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UPTAKE OF METAL IONS FROM AQUEOUS SOLUTIONS BY SEDIMENTS: A STUDY OF ION SORPTION AND PARTICLE INTERACTIONS

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UPTAKE OF METAL IONS FROM AQUEOUS SOLUTIONS BY SEDIMENTS: A STUDY OF ION SORPTION AND PARTICLE INTERACTIONS

ABSTRACT

Sorption of copper and cadmium ions from aqueous solutions by ferric oxide particles is studied using batch equilibrium and kinetic experiments. The sorption process is found to be pH dependent, with the uptake rate increasing at high pH values. Changes in the surface electrostatic potential of the ferric oxide particles during ion uptake are measured. Evidence for particle destabilization due to changes in the surface electrostatic potential during equilibrium uptake of metal ions is presented here. The two-pK Basic Stern model with background electrolyte complexation is used to describe cadmium ion sorption by hydrous ferric oxide particles. Transient electrostatic potential changes during cadmium sorption are calculated and used in particle interaction and population balance models to estimate changes in the collision efficiency and size distributions of ferric oxide particles. An increase in the collision efficiency is found for larger particles in homocoagulation simulations. A decrease in the cumulative distribution of primary particles, and an increase in the distribution of large aggregates under conditions corresponding to metal ion uptake is observed. These findings indicate a potential role of metal ion uptake on particle flocculation kinetics through alteration of the surface electrostatic potential.

INTRODUCTION

Heavy metals are one of the most commonly encountered and difficult to treat environmental pollutants. They are introduced into the environment through industrial and domestic wastes. The geochemical fate of these metals is controlled by their reactions with surfaces at the solid/water interface. Most colloidal phases in aqueous solutions comprising both abiotic and biotic organic and inorganic particles are effective sorbents of such contaminants as trace metals. These particles have a very high affinity for ions due to their small size and high surface area. Several studies (e.g., Schindler et al., 1976; Ryan and Elimelech, 1996) show that many of the inorganic colloids in subsurface environments, such as clays, metal oxides, and carbonates, are especially effective at sorbing metals through ion exchange and surface complexation reactions.

Sorption of metals by colloidal particles changes the surface properties of the particles, as well as the chemical speciation of the sorbing species. Liang (1988) found that specifically sorbed organic and inorganic species affect the surface potential and stability of hematite particles. Several other researchers (Gibbs, 1983; Tipping and Ohnstad, 1984; Roy, 1995) have also demonstrated the effect of ion sorption on stability of colloidal particles in aqueous solutions. Even though many experimental studies have been published on metal ion sorption onto hydrous iron oxide particles, relatively few models that can predict both the equilibrium and the kinetics of sorption have been developed. The most commonly used models in the assessment of sorption are the Langmuir and Freundlich equations. While a good representation of the experimental data can be obtained with these models, they fail to predict the effects of pH, ionic strength, metal ion concentration, and a number of

other factors. The surface complex formation modeling (SCFM) approach (Dzombak and Morel, 1990) takes into account all of these factors and has been found to work well in the modeling of metal ion adsorption by hydrous oxides (Davis and Leckie, 1978; Yiacoumi and Tien, 1995a).

The primary objectives of this research were to study the equilibrium and dynamics of copper and cadmium sorption on ferric oxide particles, which were considered to be representative of inorganic colloidal particles found in sediments, and the effects of sorption on particle stability. Batch equilibrium and kinetic experiments were carried out. Changes in the size distribution of particles under conditions of metal ion uptake were measured. A systematic theoretical formulation was developed to describe the sorption process based on the SCFM approach. The complexation modeling employed a kinetic algorithm (Yiacoumi and Tien, 1995a,b,c) which not only provided transient sorption calculations, but also allowed an estimation of the particle surface potential as a function of time. The transient particle surface potential was used in conjunction with particle flocculation and population dynamics models (Tsouris and Scott, 1995) to compute colloidal particle interactions under conditions of cadmium ion uptake. The uniqueness of our studies is the systematic formulation of sorption equilibrium and kinetics in conjunction to the DLVO theory to quantify the effects of sorption kinetics of metal ions on the destabilization and flocculation kinetics of colloidal particles. Results of the experimental investigation and simulation studies are presented here.

EXPERIMENTAL WORK

Materials

Ferric oxide (Polysciences Inc., Warrington, PA) was the sorbent selected in this study. Nitrate salts of copper and cadmium were used as sorbates. The ionic strength of the solution was adjusted to 0.001 M in all experiments using $NaNO_3$. Solution pH was adjusted to desired values by adding HNO_3 or NaOH as required. All the chemicals used in this study to prepare stock solutions were of reagent grade and were obtained from Fisher Scientific (Pittsburgh, PA). Ferric oxide suspensions were aged for 24 hours before all experiments. All dilutions were made with Millipore Q-water.

Particle Characterization Studies

The surface area of the ferric oxide particles was measured by the N_2-BET method, using a Gemini III 2375 surface area analyzer (Micromeritics, Norcross, GA), and was found to be 3.6 m^2/g. The effects of pH and particle concentration on the surface potential of the particles was studied by using a Lazer zee-meter model 501 (Pen Kem Inc., Bedford Hills, NY). The electrophoretic mobilities of the particles were measured and zeta potentials under different conditions were obtained. The initial size distribution of the particles was measured by dynamic light scattering techniques, using a Coulter LS 130 light scattering instrument (Coulter Corp., Hialeah, FL). The size and morphology of the particles were investigated by Scanning Electron Microscopy (SEM), using a JOEL JSM-T220A SEM. Particles were suspended in ethanol, and allowed to dry on a brass stub at room tempertature into a thin, uniform film. After drying, the sample was coated (200 angstroms) with

gold using an argon plasma sputterer (Hummer 6.2, Anatech Ltd.). The SEM pictures were taken at 20 kV at various magnifications.

Equilibrium Experiments

Stock solutions of 0.001 M copper and cadmium were prepared by dissolving required amounts of the nitrate salts in millipore-Q water. 100 mL of copper and cadmium solutions were added to 125 mL flasks. The ionic strength was adjusted to 0.001 M using $NaNO_3$, and the solution pH was adjusted to a range of initial values from 2 - 10 by adding HNO_3 or NaOH as required. Ferric oxide particles were then added to the flasks to obtain a concentration of 250 or 300 ppm. The flasks were placed in a shaking water bath with the temperature maintained at 25 ± 1°C. The suspensions were allowed to equilibrate for 60 hours. The final samples were filtered using 0.02 μm Anotop membrane filters and analyzed using Inductively Coupled Plasma (ICP) 400 emission spectrophotometer (Perkin Elmer, Norwalk, CT). The final pH and zeta potential of the suspensions were measured. For each combination of total metal ion concentration and total sorbent concentration, at least two experiments were conducted to test the reproducibility of the data.

Kinetic Experiments

A completely mixed batch reactor was used in the kinetic experiments. A schematic of the experimental set-up is shown in Figure 1. A baffled reactor with a total volume of 750 mL, and a baffled volume of 600 mL was used in this study. A He/N_2 atmosphere was maintained in the reactor headspace to purge the air from the reactor. This arrangement was found to prevent changes in the pH of the suspension due to dissolution of CO_2 from air in the headspace. An agitation rate of 180 rpm

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was employed in all the experiments. The reactor was filled with the aged ferric oxide suspension and the metal ions were added at the start of the experiment (measured as t = 0). Particle and metal ion concentrations were the same as in the equilibrium experiments. The initial pH was adjusted to be in the acidic range to avoid precipitation, and changes in the pH due to metal ion sorption were continuously monitored. Samples were withdrawn at pre-determined time intervals using a 10 mL syringe and expressed through 0.02 μm filters. After the samples were filtered, they were analyzed using the ICP for concentration changes. Sample volumes were necessarily small in order to avoid significant drawdown in the reaction vessel. Particle size distribution changes were monitored by withdrawing 1 mL samples and adding them to "freezing solutions" (NaOH solutions with pH > 10). This method has been reported to hold the particles in their flocculated state without causing further aggregation or break-up (Tsouris and Scott, 1995). The size distribution was then measured using the Coulter LS 130 instrument as described in the Section on Particle Characterization Studies.

