mass transfer of metal ions from the bulk liquid phase to the adsorbent surface, and intraparticle solid-phase diffusion which essentially involves pore diffusion and surface diffusion.
- The activated carbon particle is homogeneous with respect to shape, porosity, composition, and density; it is spherical in shape and uniform in size.
- The sorption of oxine on activated carbon particles is irreversible.
- The axial dispersion of substrate in liquid phase is important for stationary bed reactors.

The adsorption of metal ions on oxine-impregnated carbon is shown in Figure 1. The material balance for metal ions in a fixed-bed adsorber represented by the advection-diffusion phenomena coupled with adsorption can be written in general form as follows

$$\frac{\partial C_m}{\partial t} = \nabla \cdot (D_m \cdot \nabla C_m) - \boldsymbol{v} \cdot \nabla C_m - r_{\text{ad}} \tag{1}$$

In the above partial differential equation written in the tensor form, D_m is the diffusion tensor for the metal ion through the adsorber bed, $\boldsymbol{v}$ is the velocity vector representing the average linear fluid velocity, C_m represents the metal ion concentration in the adsorbent reactor at any given position and time, and r_{ad} represents the rate of metal ion removal from the liquid phase by chelation with the oxine adsorbed onto the carbon particles. It would be appropriate to assume a cylindrical coordinate system with the axial direction denoted by the z coordinate, and the radius of the adsorber represented by the radial coordinates. The Laplacian and gradient operators denote the generalized three-dimensional (3-D) case, wherein $\nabla \cdot (D_m \cdot \nabla C_m)$ denotes the diffusion term, $\boldsymbol{v} \cdot \nabla C_m$ represents the advection flux term, while r_{ad} represents the adsorption term. The above equation can be appropriately modified for the 1-D case, wherein the flow is in the axial direction. Neglecting the diffusivity of the metal in the radial direction, the above tensor equation can be written as follows

$$\frac{\partial C_m}{\partial t} = D_{zm} \nabla^2 C_m - v_z \frac{\partial C_m}{\partial z} - \frac{3k_{fm}(1-\epsilon)}{R_p \epsilon} [C_m - C_{ms}] \tag{2}$$

where D_{zm} is the axial dispersion coefficient of the metal ion within the adsorber ($\mathrm{cm \cdot s^{-2}}$) and υ_z the bulk fluid velocity in the axial direction ($\mathrm{cm \cdot s^{-1}}$). The adsorption term r_{ad} represents the rate of metal ions uptake by chelation with presorbed oxine ($\mathrm{mg \cdot L^{-1} s^{-1}}$), and is controlled by the film transfer coefficient k_{fm} for the metal ions ($\mathrm{cm \cdot s^{-1}}$). In the above equation, R_p is the adsorbent particle radius (cm), ϵ is the bed porosity (dimensionless), and C_{ms} is the metal ion concentration at the adsorbent-liquid film interface ($\mathrm{mg \cdot L^{-1}}$).

The initial and boundary conditions are based on the assumptions that at time $t = 0$ there is no metal ion in the liquid phase within the adsorber reactor, and that the concentration gradient is zero at the adsorber entrance. Therefore, the initial and boundary conditions can be represented as follows

$$C_m(z, t = 0) = 0,$$

$$C_m(z = 0^+, t) = C_{m0} + \left(\frac{D_z}{V_z}\right) \frac{\partial C_m(z = 0^+, t)}{\partial z}$$

and

$$\frac{\partial C_m(z = L^-, t)}{\partial t} = 0 \tag{3}$$

where C_{m0} is the influent concentration of metal ions ($\mathrm{mg \cdot L^{-1}}$).

The general partial differential equation representing the pore and surface diffusion model can be written as follows

$$\frac{\partial}{\partial t}\left[q_m + \frac{\theta_p}{\rho_a} C_{mp}\right] = \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 D_{sm} \frac{\partial q_m}{\partial r} + r^2 \frac{\theta_p}{\rho_a} D_{pm} \frac{\partial C_{mp}}{\partial r}\right] \tag{4}$$

In the above equation, θ_p represents the intrapore void space in the carbon particle (dimensionless), q_m denotes the solid-phase concentration of the metal ion on SMAC ($\mathrm{mg \cdot g^{-1}}$), and ρ_a is the adsorbent density ($\mathrm{g \cdot cm^{-3}}$). The initial condition for the above partial differential equation is the following

At $t = 0$, for $0 \le r \le R_p$ and $0 \le z \le L$,

$$\left[q_m + \frac{\theta_p}{\rho_a} C_{mp}\right] = 0 \tag{5}$$

The boundary conditions for the adsorbent particle within the reactor can be written as

At $r = 0$, for all t and $0 \le z \le L$,

$$\frac{\partial}{\partial t}\left[q_m + \frac{\theta_p}{\rho_a} C_{mp}\right] = 0 \tag{6}$$

The boundary condition for the adsorbent particle balancing the temporal variation of the metal ions within the adsorbent and pore liquid with the metal ion flux through the liquid film surrounding the adsorbent is the following

$$\frac{\partial}{\partial t} \int_0^{R_p} \left[q_m + \frac{\theta_p}{\rho_a} C_{ms}\right] r^2 dr = \frac{k_{fm} R_p^2}{\rho_a} [C_m - C_{ms}] \tag{7}$$

In the above partial differential equation, as well as in the initial and boundary conditions, θ_p is the intraparticle volume fraction for the adsorbent phase, r is the radial position within the spherical particle (cm), ρ_s is the solid bulk density of the adsorbent, D_{pm} is the pore diffusion coefficient of the metal ion ($\mathrm{cm \cdot s^{-2}}$), D_{sm} is the surface diffusion coefficient of the metal ion into the adsorbent particle ($\mathrm{cm \cdot s^{-2}}$), and k_{fm} is the mass-transfer coefficient for the metal ions through liquid film at the solid-liquid interface ($\mathrm{cm \cdot s^{-1}}$).

