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EFFECT OF COPPER AND CADMIUM BINDING ON FLOCCULATION OF FERRIC OXIDE PARTICLES

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ABSTRACT

The sorption of copper and cadmium ions from aqueous solutions by ferric oxide particles was studied using batch equilibrium and kinetic experiments. The sorption process was found to be pH dependent, with the uptake increasing at high pH values. An increase in equilibrium pH was observed when the initial pH was in the acidic range, and a decrease from initial values was observed in the basic range, in the case of both copper and cadmium sorption. The former phenomenon is due to competition between metal and proton binding, and the latter is due to precipitation mechanisms at high initial pH values. A large increase in the zeta potential of the particles from baseline values was observed during equilibrium sorption. This increase occurs as a result of surface charge neutralization due to metal ion uptake. Particle destabilization appears to occur as a result of metal ion sorption. Kinetic experiments indicate that the uptake of copper by

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ferric oxide particles is a slow process. The pH histories were similar to those obtained in the sorption equilibrium experiments. Changes in the size distribution of the ferric oxide particles due to aggregate formation during uptake of ions were observed in the kinetic studies. These findings indicate a potential role of metal ion uptake in 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 sizes and high surface areas. Several studies (1,2) have shown 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 and Morgan (3) found that specifically sorbed organic and inorganic species affect the surface potential and stability of hematite particles. Several other researchers (4,5,6) have also demonstrated the effect of ion sorption on the stability of colloidal particles in aqueous solutions. This study focusses on sorption of metal ions such as copper and cadmium on inorganic metal oxides, specifically ferric oxide particles. These particles are widely prevalent in aquatic systems as such, or as coatings on other particles such as clays, other mineral phases, particulate matter, and cell surfaces (7).

The specific objectives of this research were to study the dynamics and equilibria of copper and cadmium sorption on ferric oxide particles, and the effects of sorption on particle stability. Batch equilibrium and kinetic experiments were carried out. Changes in the zeta potential and size distribution of the particles under conditions of metal ion uptake were measured. The uniqueness of our studies is in the investigation of sorption equilibrium and kinetics in conjunction with particle interactions to understand the effects of metal ion sorption on the destabilization and flocculation kinetics of colloidal particles.

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 $NaNO_3$. The 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 h before being used in 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 were 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 picture was taken at 20 kV at a magnification of 15000X.

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. Then, 100-mL volumes 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 to 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 h. The final samples were filtered using 0.02-μm Anotop membrane filters and analyzed using an 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 were used in this study. An 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 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 time (measured as $t = 0$). Particle and metal ion concentrations were the same as those 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 predetermined time intervals using a 10-mL syringe and expressed through 0.02-μm filters. After the samples had been filtered, they were analyzed using the ICP for concentration changes. Sample volumes were necessarily small in order to

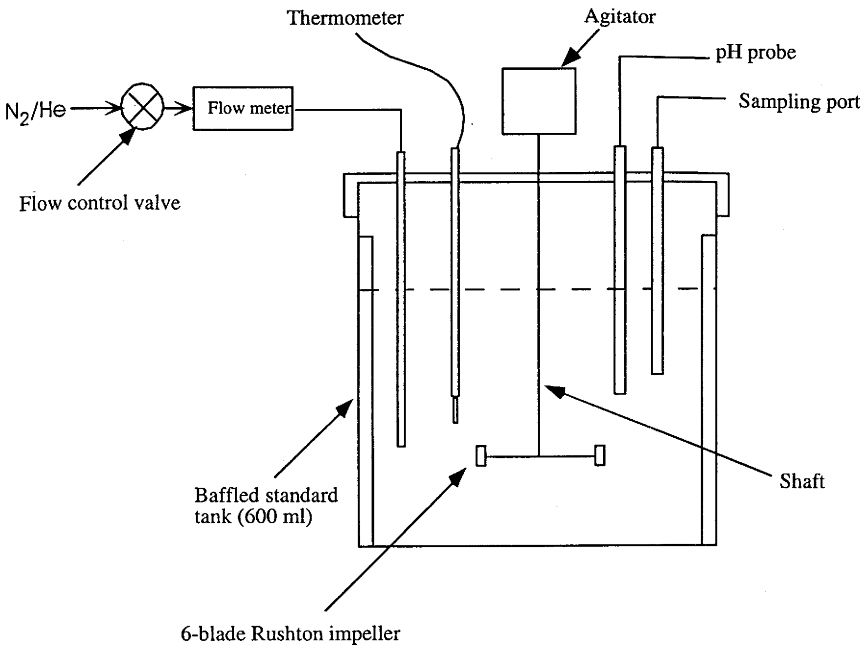


FIGURE 1. Schematic of completely mixed batch reactor.