THEORETICAL FORMULATION

Equilibrium and Kinetic Modeling of Sorption

The uptake of metal ions by hydrous iron oxides in aqueous solutions has been found to occur as three interrelated processes (Yiacoumi and Tien, 1995a). These include particle surface ionization, formation of an electrical double layer adjacent to the surface, and metal ion complexation with surface sites. The reactive sites on the sorbent are treated as analogs of the complexing ligands in solution. The two-pK Basic Stern model with background electrolyte complexation was employed in this

study to describe the sorption of metal ions onto ferric oxide particles. The surface species are represented as SOH, SO^-, and SOH_2^+, and the surface protolysis reactions with the associated equilibrium constants, K_{H1} and K_{H2}, are shown in Table 1. The exponential terms shown in Table 1 are due to the formation of the electrical double layer. Removal of cadmium ions can be represented by different mechanisms. In this formulation, the removal of metal ions from solution was considered to be due to sorption of the free metal ion (Cd^{2+}). The surface complex formed was represented as SO^-Cd^{2+}. The electrolyte added to adjust the ionic strength was $NaNO_3$. The complexation reactions for both the metal ions, as well as for the background electrolyte are presented in Table 1. In Table 1, the solution phase reactions for cadmium are also given. The equations from Table 1 may be used in conjunction with mass balances to predict the distribution of ions in both solid and liquid phases by using a kinetic algorithm, KINEQL (Yiacoumi and Tien, 1995a).

Estimation of model parameters such as the equilibrium constants for the surface reactions can be obtained from experimental data by using optimization techniques. KINEQL and a sequential quadratic programming (SQP) technique (Biegler, 1985) can be used to minimize the objective function, SHAT, shown in Equation (1).

$$SHAT = \left(\frac{\sum_{j=1}^{NP}\left(\frac{y_{j,measured} - y_{j,calculated}}{y_{j,measured}} \right)^2}{NP - NPAR - 1} \right)^{0.5}$$ (1)

where $y_{j,measured}$ and $y_{j,calculated}$ are experimentally measured and theoretically determined quantities respectively. NP is the number of experimental data points and NPAR is the number of parameters to be determined by optimization. With the

determination of the required parameters, the speciation of ions due to sorption becomes a well-defined problem.

For studying the kinetics of adsorption of metal ions, KINEQL (Yiacoumi and Tien, 1995a,b,c) can be used under conditions where sorption reaction or mass transfer may be the dominant mechanism. These two scenarios are referred to as the reaction-controlled and transport-controlled cases, respectively. Modeling the uptake of cadmium ions by hydrous ferric oxide particles is presented in this study. Rate parameters (such as diffusion coefficient or mass transfer coefficient), and any other additional parameters may be obtained by using the results from kinetic experiments in conjunction with an optimization search procedure similar to the one described by Equation (1). This approach enables prediction of the concentrations of sorbed species, and their charge densities as a function of time. Transient electrostatic potentials calculated from the charge densities are then used in particle interaction models to determine the inter-relationships between metal ion sorption and particle interactions. This is the unique feature of the sorption modeling approach used to predict particle behavior in this study.

Particle Interaction Modeling

The particle forces considered in this work include external forces acting on individual particles, such as gravity, and interparticle forces, such as van der Waals, electrostatic, and hydrodynamic. Brownian relative diffusivity is also considered. In dilute suspensions, the forces acting between two particles change in strength as one particle approaches the other. The forces acting on a particle pair with radii a_i and a_j will be examined and quantified. In order to use them in a theoretical model, the relations among the various forces have to be delineated, and like forces grouped

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together. The relative diffusivity due to Brownian motion for two particles can be expressed as:

$$D_{ij}^{(0)} = \frac{kT\left(1 + {a_j}/{a_i}\right)}{6\pi\eta a_i}$$ (2)

where η is the viscosity of the liquid, k is the Boltzmann constant, and T is the absolute temperature. The far-field relative velocity due to the external gravitational force is given by

$$V_{ij}^{(0)} = \frac{2[(\rho_j - \rho)a_j^2 - (\rho_i - \rho)a_i^2]g}{9\eta}$$ (3)

where ρ is the density of the liquid, ρ_i is the density of the ith particle, and g is the gravitational acceleration. The relative diffusivity and the far-field relative velocity were related by Davis (1984) through two dimensionless parameters, the interparticle force parameter, Q_{ij}, and the Péclet number, Pe:

$$Q_{ij} \equiv \frac{\frac{1}{2}(a_i + a_j)V_{ij}^{(0)}}{{AD_{ij}^{(0)}}/{kT}}$$ (4a)

$$Pe \equiv \frac{\frac{1}{2}(a_i + a_j)V_{ij}^{(0)}}{D_{ij}^{(0)}}$$ (4b)

where A is the Hamaker constant.

The relative velocity can be found based on a force balance. In the case of creeping flow, the overall dimensionless relative velocity, u_{ij}, is obtained from the relative velocity when it is divided by $V_{ij}^{(0)}$ as

$$u_{ij} = [-L(s)\cos(\theta)e_r + M(s)\sin(\theta)e_\theta] - \frac{1}{Q_{ij}} G(s) \frac{d\left(\Phi_{ij}/A\right)}{ds} e_r$$

$$- \frac{1}{Pe}[G(s)\frac{\partial}{\partial s}(\ln p_{ij})e_r + \frac{H(s)}{s}\frac{\partial}{\partial \theta}(\ln p_{ij})e_\theta] \qquad (5)$$

where $s = 2r/(a_i + a_j)$, r is the center-to-center particle separation, e_r and e_θ are

unit vectors in the radial and tangential directions respectively, Φ_{ij} is the total

interparticle potential given by the summation of electrostatic and van der Waals

potentials, $L(s)$, $G(s)$, $M(s)$, and $H(s)$ correspond to the hydrodynamic functions, and

p_{ij} represents the normalized probability that particle i is at a given position relative

to particle j. A general solution of this equation, which is useful for particles in the

micron size range, may be obtained using perturbation methods (Tien, 1989). The

effect of the probabilistic term is determined by the Péclet number (Pe), which

defines whether Brownian diffusion or gravity dominates.

Brownian Flocculation: In the case of flocculation due to Brownian diffusion,

$Pe \ll 1$ (small particles), the flocculation frequency can be determined by (e.g.

Valioulis and List, 1984; Zhang and Davis, 1991):

$$F_{ij} = \frac{4\pi D_{ij}^{(0)}}{\int\limits_{a_i+a_j}^{\infty} \frac{\exp\left(\Phi_{ij}/kT\right)}{r^2 G(s)} dr} \qquad (6)$$

Turbulent Shear Flocculation: By finding the numerical solution to the

trajectory equation obtained from a force balance, the trajectory of a particle can be

traced from an arbitrary starting position and its eventual fate (flocculation or non-

flocculation with the other particle placed at the origin) can be determined (Chin,

1997). Furthermore, by repeated applications of this numerical solution, the limiting

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or critical trajectory separating the fate of the two particles can be found. From Equation (5), it is clear that the limiting trajectory shows cylindrical symmetry about the z-axis. Thus, trajectories that result in flocculation will originate within a certain horizontal distance y_c^* of the z-axis. From this critical radius parameter, the flocculation frequency can be found (Zhang and Davis, 1991):

$$F_{ij} = V_{ij}^{(0)} \pi y_c^{*2} \tag{7}$$

The definitions and equations presented in this section yield a theoretical framework for a particle-particle trajectory-analysis model that would be sufficient to achieve useful numerical simulations. The flocculation frequency can then be used in a population balance model to study particle population properties with time. It is worth mentioning here that, since electrostatic potential is a function of time, particle flocculation frequencies are also functions of time in the above formulations. Thus, prediction of the transient flocculation frequency is possible using this approach.