It can be assumed that equilibrium exists between the adsorbent and the liquid phases with respect to the sorption of the chelate. The adsorption of chelating agent on activated carbon can be assumed irreversible during the operation of the adsorber, although the spent adsorbent can be processed under low pH conditions for adsorbent regeneration.

The adsorption equilibrium for the metal-chelate complex is described by the Freundlich equation, according to which

$$q_m = K_F C_{ms}^n(z, t) \tag{8}$$

where K_F and n denote the Freundlich capacity parameter $(\mathrm{mg \cdot g^{-1}})(\mathrm{mg \cdot L^{-1}})^{-n}$ and intensity parameter (dimensionless), respectively. Mass balance must be established as the rate of accumulation of the metal ions within the adsorbent particle is balanced by the rate of substrate transport of metal ions from the bulk liquid phase through the liquid film. This relationship can be represented by the partial integro-differential equation

$$\frac{\partial}{\partial t} \int_0^{R_p} 4\pi r^2 q_m dr = \frac{k_{fm} A_p R_p^3}{3 V_c \rho_a} (C_m - C_{ms}) \tag{9}$$

The adsorption equilibrium of the substrate onto the adsorbent is represented by the Freundlich isotherm model. The estimation of pore diffusivity D_{pm} for the metal ions is based on the free liquid diffusivity D_{lm} ($\mathrm{cm \cdot s^{-2}}$), intraparticle porosity θ_p, and the tortuosity factor τ (dimensionless), adopting the formula employed by Crittenden and coworkers for soil particles (Crittenden et al., 1986; Hutzler et al., 1986) and for granular activated carbon particles (Hand et al., 1987)

$$D_{pm} = \frac{D_{lm}}{\theta_p \tau} \tag{10}$$

The free liquid diffusivity can be estimated using the following correlation adapted from Perry and Green (1984)

$$D_{lm} = \frac{RT}{F^2 Z_1} \left(\frac{\nu_1 + \nu_2}{\nu_1}\right) \left(\frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}\right) \tag{11}$$

where F is the Faraday's constant [96489 coul$\cdot$(g$\cdot$equiv.)$^{-1}$],

R is the gas constant, T is the absolute temperature (K), Z_1 is the valency of the metal ion, ν_1 and ν_2 are the numbers of the metal ions and the corresponding anions, respectively, in one molecule of the metallic salt, and λ_1 and λ_2 are the limiting equivalent conductances of the metal ion and the corresponding anions, respectively (mho·equiv^{-1}). The surface diffusion coefficient D_{sm} and the batch reactor film transfer coefficient k_{fbm} (cm·s^{-1}) is estimated from the adsorption rate data obtained from completely mixed batch reactor studies. The adsorption rate data are fitted with the batch reactor model simulation results to estimate these mass-transfer parameters (Kim and Pirbazari, 1989). It must be noted that the batch reactor film-transfer coefficient will provide only an estimate of the adsorber column film-transfer coefficient k_{fcm}, which is referred to as k_{fm} in the above adsorber equations. However, the least-square curve-fitting techniques on the batch reactor data can provide accurate determinations for the surface diffusion coefficient.

The adsorber column film-transfer coefficient for the metal ions k_{fcm} is estimated from different correlations relating the Sherwood number Sh (dimensionless) to a function of the Reynolds number Re (dimensionless) and the Schmidt number Sc (dimensionless). In these studies, the correlation of Williamson et al. (1963) was found appropriate for evaluating the adsorber column film transfer coefficient

$$Sh = 2.4\,\epsilon\, Re^{0.34} Sc^{0.42} \quad \text{for} \quad 0.08 < Re < 125 \quad \text{and} \quad 150 < Sc < 1{,}300 \tag{12}$$

The Reynolds, Schmidt and Sherwood numbers are defined by the relations

$$Re = d_p v_z \rho_1/(\epsilon\mu), \quad Sc = \mu/(\rho_1 D_{lm}) \quad \text{and } Sh = d_p k_{fcm}/D_{lm} \tag{13}$$

where d_p represents the diameter (cm) of the adsorbent particle, D_{lm} represents the free liquid diffusivity of the metal ions, ρ_1 denotes the density of the fluid (g·cm^{-3}), μ denotes the viscosity of the fluid (g·cm^{-1}·s^{-1}), and D_{lm} is the free liquid diffusivity of the metal ion.

Numerical technique for solving the model equations

The system of differential equations along with initial and boundary conditions should be nondimensionalized before being solved numerically. In this work, a hybrid numerical technique combining finite difference and orthogonal collocation methods was used for solving the adsorber model. This method was employed successfully by Kim and Pirbazari (1989) for modeling bioactive fixed-bed and fluidized-bed adsorbers. This technique was found numerically stable, consistent, and efficient in comparison to finite difference methods. Subsequently, Pirbazari and coworkers (Ravindran et al., 1996, 1997) observed that this technique required less computational time than the pure orthogonal collocation technique for solving problems involving surface diffusion, film transfer, biofilm diffusion, and biofilm degradation of the contaminants. In this study, a similar hybrid technique was employed for solving the differential equations pertaining to the pore-surface diffusion adsorption and chelation model.

The orthogonal collocation method was used for solving differential equations with appropriate boundary conditions corresponding to intraparticle diffusion. This technique transformed the partial differential equations into ordinary differential equations which could be easily numerically integrated using the GEAR software, theoretical aspects of which are discussed by Gear (1971a,b). The orthogonal collocation grid points were used for the adsorber liquid-phase transport equations. The choice of grid points in the axial and radial directions are based on the roots of shifted asymmetric Legendre polynomials. The theoretical aspects regarding the application of Legendre polynomials as trial functions with orthogonality properties are discussed by Finlayson (1972, 1980). The cylindrical shells in radial direction are denoted by curvilinear and parallel cylindrical planes, while the axial grids are represented by parallel planes, orthogonal to the axial direction (z direction).

The Crank-Nicholson grid was used for obtaining finite-difference approximations to the advection-diffusion equation. The rationale for this hybridization scheme was that pore diffusion and surface diffusion were relatively slow processes as compared to advection and axial dispersion. Finite difference approximations seemed appropriate, because the concentrations along the adsorber bed were expected to vary sharply, especially in the transition from the saturated zone to the mass-transfer zone where the sorption occurs. On the other hand, concentration profiles in adsorbent pore volume and the adsorbent surface are comparatively smooth, and could be approximated by larger grid intervals using a relatively sparse collocation mesh, resulting in a saving of computing time.