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 breakup (8). The size distribution was then measured using the Coulter LS 130 instrument as described in the section on Particle Characterization Studies.

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

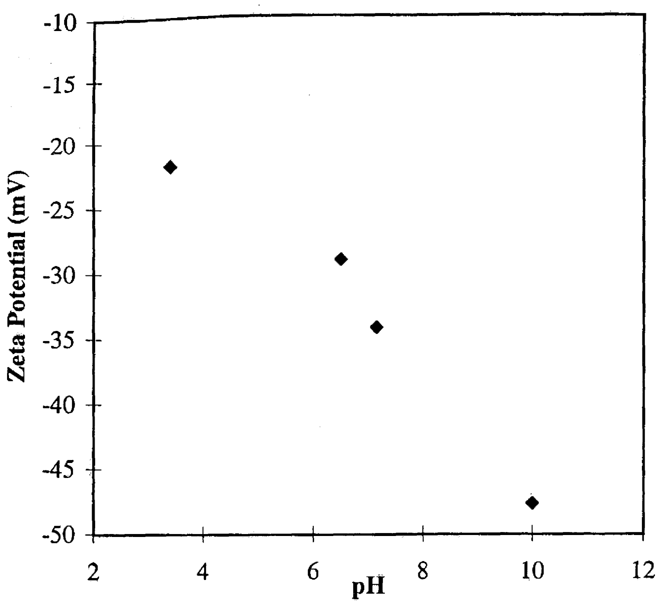


FIGURE 2. Effect of pH on zeta potential of ferric oxide particles.

300 ppm. The zeta potential was found to vary from -22 to -48 mV over a pH range from 3 to 10. Typical values for stabilized suspensions in natural systems are documented as -20 mV to -40 mV in the literature (9). 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 as particle concentration increases. 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 data from 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).

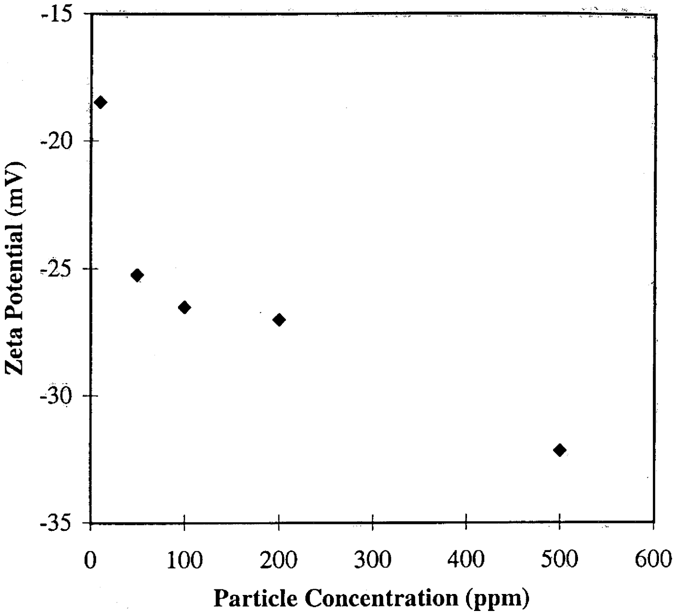


FIGURE 3. Effect of particle concentration on zeta potential of ferric oxide particles.

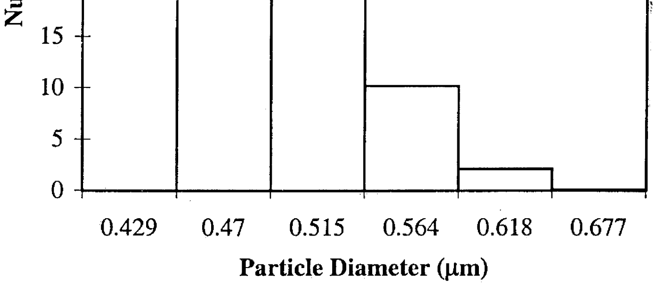


FIGURE 4. Initial size distribution of ferric oxide particles.