Kinetics of Particle Flocculation

The flocculation frequency obtained as described in the previous section can be used in a population-balance equation to predict the particle population state with time (e.g., Tsouris and Scott, 1995):

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} n_i n_j F_{ij} - \sum_{i=1}^{\infty} n_i n_k F_{ik} \tag{8}$$

where n_k is the number of particles of size k and t is the time. Equation (8) is a population balance of particles of size k. The first term represents accumulation, the second is gain resulting from flocculation of smaller particles, and the third is loss due to flocculation with other particles. An extension of this model is a bivariate

population-balance equation in which each particle is designated by size and another property, such as particle surface charge, concentration of a certain species, or residence time in a specific system. This model can accommodate not only a distribution of particle sizes but also a distribution of another property, such as surface charge, for each particle size. This feature was used in this study because it allowed calculations of flocculation kinetics among particles of different electrostatic potential and size. The discrete bivariate population-balance equation for a batch system can be written as (Tsouris et al., 1995):

$$\frac{dn_{ij}}{dt} = \frac{1}{2}\sum_{l=1}^{i-1} n_{lm} n_{(i-l)(j-m)} F_{lm,(i-l)(j-m)} - \sum_{l=1}^{Ns-i} \sum_{m=1}^{l+Nc-1} n_{ij} n_{lm} F_{ij,lm}$$ (9)

where n_{ij} is the number of particles of size i and electrostatic potential j (class ij), $F_{ij,lm}$ is the flocculation frequency of particles in class ij with particles in class lm, and N_s, N_c are the total numbers of size and electrostatic potential classes, respectively. Equation (9) was used to calculate flocculation kinetics of both homogeneous and heterogeneous suspensions, accommodating the continuously varying electrostatic potential in the discretization scheme.

RESULTS AND DISCUSSION

Particle Characterization Studies

Figure 2 shows the zeta potential of the ferric oxide particles used in this work, as a function of pH. The concentration of the ferric oxide particles in these experiments was 300 ppm. The zeta potential was found to vary from -22 to -48 mV over a pH range from 3-10. Typical values for stabilized suspensions in natural systems are documented as -20 to -40 mV in the literature (American Water Works

Association, 1990). The effect of particle concentration on the surface potential of the particles at a constant ionic strength of 0.001 M is shown in Figure 3. The zeta potential of the particles is seen to decrease with an increase in the particle concentration. The initial size distribution of the particles is shown in Figure 4. The findings from the characterization studies are used as baseline measurements to compare with metal ion sorption studies. The microstructure of the ferric oxide particles is shown in Figure 5. The particles were found to be fairly homogeneous, and the size distribution ranges agreed well with those presented in Figure 4, as well as with the manufacturer's literature (0.3 to 0.8 μm).

Equilibrium Experiments

Figures 6a and 6b depict the sorption edges for cadmium and copper as a function of pH. 250 ppm ferric oxide particles were used in the copper sorption experiments, and 300 ppm concentration was used with the cadmium ions. A higher concentration of sorbent implies an increase in the number of available sorption sites and hence an increase in the extent of sorption, for ions having the same charge. This process would explain the greater sorption seen in the case of cadmium ions at lower pH values. In both cases, sorption appears to be a pH-dependent process with an increase in the extent of sorption at high pH values. This occurrence is possibly due to an increase in the number of negatively charged surface sites at higher pH values due to ionization of surface sites.

The changes in the pH of the suspensions due to equilibrium sorption of metal ions are represented in Figures 7a and 7b for cadmium and copper, respectively. In both cases, control experiments were carried out without metal ions to measure baseline changes in the pH of ferric oxide under identical conditions. Two different

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metal ion concentrations were investigated in the experiments with cadmium to investigate the effects of changing initial metal ion concentration. In all cases, it was found that the final pH was higher than the initial pH in the acidic range, and lower than the initial pH in the basic range. One possible explanation is that when the initial pH is very high, the metal ions have a tendency to precipitate out. Indeed, in some of our suspensions, formation of precipitates was clearly visible. In these cases, free metal ionic species are not available for sorbing onto the ferric oxide particles. Also, there is a decrease in the concentration of hydroxyl ions due to formation of $Cd(OH)_2(s)$. Thus, a corresponding decrease in pH is observed. At low initial pH values, both metal ions and protons can bind onto the surface active sites, thus indicating an increase in the pH. It is also worth noting that the pH variations were more for Cd binding than for Cu. Cu, being a divalent transition metal, exhibits a stronger affinity for binding sites through covalent as well as electrostatic interactions. Cd is a Class B metal cation which is easily polarizable and undergoes primarily covalent interactions. Thus, competition due to proton binding for the same sorbent sites appears to be to a lesser degree with copper than with cadmium. Furthermore, based on stability constants, it was found that Cd^{2+} was by far the dominant dissolved Cd species, and that Cu^{2+} and $CuOH^+$ were the dominant dissolved Cu species at the pH values studied here. This reasoning does not include the highly basic pH ranges where precipitation is clearly seen.

Zeta potential changes due to sorption are shown in Figures 8a and 8b for cadmium and copper, respectively. In the case of both metals, the zeta potential was found to increase with pH in contrast to baseline measurements for the particles alone. The increase was more pronounced in the case of copper ion sorption than for cadmium ion sorption. As metal ions sorb onto the ferric oxide particles, surface charge neutralization takes place. This charge neutralization results in the particles

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having higher values of zeta potential corresponding to increasing quantities of metal sorption. An interesting observation is at a pH of around 10, where the zeta potential value under conditions of cadmium ion uptake did not change from baseline values. This finding appears to corroborate our theory about precipitation at higher pH values. When the initial pH was around 10.8, metal ions precipitated out as the corresponding hydroxide species. The precipitated $Cd(OH)_2(s)$ species was not available for sorption and hence did not affect the zeta potential of ferric oxide. This precipitation prevented metal ion sorption and thereby, the zeta potential remained at the baseline value. The changes in the zeta potential (approaching a value of 0 mV or higher) would result in a destabilization of these particles due to charge neutralization. This phenomenon indicates a possible increase in the rates of interparticle collisions, as repulsive forces would be overcome to a large extent, causing flocculation of particles.

Kinetic Experiments

The history of copper ion sorption onto ferric oxide particles is shown in Figure 9. It is clear that the kinetics of copper ion uptake is very slow. The extent of sorption was found to be around 60 % at the end of 150 hours. Dzombak and Morel (1990) reported that sorption kinetics may be considerably slow in cases where the sorbate/sorbent ratio is high. This process may have been operative in our experiments where the sorbate/sorbent ratios were relatively high. Sensitivity analysis experiments at different metal ion and ferric oxide concentrations have to be carried out to determine the mechanism governing the sorption phenomenon as a diffusion-limited or a rate-limited process (Yiacoumi and Tien, 1995a,b,c).

Changes in the particle size distribution during the initial stage of dynamic sorption experiments for cadmium and copper are shown in Figures 10a and 10b, respectively. In both cases, the size distribution changes were measured over a period of 3 hours. A decrease in the cumulative number distribution of primary particles, and a corresponding increase in the cumulative number distribution of larger size fractions were observed during both cadmium and copper uptake. This finding indicates that particle aggregation may occur during metal ion sorption. The flocculation process was more profound in the case of cadmium, where aggregates more than 200 times larger than the primary particles (0.3 μm to 0.8 μm) were formed. Some evidence for particle break-up was also seen in the cadmium uptake experiments, which may have been caused by the agitation in the reaction vessel.

Changes in the suspension pH monitored over a period of 50 hours for both cadmium and copper uptake are presented in Figures 11a and 11b. In the case of Cd uptake, a pH increase by about 3 units was observed when the initial pH was around 4.5. An increase by 1 pH unit was seen during Cu ion uptake when the initial pH was 5.2. These findings are consistent with the pH profiles obtained from the equilibrium experiments (Figures 7a and 7b) and the findings of other researchers (Chen et al., 1996).