Experimental Techniques

Materials

Activated Carbon. The activated carbon used in these studies was granular type Filtrasorb 400 (Calgon Corporation, Pittsburgh, PA), obtained from bituminous coal. Each batch of granular carbon was ground and sieved for size classification through Tyler meshes. The desired size fraction of carbon was then washed with organic free water (OFW) and dried in an oven at 120°C. The carbon was subsequently cooled in a desiccator and stored in air-tight glass containers prior to use. The size range of activated carbon used for adsorption equilibrium studies was 100/200 mesh, while those used in adsorption rate studies and adsorber column experiments were 40/50 mesh.

For these studies, the surface-modified adsorbent was prepared by immobilizing oxine on the granular activated carbon. In each case the adsorbent of the appropriate particle size was equilibrated for a duration of 24 h in completely mixed batch reactors with ozine solution prepared in OFW. Subsequently, the oxine-impregnated activated carbon was employed in various adsorption experiments described in this section.

Organic Free Water. The organic free water employed in the experiments was prepared by passing de-ionized distilled water through a granular activated carbon bed at an empty bed contact time (EBCT) of over 15 min.

Metal Ions Solutions. In order to prepare the metal ion solutions for various adsorption experiments, organic free water was employed. Different buffer systems were employed for the three metal ions of interest: an alkaline borate buffer for cadmium solutions at pH 9; a phosphate buffer for lead solutions at pH 6; and, a phthalate buffer for zinc solutions at pH 5.8.

Divalent Metal Standards. The standards for cadmium, lead, and zinc were prepared from spectrometric grade solutions of those ions (Fisher Scientific Co., Tustin, CA).

Oxine and Other Chemicals. The 8-hydroxyquinoline (oxine) employed in these studies was obtained from Matheson, Coleman and Bell Chemical Co. (Cincinnati, OH). Other chemicals such as hydrochloric acid, sodium hydroxide, sodium borate, sodium biphosphate, and potassium biphthalate that were used were of Baker analyzed reagent grade (J.T. Baker and Co., Phillipsburg, NJ).

Experimental methodologies

Analytical Techniques. All quantitative determinations of samples for cadmium, lead, and zinc were conducted using atomic absorption spectrometry. Samples containing metal concentrations in excess of 1 mg/L were analyzed using a Perkin Elmer Model 305 atomic absorption spectrophotometer (Perkin Elmer Corp., Norwalk, CT), equipped with a standard flame nebulizer. For samples containing low metal concentrations less than 1 mg/L, a Perkin Elmer Model 460 atomic absorption spectrophotometer equipped with a flameless graphite furnace was employed. The analyses for these metals followed the procedures described in Standard Methods (1995).

The analyses for 8-hydroxyquinoline (oxine) in solution was based on the Koppeschar technique involving the titration of phenols, as described by Kolthoff et al. (1969). In this technique, the analyte solution is acidified in 3-M hydrochloric acid and standard potassium bromate solution is added dropwise until excess bromate is present, as indicated by the yellow color of the dilute bromine formed. Potassium iodide crystals are then added and the liberated iodine is determined by titration with sodium thiosulfate solution as outlined in Standard Methods (1995). The equivalents of iodine in solution is the same as the equivalents of excess potassium bromate. Hence, the equivalents of oxine present can be determined by determining the difference between the total equivalents of bromate added and the excess equivalents of bromate present.

Adsorption Equilibrium Studies. Adsorption isotherm tests were conducted using the completely mixed batch reactor technique for the determination of the equilibrium parameters (Pirbazari et al., 1992, 1993). These experiments were conducted in 250-mL glass reactors to which accurately weighed 100/200 mesh activated carbon was added, before being filled with 100 mL of the adsorbate solution with the desired concentration of heavy metal (cadmium, lead, or zinc). The adsorbate solution was buffered in OFW to the desired pH conditions, as previously discussed. The reactors were then carefully sealed with Teflon screw-caps and agitated in a rotary tumbler for an equilibration time of two days. The samples were then withdrawn from the reactor using a volumetric syringe and analyzed for metal concentration by atomic absorption spectrometry.

Adsorption Rate Studies. Adsorption rate studies were conducted in 4-L completely mixed batch reactors made of glass, equipped with a propeller-type mixer. The 3-L of a buffered solution of adsorbate containing a known heavy metal concentration was transferred into the reactor. Appropriate amounts of 40/50 mesh activated carbon (with or without impregnated oxine) was added to the reactor contents. The reactor was stirred at sufficient speed to maintain the contents completely mixed so that the carbon particles were suspended throughout the entire reactor. Samples were withdrawn at regular intervals of a few hours and analyzed by atomic absorption spectrometry.

Adsorber Studies. Fixed-bed reactor studies were conducted to determine the dynamics of the adsorbers for the heavy metals of interest under various conditions. These experiments were conducted in glass columns of length 30 cm and of diameter 1 cm. The adsorbers were charged with appropriate amounts of 40/50 mesh activated carbon (impregnated with oxine). The carbon bed was supported by glass beads, which in turn was maintained in position by a small bed of glass wool. The actual depth of adsorber bed varied with the heavy metal and the initial concentration of the metal in the feed solution. Nevertheless, the adsorber diameter-to-depth ratio was maintained greater than 1/20 to minimize wall effects. The feed solutions were prepared in large 20-L glass containers that served as feed reservoirs. The feed reservoir was equipped with a magnetic stirrer to maintain the metal solution agitated. The feed solution was pumped into the adsorber column at the desired flow rate by means of a peristaltic pump. The adsorber effluent was periodically sampled and analyzed for the metal of interest by atomic absorption spectrometry.