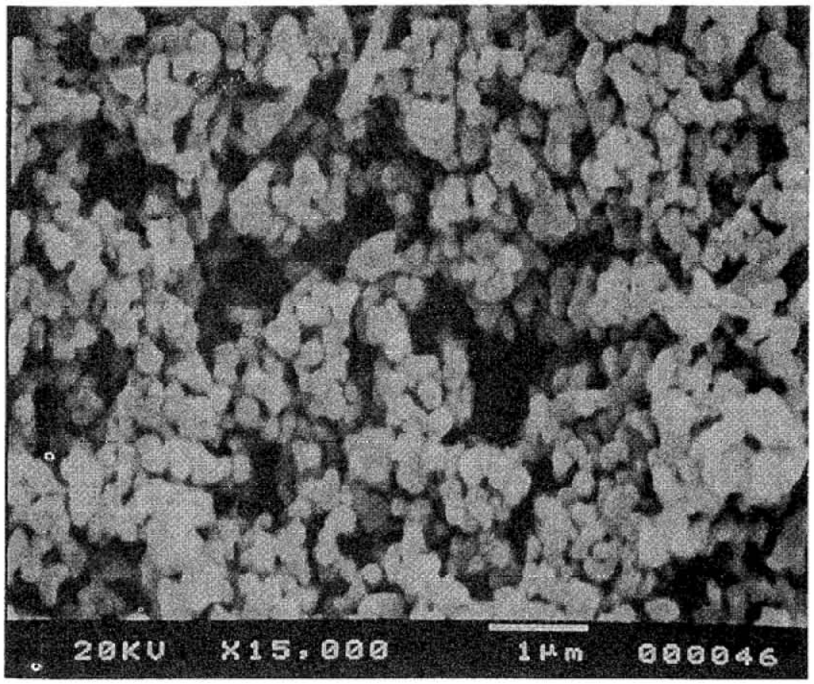


FIGURE 5. Microstructure of ferric oxide particles.

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 extent of sorption seen in the case of cadmium ions at lower pH values. In each case, 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.

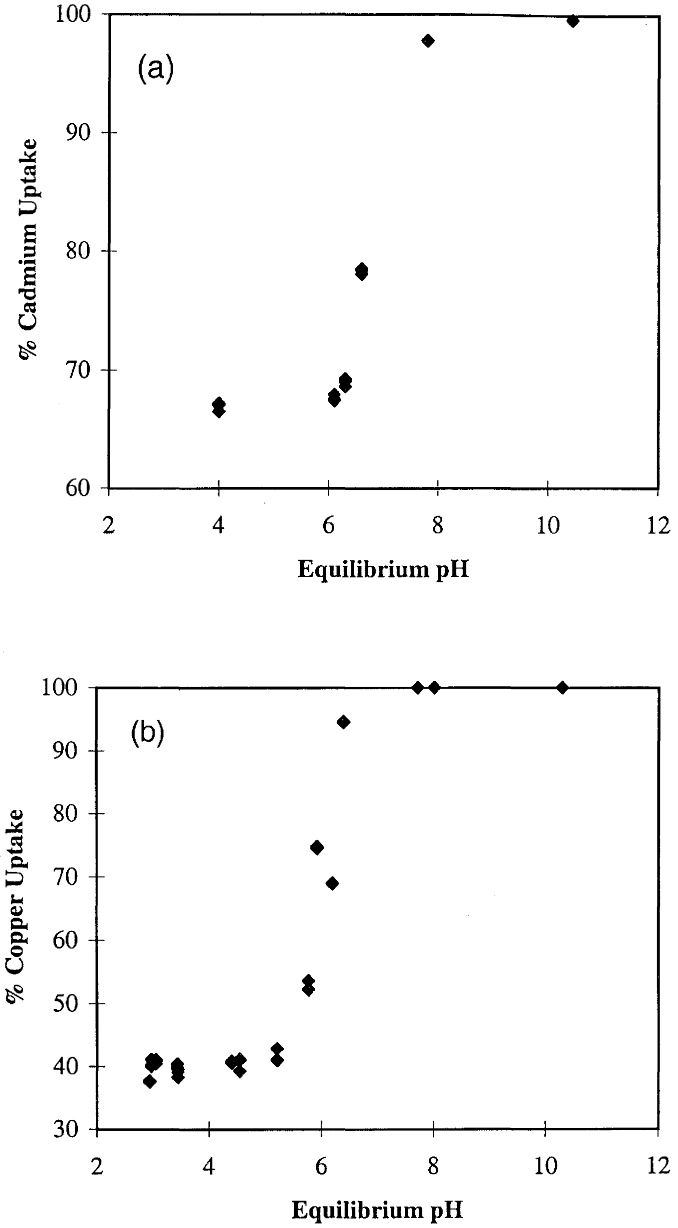


FIGURE 6. pH edge during equilibrium (a) cadmium and (b) copper sorption.