Equilibrium Modeling

Cadmium ion uptake from aqueous solutions by hydrous ferric oxide (HFO) was studied using the model described in the Theoretical Formulation Section. Model parameters for these simulations were obtained from Yiacoumi and Tien (1995a) and are presented in Table 2. Figure 12 shows the effect of initial cadmium concentration on equilibrium uptake by HFO. It was found that as the metal ion concentration

increased, the percent uptake by the sorbent at a constant pH decreased. Also, the uptake increased with an increase in pH, which is similar to the experimental findings of this study (Figures 6a and 6b). At low concentrations, the ratio of sorptive surface to total metal ions available is high and nearly all ions in solution may be bound and removed. As metal ion concentration increases, percent uptake decreases due to a decrease in the availability of binding sites. It appears that such sorbent particles can deal more effectively with dilute solutions if a high percent removal is required for extended periods of time.

Kinetic Modeling

The sorption and surface potential histories for the transport-controlled sorption of cadmium ions are presented in Figure 13a. The dimensionless time (θ) shown in the graphs is defined as

$$\theta = \frac{D_j t}{a_p^2} \tag{10}$$

where t is the real time, a_p is the radius of the particle, and D_j is the diffusion coefficient. With an increase in sorption, the zeta potential is seen to increase to positive values, which agrees well with the experimental observations of Figures 8a and 8b. These findings indicate that with an increase in the metal ion uptake, the particle surface potential changes, thereby altering the stability of the particles. This observation is similar to the changes in size distribution during sorption kinetics experiments, as shown in Figures 10a and 10b.

The changes in the surface electrostatic potential of HFO during cadmium sorption was simulated at three different pH values. These findings are presented in Figure 13b. As the pH of the suspension increases, the proton concentration in the

solution decreases. At low pH values, a high concentration of protons in the water may result in competition between the protons and metal ions for the binding sites, thereby decreasing metal ion uptake. At these pH values, the sorbent sites would be closely associated with H^+ ions, thereby the metal ions experience repulsive forces. As pH increases, more negatively charged sites would be exposed with a subsequent increase in attraction for the positively charged metal ions. The surface potential of the particles is also seen to change corresponding to the variations in the extent of metal ion sorption.

Figure 14 shows the effect of surface electrostatic potential on the collision efficiency of homogeneous HFO particles in the Brownian diffusion regime. Three different particle sizes were studied. The particles were seen to be stabilized due to electrostatic repulsion when the surface potential was less than -20 mV or greater than +20 mV. Within this range, particles were observed to be destabilized and there was an increase in the collision efficiency of particles leading to floc formation. The extent of collision was found to be greater for larger particles.

Figure 15 is an example of the changes in the cumulative size distribution of hydrous iron oxide particles as a function of particle size and time for the Brownian flocculation regime. The transient electrostatic potentials obtained from sorption modeling were incorporated in the discretization scheme used for calculating changes in particle size distribution with time over a period of 1.86 dimensionless time units. With an increase in time, a decrease in the number of primary particles and an increase in the number of larger sized particles are seen. These findings indicate a possibility of particle aggregation due to changes in the surface potential of the particles due to metal ion sorption, and consequently, changes in the collision efficiency of the particles.

SUMMARY AND CONCLUSIONS

The findings from an experimental and modeling investigation of metal ion sorption onto inorganic colloidal particles are reported in this work. Based on preliminary experimental and modeling efforts, it is clear that copper and cadmium ion sorption alters the surface potential of ferric oxide particles. Destabilization of the ferric oxide particles is seen to occur under conditions of suspension pH and ionic strength commonly encountered in natural systems. Modeling studies indicate possibilities of particle aggregation under conditions of metal ion uptake due to alteration of surface electrostatic potential. Experimental work to validate these findings is in progress in our laboratories.

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TABLES AND FIGURES

Table 2. Model Parameters for Cadmium Sorption by Hydrous Ferric Oxide Particles (Yiacoumi and Tien, 1995c)