Results and Discussion

Adsorption equilibria

The objective of conducting adsorption equilibrium studies in this research was threefold: (i) comparison of the carbon adsorption capacities with and without oxine impregnation for cadmium, lead, and zinc ions; (ii) *a-priori* estimation of metal ion sorption on the two adsorbents over a range of liquid-phase concentrations of practical interest; (iii) evaluation of the isotherm parameters for predictive modeling and design of real adsorbers. In this study the Freundlich model was found appropriate for evaluating the equilibrium relationships, and, therefore, the Freundlich capacity and intensity constants were incorporated as equilibrium parameters into the adsorber model for predicting the dynamics of fixed-bed adsorbers. These experiments were conducted at optimal conditions for maintaining stable oxine-metal chelates for each ion. The equilibrium tests employed a strategy in which the initial metal ion concentration was maintained constant, and the adsorbent concentration was varied in each isotherm reactor. The results of adsorption equilibrium studies for cadmium, lead, and zinc ions on oxine-impregnated carbon and virgin carbon are presented in Figures 2, 3, and 4, respectively, in which the linear regression fit of the data is represented by the solid line. Comparisons of the results in-

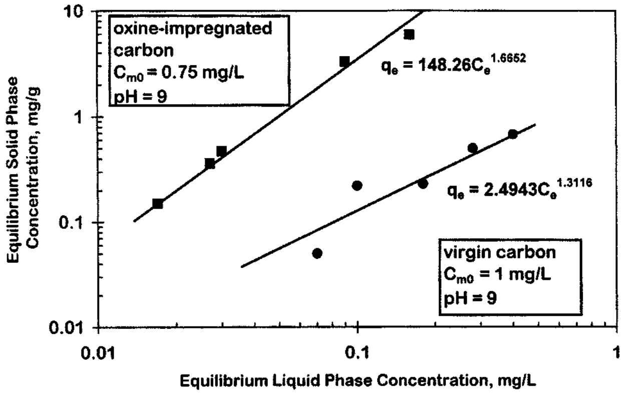

Figure 2. Experimental data and Freundlich isotherm model for adsorption of cadmium on virgin and oxine-impregnated carbon.

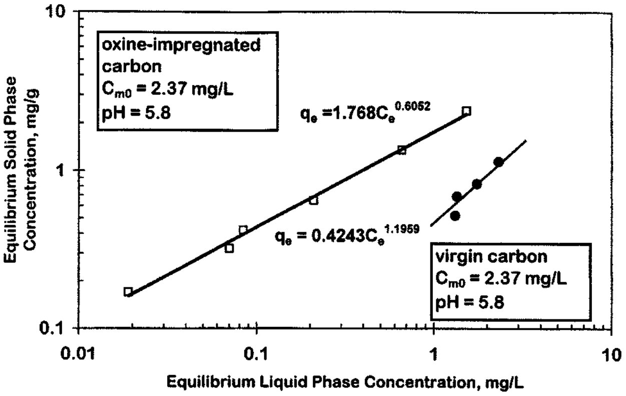

Figure 4. Experimental data and Freundlich isotherm model for adsorption and zinc on virgin and oxine-impregnated carbon.

dicate that adsorption capacities of oxine-impregnated carbon are greater than those of virgin carbon for the three metal ions by an order of magnitude. Additionally, the isotherms for cadmium and zinc (Figures 2 and 4, respectively) show that the residual metal ion concentrations were significantly lower for oxine-impregnated carbon than for virgin carbon, indicating that significantly higher removals could be achieved by the former at trace levels.

The Freundlich isotherms also present qualitative information on the adsorption of cadmium, lead and zinc on oxine-impregnated carbon. It can be seen from the Figures 2 through 4 that the Freundlich intensity constants n are greater than unity for cadmium and lead, but less than unity for zinc. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between the adsorbate species (Adamson, 1976; Voice and Weber, 1983). In the case of cadmium and zinc ions ($n > 1$), the adsorbent shows an increasing tendency for sorption with increasing solid-phase concentration. This could be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the adsorbate ions such as van der Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion, and, consequently, the metal ions manifest a stronger tendency to bind to the adsorbent sites (Adamson, 1976). However, in the case of lead ions ($n < 1$), the adsorbent manifests a decreasing tendency for sorption with increasing solid-phase concentration. This follows the general rule of adsorption, when the repulsive forces between the adsorbate ions increase more rapidly than the attractive forces are more adsorbent sites are covered, and, eventually, the adsorbate ions manifest a weaker tendency to bind to the adsorbent sites (Adamson, 1976). Nevertheless, more detailed studies are needed to arrive at definite conclusions regarding the sorption behavior of divalent metal ions on oxine-impregnated carbon.

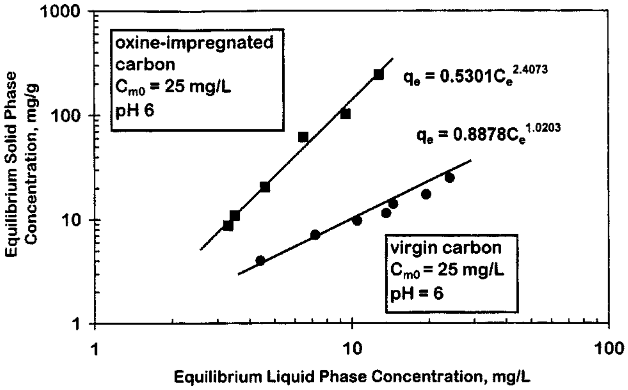

Figure 3. Experimental data and Freundlich isotherm model for adsorption of lead on virgin and oxine-impregnated carbon.

Adsorption kinetics

The purpose of the adsorption rate studies was to determine the mass-transfer parameters for the pore-surface diffusion model, namely, the surface diffusivity D_{sm}, and the film-transfer coefficient k_{fm}. The rate data were employed to determine these mass-transfer parameters using the model for batch reactor configuration using a two-parameter search regression procedure (Pirbazari et al., 1991). Typical experimental data for adsorption kinetic study, and the model predictions obtained from the batch reactor pore-surface diffusion model corresponding to the adsorption of cadmium ions are shown in Figure 5. A two-parameter search algorithm was employed for evaluating the mass-transfer parameters. Similar model simulations and mass-transfer parameter evaluations were conducted for the sorption kinetics of lead and zinc ions on oxine-impregnated carbon. The surface diffusivity D_{sm} manifested variability for different metal ions: 5×10^{-10} cm²/s for cadmium, 1.0×10^{-10} cm²/s for lead, and 8.0×10^{-11} cm²/s for zinc. The column film-transfer coefficients k_{fmc} were estimated using the correlation of Williamson et al. (1963). These values were slightly different for the three metal ions as follows: 6.17×10^{-3} cm/s for cadmium, 6.72×10^{-3} cm/s for lead, and 6.88×10^{-3} for zinc. These values were employed in the mathematical model for predicting the adsorber dynamics.

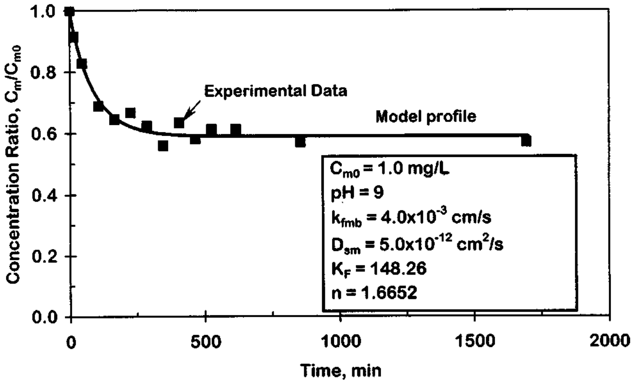

Figure 5. Experimental rate data and predicted model profile for adsorption of cadmium on oxine-impregnated carbon.

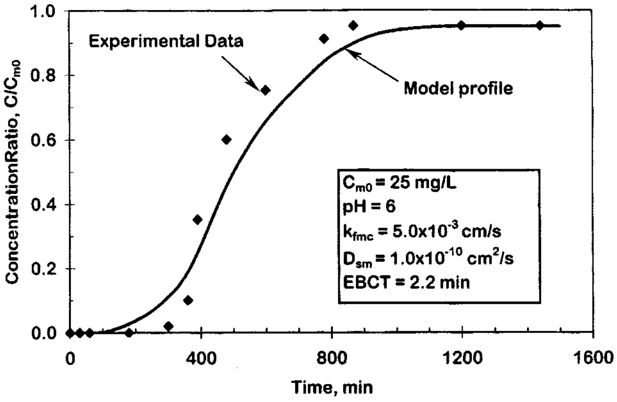

Figure 7. Experimental adsorber column data and predicted model profile for adsorption of lead on oxine-impregnated carbon.

Adsorber column experiments

The purpose of adsorber column studies was to acquire experimental data to simulate the uptake of metal ions in real adsorbers, and to validate the predictive capability of the adsorber model. The results of these experiments for cadmium, lead, and zinc are presented in Figures 6, 7 and 8, respectively, wherein the nondimensionalized effluent concentration (effluent-to-influent concentration ratio) is plotted as a function of adsorber operation time to obtain the breakthrough profiles. The predictions of adsorber dynamics using the pore and surface diffusion model are also provided to facilitate an evaluation on the predictive capability of the model (discussed in a later section). Table 2 presents the adsorber characteristics including adsorber dimensions and adsorbent properties, as well as the parameters employed in the pore-surface diffusion model.

The adsorber data for cadmium ions at an influent concentration of 0.93 mg/L, pH of 9.0, and an EBCT of 4.4 min are presented in Figure 6. It is evident from the adsorber effluent data that the removal efficiency exceeded 95% even after 8,000 min of column operation, corresponding to a treatment of over 1,800 adsorber bed volumes of throughput. The adsorber data indicate that oxine-impregnated carbon can be effectively employed as adsorbent for eliminating cadmium ions from water at trace levels.

The adsorber data for lead ions corresponding to an influent concentration of 25 mg/L are shown in Figure 7. The results indicate that the lead concentration is below the detection limit for the first 320 min of adsorber operation, corresponding to 140 adsorber bed volumes of throughput. The effluent concentration after 320 min of operation corresponds to a lead removal efficiency of over 99.9%.

The adsorber data for zinc ions corresponding to an influent concentration of 3.7 mg/L are shown in Figure 8. It is evident that the effluent zinc concentrations are below detection limit during the first 100 min of adsorber operation, corresponding to a removal efficiency of nearly 100%. As the adsorbent becomes saturated, the concentration ratio reaches 0.85 after 1,200 min, corresponding to an overall adsorber throughput of 108 bed volumes. The adsorber experiences breakthrough after 120 min according to the predicted profile.

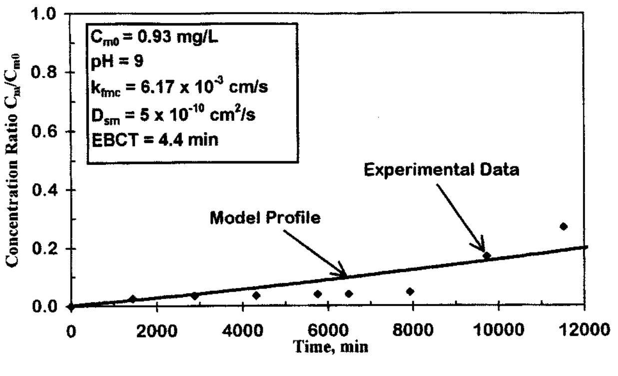

Figure 6. Experimental adsorber column data and predicted model profile for adsorption of cadmium on oxine-impregnated carbon.

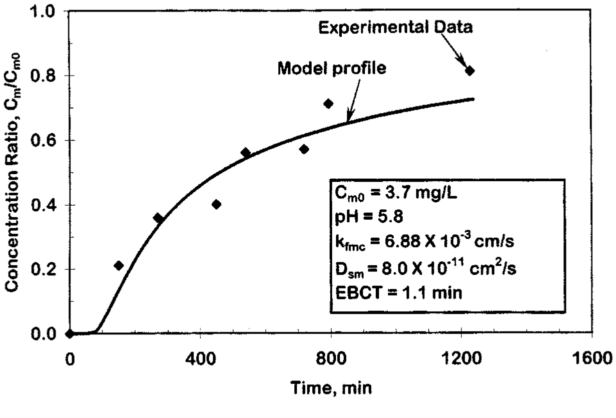

Figure 8. Experimental adsorber column data and predicted model profile for adsorption of zinc on oxine-impregnated carbon.