Name of Parameter	Value of Parameter
pK_{H1}	7.72
pK_{H2}	-8.08
pK_{Na}	-8.58
pK_{NO3}	7.07
pK_{Cd}	-3.61
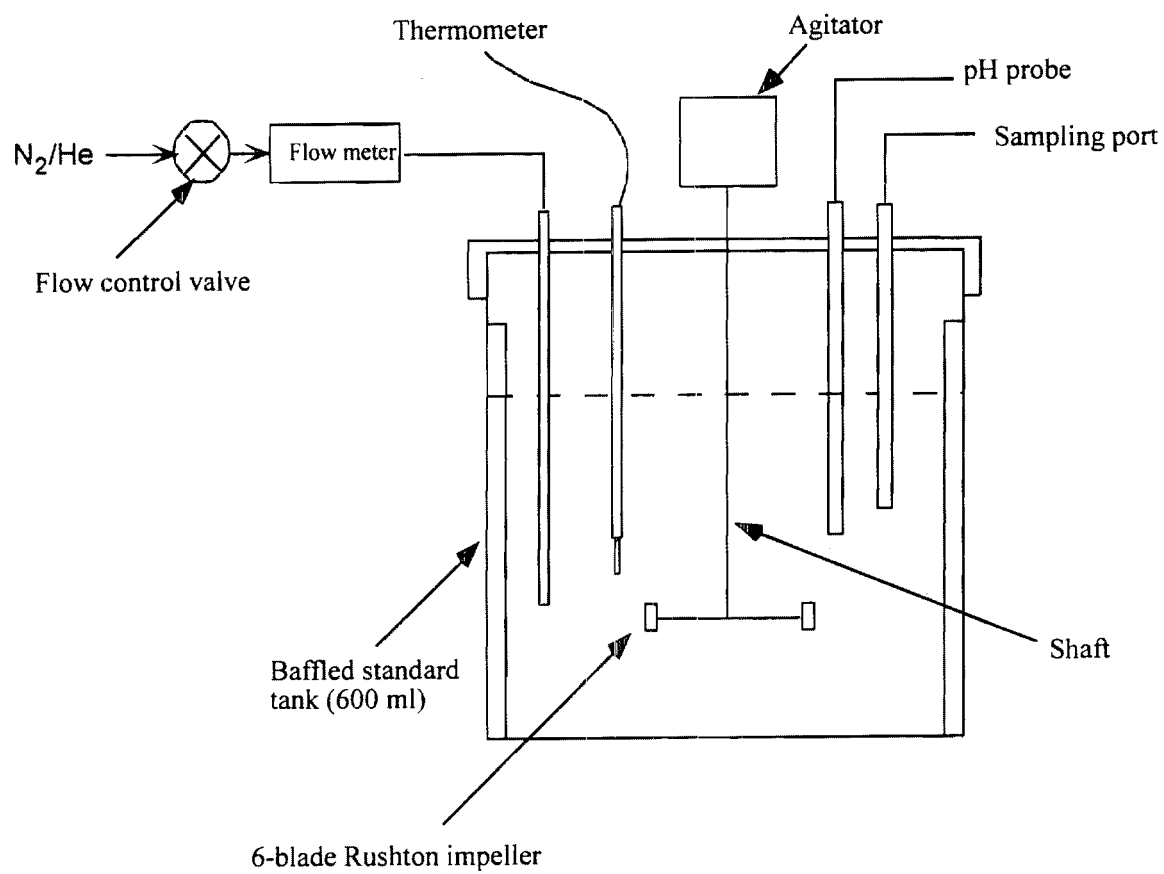
Figure 1. Schematic of continuously mixed batch reactor.
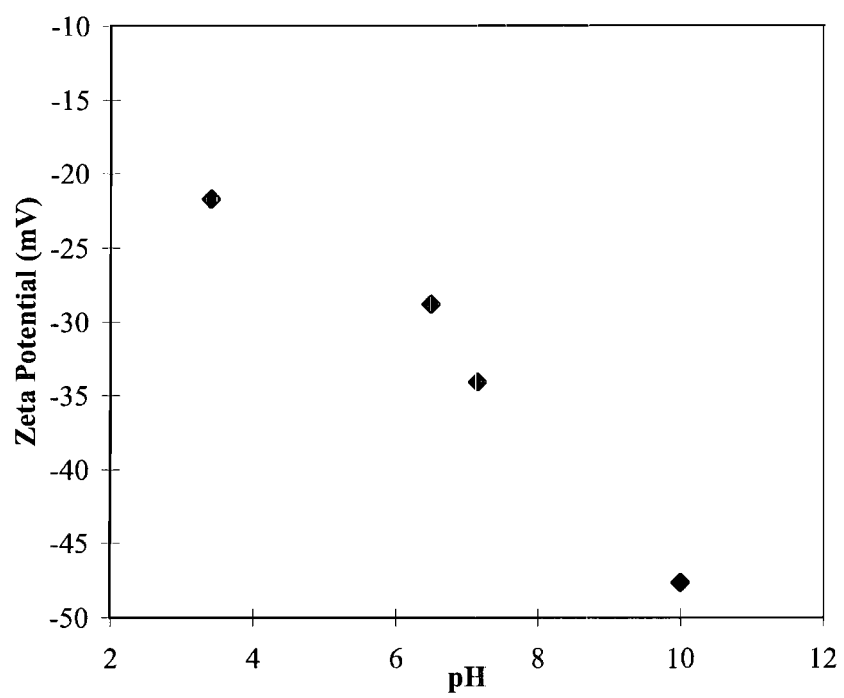
Figure 2. Effect of pH on zeta potential of ferric oxide particles.
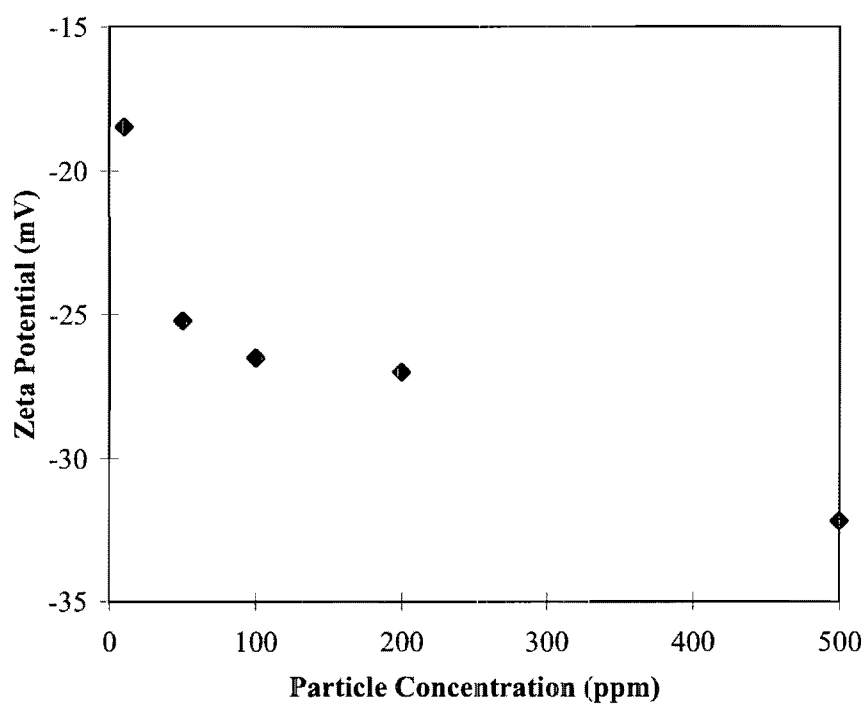
Figure 3. Effect of particle concentration on zeta potential of ferric oxide particles.
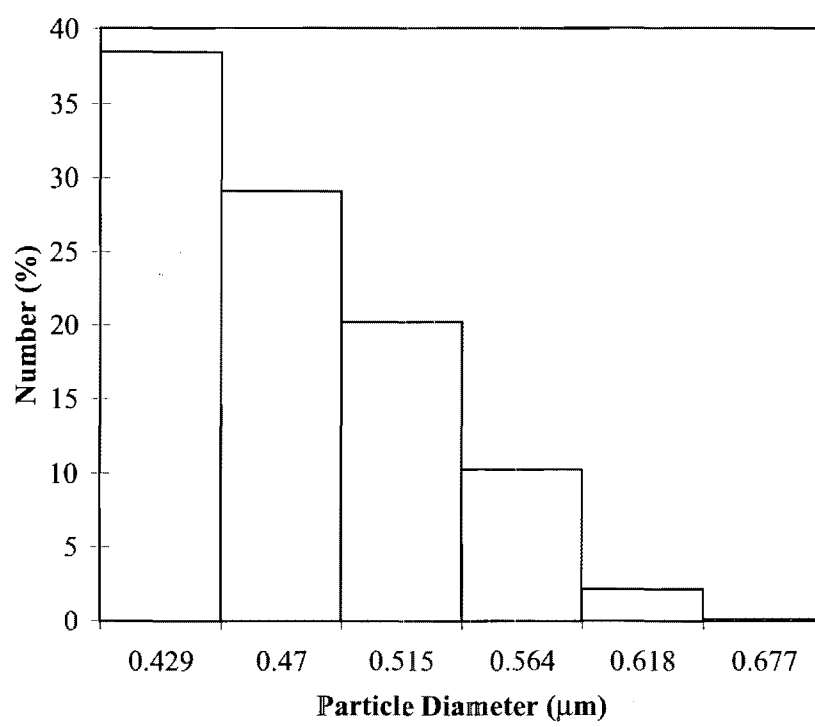
Figure 4. Initial size distribution of ferric oxide particles.
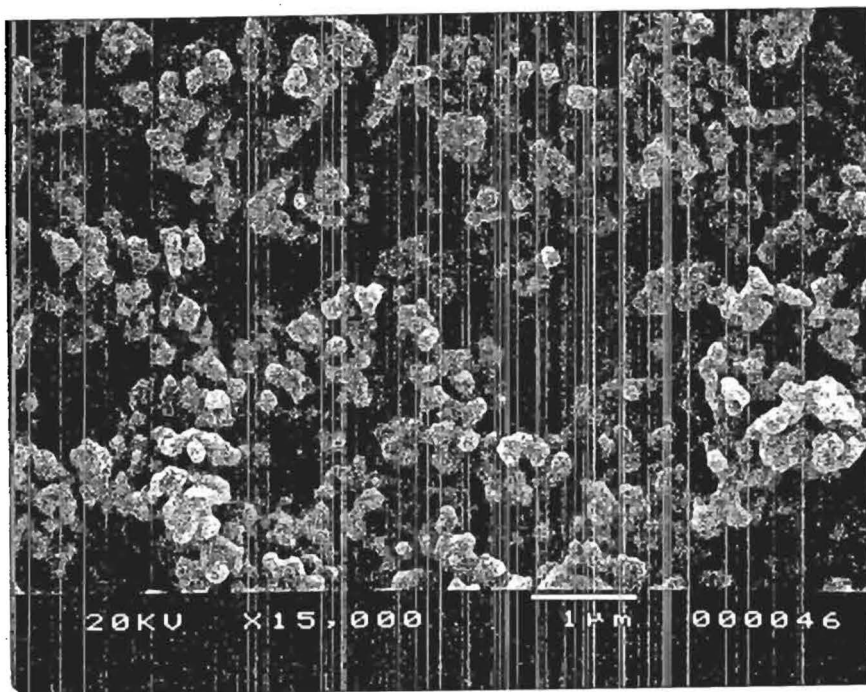
Figure 5. Microstructure of ferric oxide particles.
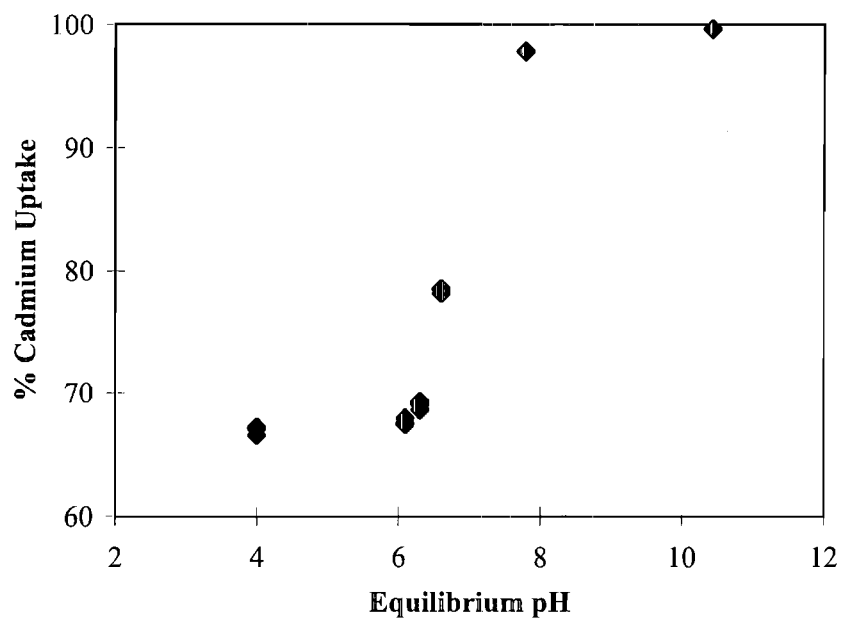