Table 2. Parameters for the Pore and Surface Diffusion Model for Chelation and Adsorption

Parameter	Units	Cadmium	Lead	Zinc
Adsorber Column Characteristics				
Column dia.	cm	1.0	1.0	1.0
Column length, L	cm	17.8	17.8	8.9
Carbon weight	g	6.4	6.4	3.2
Empty bed contact time	min	4.4	2.2	1.1
Adsorbent Property				
Particle diameter, d_p	cm	0.078	0.078	0.078
Influent Characteristics				
Influent model ion conc., C_{mo}	$mg \cdot L^{-1}$	0.93	25	3.7
Influent pH	None	9	6	5.8
Influent/effluent flow rate, Q	$mL \cdot min^{-1}$	3.2	6.4	6.4
Adsorption Equilibria				
Freundlich capacity const., K_F	$mg \cdot g^{-1}(mg \cdot L^{-1})^n$	148.26	0.5301	1.768
Freundlich intensity const., n	None	1.6652	2.4073	0.6052
Adsorption Kinetics				
Free liquid diffus., D_{lm}	$cm^2 \cdot s^{-1}$	1.21×10^{-5}	1.40×10^{-5}	1.19×10^{-5}
Surface diffusion coeff., D_{sm}	$cm^2 \cdot s^{-1}$	5×10^{-10}	1.0×10^{-10}	8×10^{-11}
Pore diffusion coeff., D_{pm}	$cm^2 \cdot s^{-1}$	1.21×10^{-5}	1.40×10^{-5}	1.19×10^{-5}
Column film transfer coeff., k_{fcm}	$cm \cdot s^{-1}$	6.17×10^{-3}	6.72×10^{-3}	6.88×10^{-3}
Axial dispersion coeff., D_{zm}	$cm^2 \cdot s^{-1}$	0.0218	0.0212	0.0329

Adsorbent regenerability

Adsorber regeneration experiments were conducted to determine the reversibility of the chelated metal ions and the desorption of oxine from the carbon surface under acidic conditions. The spent adsorbent from adsorber column studies discussed earlier were employed in these tests. These experiments employed hydrochloric acid solutions at concentrations ranging from approximately 10^{-2} to 2 mol/L. The regeneration studies employed the same mass of the adsorbent, flow regimes, and EBCT used in the adsorber experiments. Typical results of desorption column experiments for cadmium are presented in Figure 9. A comparison of the adsorbent capacity utilization from the column experiments for cadmium (Figure 6) with the amount of metal desorbed from the spent adsorbent (Figure 9) reflects a metal recovery of about 98–99%. Thus, the results showed that almost complete recovery of cadmium ions from the spent carbon could be accomplished. Furthermore, it must be noted that no detectable amount of oxine was observed in the regenerate solutions. These studies clearly demonstrated the regenerability of the oxine-impregnated carbon, and established the feasibility of this adsorbent for metal recovery from aqueous solutions at trace levels.

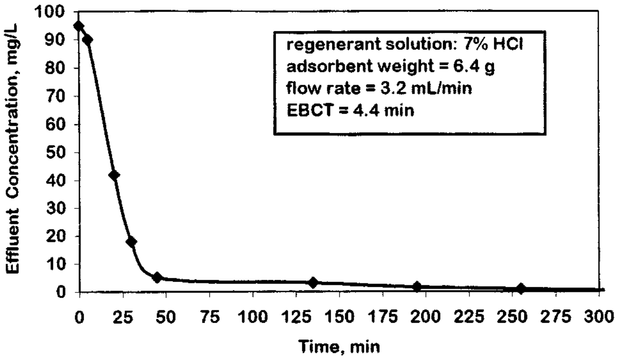

Figure 9. Effluent concentration profile for cadmium desorption during regeneration cycle.

Predictive capability of the adsorber model

The predictive capability of the pore-surface diffusion model for the chelation of metal ions on oxine-impregnated carbon was examined in this research. The model parameters employed for both models are presented in Table 2 for the three metal ions of interest, and these include the following: Freundlich adsorption equilibrium parameters, mass-transfer parameters, and reactor characteristics such as bed porosity, reactor residence time (represented by empty bed contact time), particle size, particle density, oxine concentration for carbon impregnation, and flow characteristics.

There is a certain element of empiricism in the modeling approaches describing the intraparticle diffusion phenomenon due to microporous and complex structure of activated carbon, and the nature of sorption of oxine on activated carbon. Nonetheless, it is important to determine whether pore diffusion or surface diffusion or both mechanisms play an important role. In order to investigate the relative importance of these mechanisms, the pore and surface diffusion model was implemented under three different scenarios. In the first case, both pore and surface diffusion coefficients were estimated for the metal ions and used as model inputs. In the second case, the pore diffusion coefficient alone was used, and the surface diffusion coefficient was set to zero. In the third case, the surface diffusion coefficient alone was employed, while the pore diffusion coefficient was set to zero. The results from the first and second cases showed no agreement with the experimental data. However, the model predictions obtained from the third case (only surface diffusion) were in excellent agreement with the experimental data, as evident from Figures 6, 7, and 8. These results indicate a reasonably good predictive capability of the model when sur-

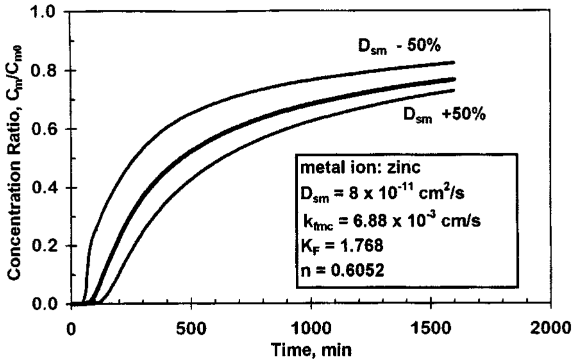

Figure 10. Sensitivity of the adsorber model breakthrough profile to the surface diffusion coefficient D_{sm}.

face diffusion was considered as the sole mechanism for the intraparticle transport of metal ions into the adsorbent. This is an important aspect that merits discussion. The modeling studies indicate that surface diffusion is the most significant mechanism associated with intraparticle diffusion of metal ions into the adsorbent, and subsequent chelation of these ions with oxine sorbed on the carbon surface. These studies appear to indicate that the transport of the metal ions within the adsorbent particle, and subsequent chelation with oxine molecules is a process mainly controlled by the surface diffusion mechanism.