Figure 6a. pH edge during equilibrium cadmium sorption.
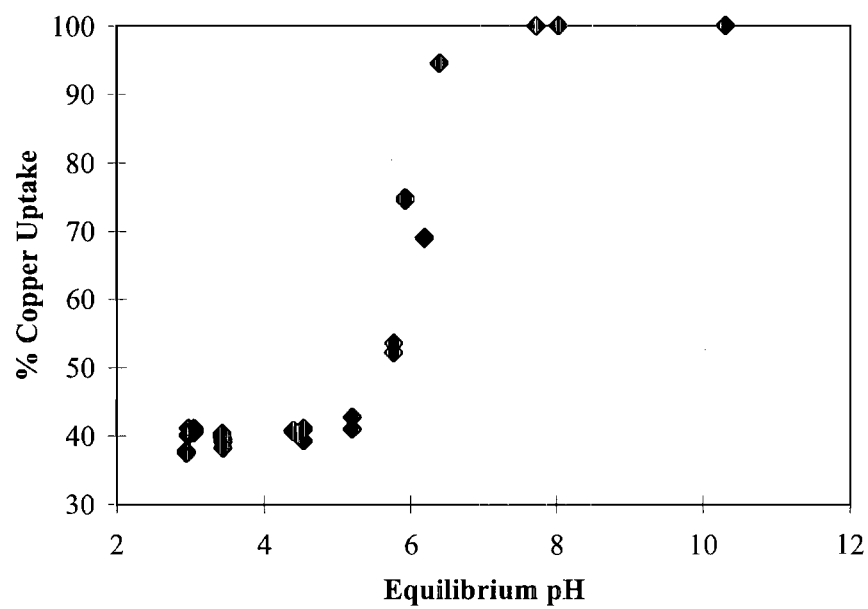
Figure 6b. pH edge during equilibrium copper sorption.
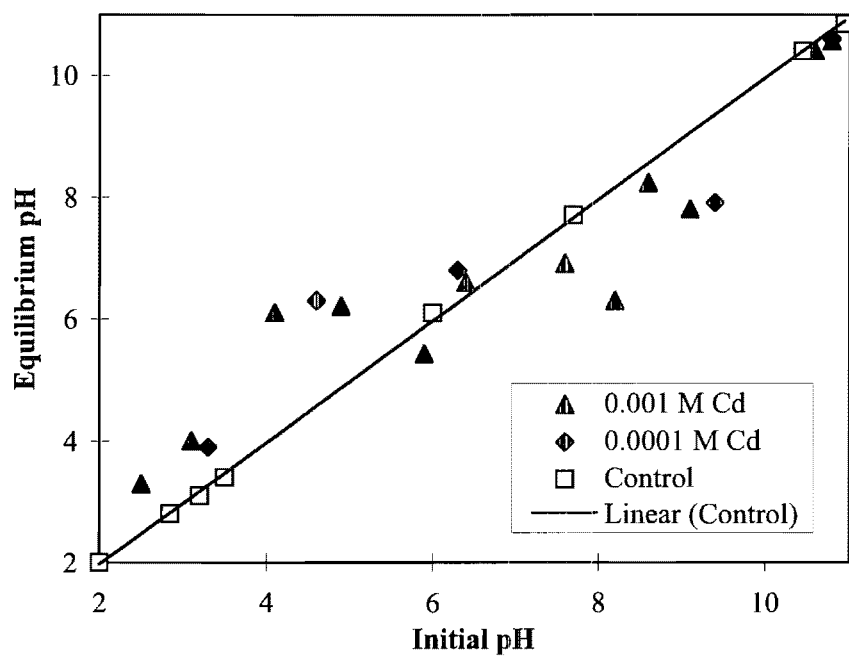
Figure 7a. Variations in pH during equilibrium cadmium sorption.
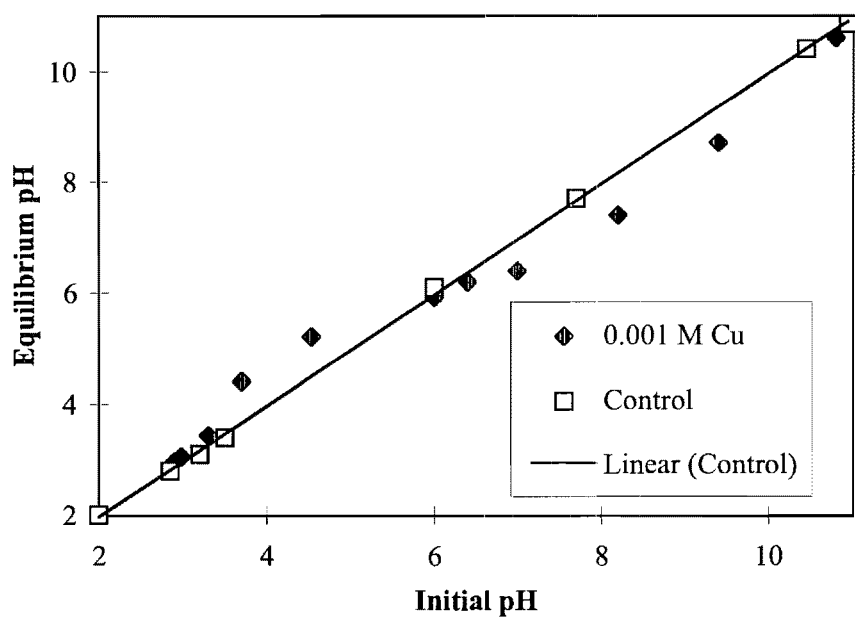
Figure 7b. Variations in pH during equilibrium copper sorption.
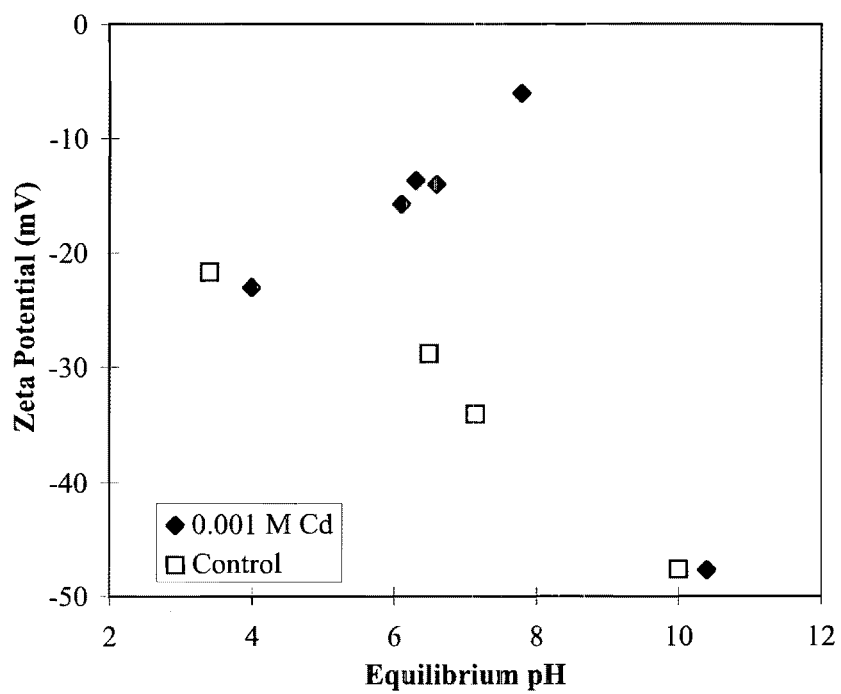
Figure 8a. Changes in zeta potential due to equilibrium cadmium sorption.
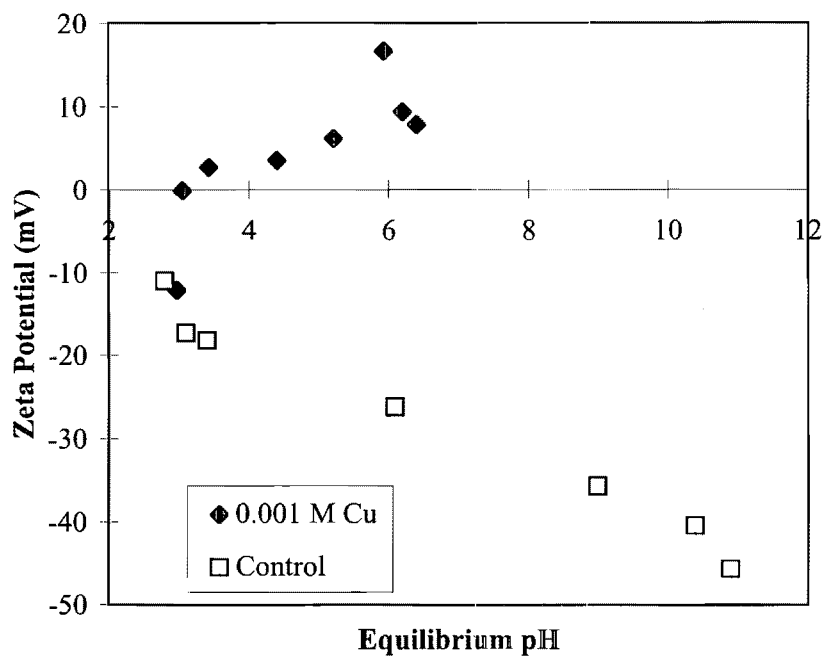
Figure 8b. Changes in zeta potential due to equilibrium copper sorption.
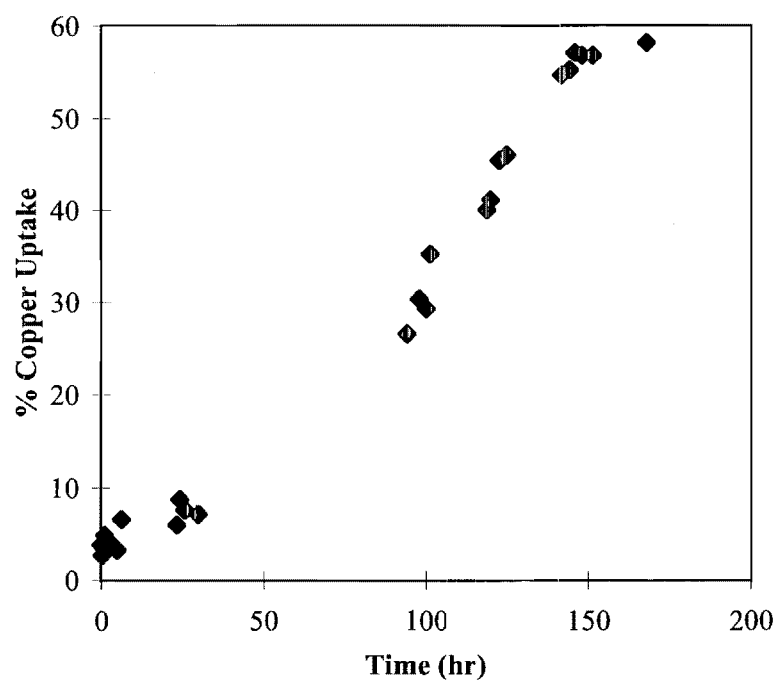
Figure 9. Sorption history of copper ion uptake by ferric oxide particles.
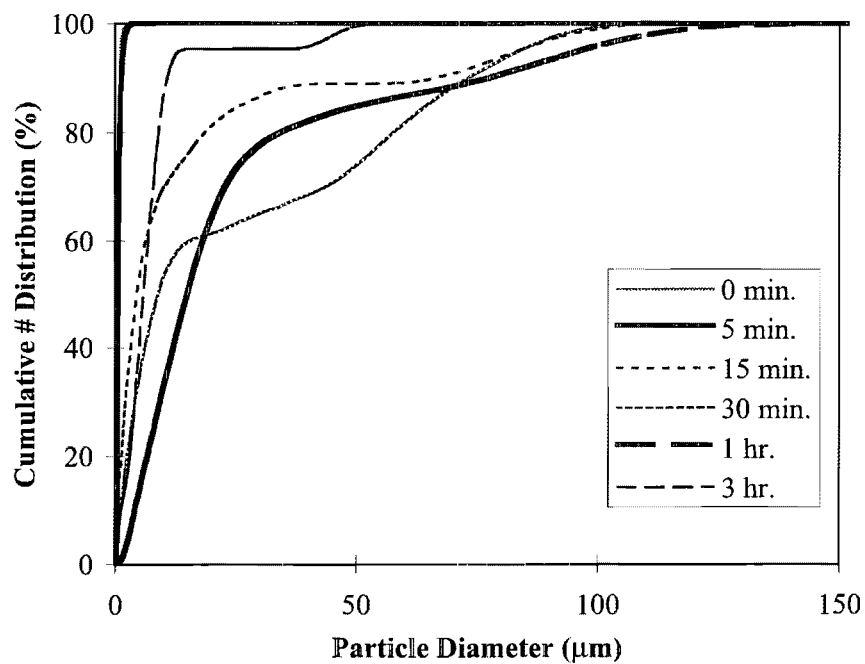
Figure 10a. Size distribution changes during cadmium kinetic experiments.
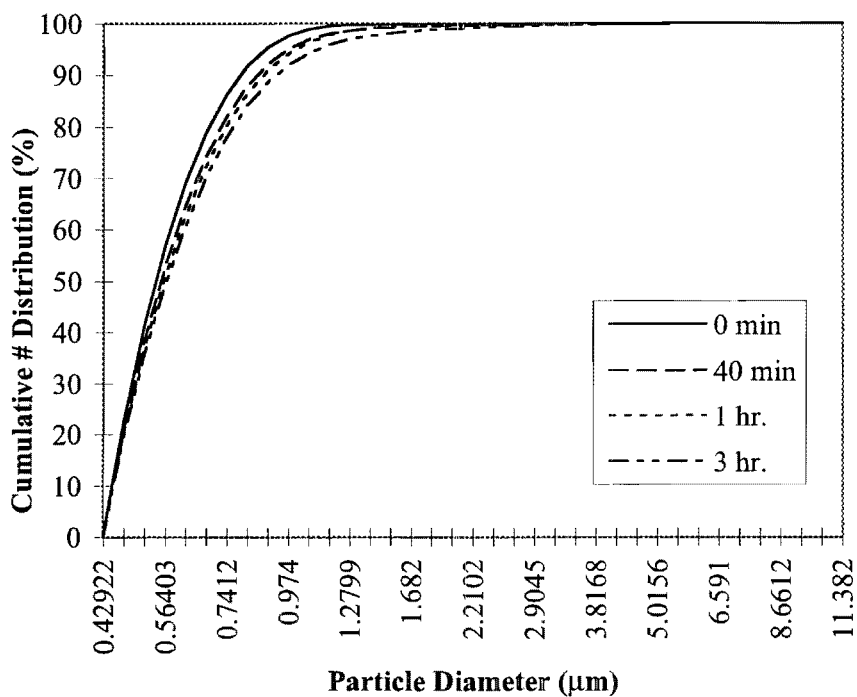
Figure 10b. Size distribution changes during copper kinetic experiments.
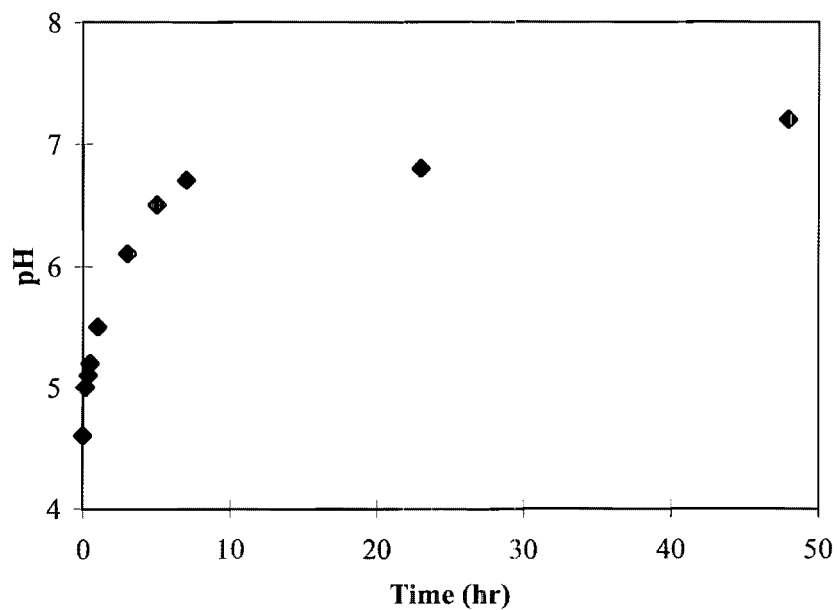
Figure 11a. pH histories during cadmium kinetic experiments.
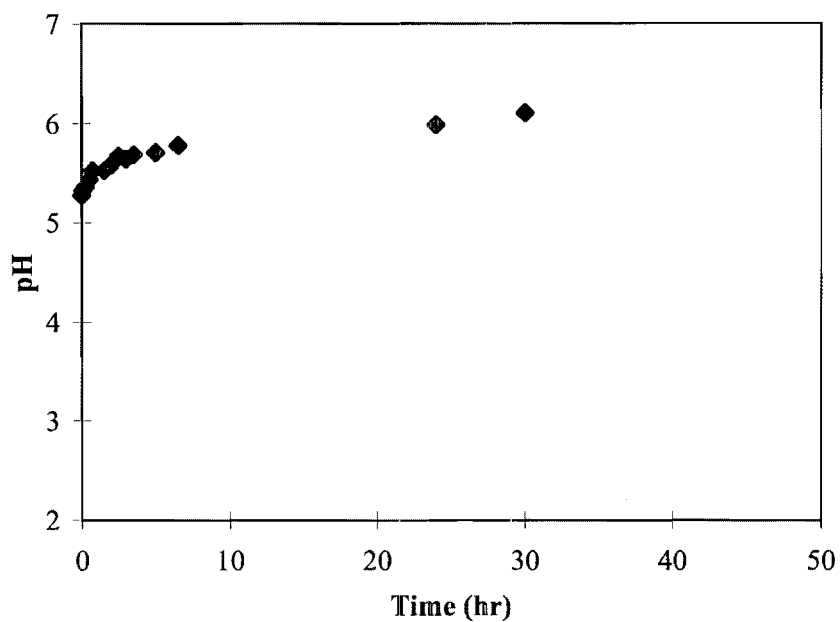
Figure 11b. pH histories during copper kinetic experiments.
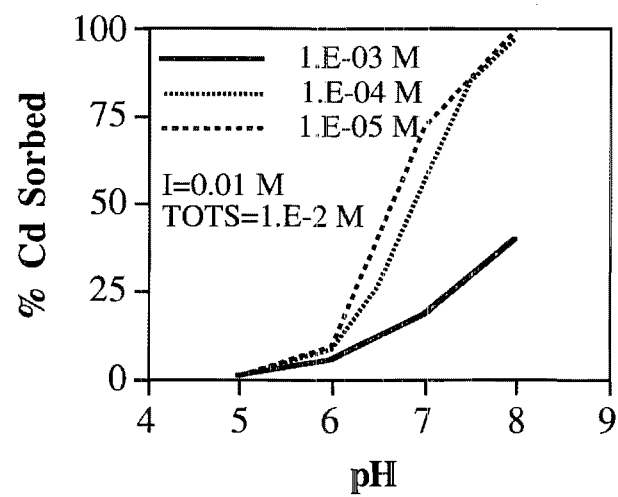
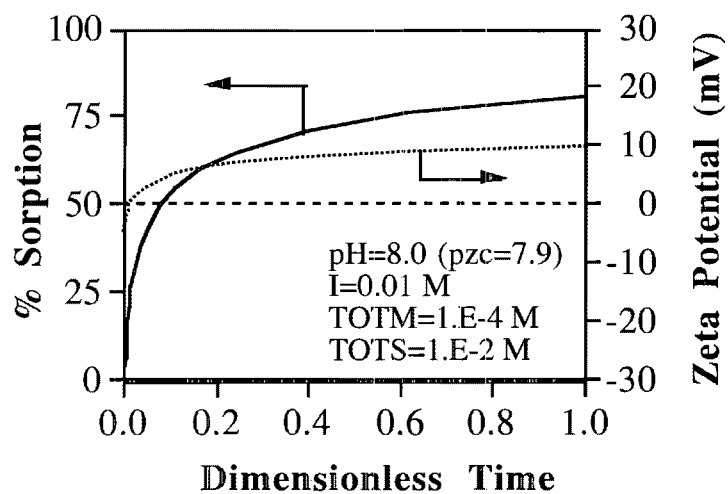**Figure 12.** Effect of initial copper concentration on equilibrium uptake by HFO particles.