Model sensitivity studies

The objective of sensitivity analyses was twofold: (i) to obtain a qualitative appreciation of the influence of various parameters on the overall reactor dynamics of fixed-bed adsorbers employing oxine-impregnated carbon; (ii) to examine the level of accuracy required for the estimation of each parameter for adsorber modeling. The parameters investigated were the following: the Freundlich capacity constant K_F; the Freundlich intensity constant n; the surface diffusion coefficient D_{sm}; the column film-transfer coefficient k_{fcm}; the axial dispersion coefficient D_{zm}. Typical results of adsorber sensitivity studies for zinc are presented in Figures 10 through 12.

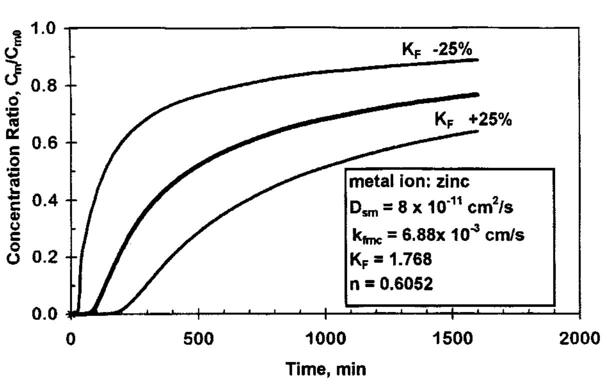

Figure 11. Sensitivity of the adsorber model breakthrough profile to the Freundlich capacity constant K_F.

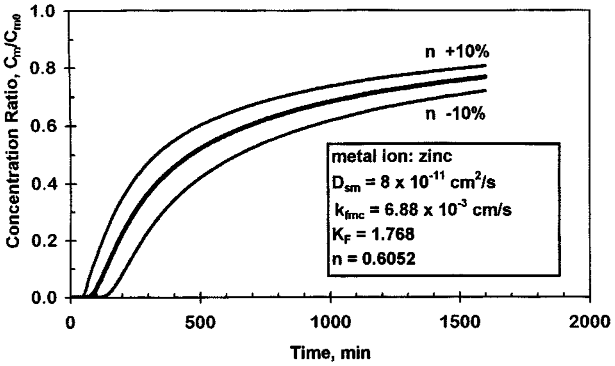

Figure 12. Sensitivity of the adsorber model breakthrough profile to the Freundlich intensity constant *n*.

The changes in the adsorber profiles with respect to an increase and decrease of 50% in the surface diffusion coefficient D_{sm} (Figure 10) clearly indicate that the model is very sensitive to this parameter, confirming that surface diffusion is an important phenomenon in the adsorption and chelation process. Similarly, the results of sensitivity studies for the Freundlich isotherm constants K_F and n depicted in Figures 11 and 12, respectively, indicate high sensitivities to variations in these parameters. Sensitivity studies were also conducted for variations in the column film-transfer coefficient k_{fcm} and the axial dispersion coefficient D_{zm}. It was, however, observed that the adsorber dynamics was relatively insensitive to these parameters. Qualitatively similar results were observed in the case of cadmium and lead ions as well.

Summary and Conclusions

- The adsorption equilibrium studies demonstrated that oxine-impregnated carbon manifested distinctly superior sorption properties as compared to virgin carbon for the removal of all the metal ions of interest, namely, cadmium, lead, and zinc, at trace levels.
- A comparison of the experimental data with the adsorber model predictions established a reasonably good predictive capability of the pore and surface diffusion model. The study further demonstrated that surface diffusivity was the predominant mechanism in the intraparticle transport of the metal ions.
- The results of sensitivity studies showed that the adsorber profiles were highly sensitive to the Freundlich isotherm parameters K_F and n, and the surface diffusion coefficient D_{sm}.
- Adsorber regeneration studies demonstrated that almost complete metal recovery could be achieved. Furthermore, there was no detectable desorption of oxine during the regeneration process.

Acknowledgment

This article is dedicated to the memory of Dr. Mario R. Stevens (our deceased coauthor). Part of this research was presented at the AIChE Annual Meeting in Chicago, November 1990. The remaining portion of this work was presented at the AIChE Annual Meeting in Los Angeles, November 1997.

Notation

C_m = metal ion concentration in the adsorbent reactor at any given position and time, mg·L^{-1}
C_{mp} = metal ion concentration within the adsorbent pore in equilibrium with adsorbent surface, mg·L^{-1}
k_{fbm} = mass-transfer or film-transfer coefficient in a batch reactor for metal ions through liquid film at solid-liquid interface, cm·s^{-1}
L = length of the adsorber bed, cm
ρ_s = solid bulk density of the adsorbent, g·cm^{-3}
q_{ms} = adsorbent phase concentration of metal ions at the adsorbent-liquid film interface in equilibrium with the liquid phase metal ion concentration C_{ms}, mg·g^{-1}
Q = adsorber flow rate, mL·min^{-1}
t = time coordinate, s, min, h
τ = tortuosity factor within the adsorber pores, dimensionless
z = coordinate along the axial direction for the adsorber, cm

Literature Cited

Abollino, O., E. Mentast, V. Porta, and C. Sarzanini, "Immobilized 8-Oxine Units on Different Solid Sorbents for the Uptake of Metal Traces," *Analy. Chemistry*, **62**, 21 (1990).