Figure 13a. Sorption and surface potential histories for the transport-controlled sorption of cadmium ion.
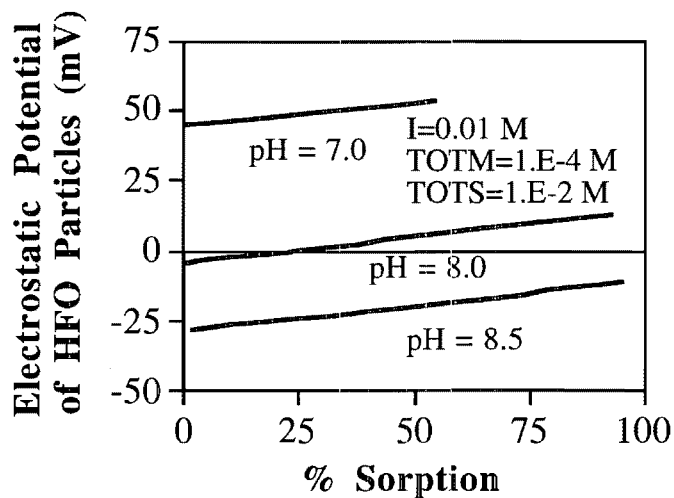

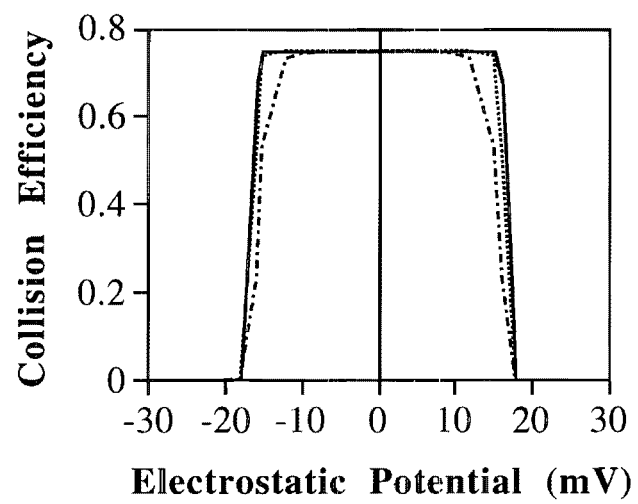**Figure 13b.** Surface potential variations of HFO particles as a function of pH.

Figure 14. Effect of surface potential on the collision efficiency of homogeneous HFO particles in the Brownian diffusion regime.