Adamson, A. W., *Physical Chemistry of Surfaces*, Wiley, New York (1976).

Boehm, H. P., "Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons," *Carbon*, **32**, 759 (1994).

Clifford, D., S. Subramonian, and T. J. Sorg, "Removing Dissolved Inorganic Contaminants from Water," *Environ. Sci. Technol.*, **20**, 1072 (1986).

Crittenden, J. C., N. J. Hutzler, D. G. Geyer, J. L. Oravitz, and G. Friedman, "Transport of Organic Compounds with Saturated Groundwater Flow: Model Development and Parameter Sensitivity," *Water Resour. Res.*, **22**, 271 (1986).

Dwyer, F. P., and D. P. Mellor, eds., *Chelating Agents and Their Metal Chelates*, Academic Press, New York (1964).

Finlayson, B. A., *The Method of Weighted Residuals and Variational Principles*, Academic Press, New York (1972).

Finlayson, B. A., *Nonlinear Analysis in Chemical Engineering*, McGraw-Hill, New York (1980).

Gear, C. W., "DIFSUB for Solution of Ordinary Differential Equations," *Comm. of Association of Computing Machinery*, **14**, 185 (1971a).

Gear, C. W., "The Automatic Integration of Ordinary Differential Equation," *Comm. of Association of Computing Machinery*, **14**, 176 (1971b).

Hand, D. W., J. C. Crittenden, D. R. Hokanson, and J. L. Bulloch, "Predicting the Performance of Fixed-Bed Granular Activated Carbon Adsorbers," *Water Sci. and Technol.*, **35**, 235 (1997).

Hutzler, N. J., J. C. Crittenden, J. S. Gierke, and A. Johnson, "Transport of Organic Compounds with Saturated Groundwater Flow: Experimental Results," *Water Resour. Res.*, **22**, 285 (1986).

Jevtitch, M. M., and D. Bhattacharya, "Separation of Heavy Metals Chelates by Activated Carbon: Effects of Surface and Species Charge," *Chem. Eng. Comm.*, **23**, 191 (1983).

Kim, S. H., and M. Pirbazari, "Bioactive Adsorber Model for Industrial Wastewater Treatment," *J. Environ. Eng.*, **115**, 1235 (1989).

Kolthoff, I. M., E. B. Sandell, E. J. Meehan, and S. Bruckstein, *Quantitative Chemical Analysis*, 4th ed., Macmillan, New York (1969).

Motojima, K., E. Tachikawa, H. Kamiyama, and T. Imahashi, "Removal of Radiocobalt in Waste Water by Activated Charcoal Using Oxine as a Chelating Agent," *Annals of Nucl. Energy*, **5**, 5 (1978).

Motojima, K., E. Tachikawa, and H. Kamiyama, "Elimination of Manganese-54 in Waste Water by Oxine-Impregnated Carbon," *J. of Nucl. Sci. and Technol.*, **16**, 356 (1979a).

Motojima, K., E. Tachikawa, and H. Kamiyama, "Removal of Radiocobalt Ion in Waste Water by Oxine-Impregnated Activated Charcoal: II. Column Experiments," *Nucl. Technol.*, **42**, 172 (1979b).

Perry, R. H., and D. W. Green, eds., *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York (1984).

Phillips, J. P., "The Reactions of 8-Quinolinol," *Chem. Rev.*, **56**, 271 (1956).

Pirbazari, M., B. N. Badriyha, and R. J. Miltner, "GAC Adsorber Design for Removal of Chlorinated Pesticides," *J. of Environ. Eng.*, **117**, 80 (1991).

Pirbazari, M., B. N. Badriyha, S. H. Kim, and R. J. Miltner, "Evaluating GAC Adsorbers for the Removals of PCBs and Toxaphene," *Amer. Water Works Assoc. J.*, **84**(2), 95 (1992).

Pirbazari, M., V. Ravindran, B. N. Badriyha, S. L. Craig, and M. J. McGuire, "GAC Adsorber Design Protocol for the Removal of Off-Flavors," *Water Res.*, **27**, 1153 (1993).

Ravindran, V., M. Pirbazari, S. H. Kim, and B. N. Badriyha, "Modeling of Bioactive Carbon Adsorbers: A Hybrid Weighted Residual-Finite Difference Numerical Technique," *Appl. Math. and Comput.*, **76**, 99 (1996).

Ravindran, V., S. H. Kim, B. N. Badriyha, and M. Pirbazari, "Predictive Modeling for Bioactive Fluidized Bed and Stationary Bed Reactors: Application to Dairy Wastewater," *Environ. Technol.*, **18**, 861 (1997).

Standard Methods for the Examination of Water and Wastewater, 19th ed., APHA, AWWA and WERF, Washington, DC (1995).

Stevens, M. R., "Removal of Trace Toxic and Carcinogenic Organic and Inorganic Contaminants from Water," PhD Diss., Univ. of Southern California, Los Angeles (1987).

Stumm, W., and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 3rd ed., Wiley, New York (1996).

Vanderborght, B. M., and R. E. Van Grieken, "Enrichment of Trace Metals in Water by Adsorption on Activated Carbon," *Analy. Chemistry*, **49**, 311 (1977).

Vogt, V. H., "Das Adsorptionsvermögen von Kohle und anderen Stoffen gegen 8-Oxychinolin in wasseriger Lösung als Adsorbendem [in German (Adsorptive Power of Carbon and Other Substances for 8-Hydroxyquinoline in Aqueous Solution)]," *Pharmazeutische Zentralhalle für Deutschland*, **87**, 38 (1948).

Voice, T. C., and W. J. Weber, Jr., "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids: I. Theory and Background," *Water Res.*, **17**, 1433 (1983).

Williamson, J. E., K. E. Bazaire, and C. J. Geankoplis, "Liquid-Phase Mass Transfer at Low Reynolds Numbers," *Ind. and Eng. Chemistry Fund.*, **2**, 126 (1963).

Manuscript received Aug. 10, 1998, and revision received Jan. 19, 1999.