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 metal ion concentrations were investigated in the experiments with cadmium to determine 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, the formation of precipitates was clearly visible. In these cases, free metal ionic species were not available for sorbing onto the ferric oxide particles. Also, there was a decrease in the concentration of hydroxyl ions due to the formation of $Cd(OH)_2(s)$. Thus, a corresponding decrease in pH was 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 cadmium binding than for copper. Copper, which is a divalent transition metal, exhibits a stronger affinity for binding sites through covalent as well as electrostatic interactions. Cadmium 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, it is worth mentioning here that, based on stability constants, it was found that Cd^{2+} was by far the dominant dissolved cadmium species, and that Cu^{2+} and $CuOH^{+}$ were the dominant dissolved copper 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 having higher values of

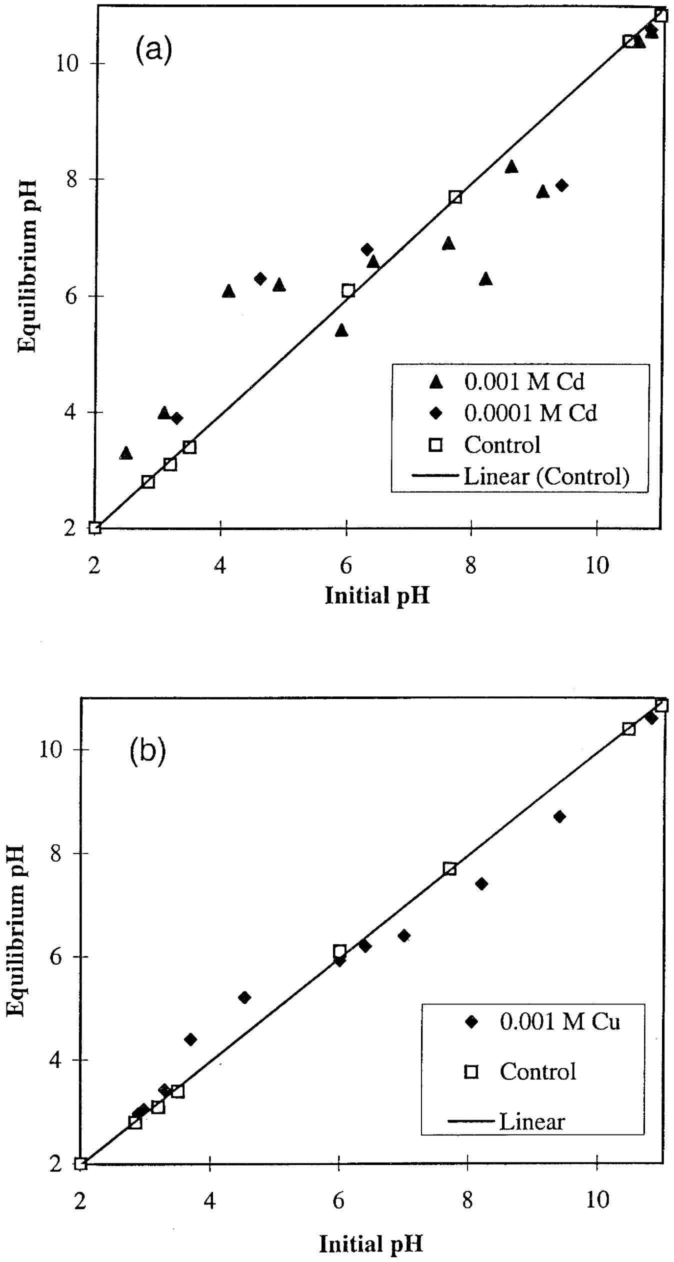


FIGURE 7. Variations in pH during equilibrium (a) cadmium and (b) copper sorption.

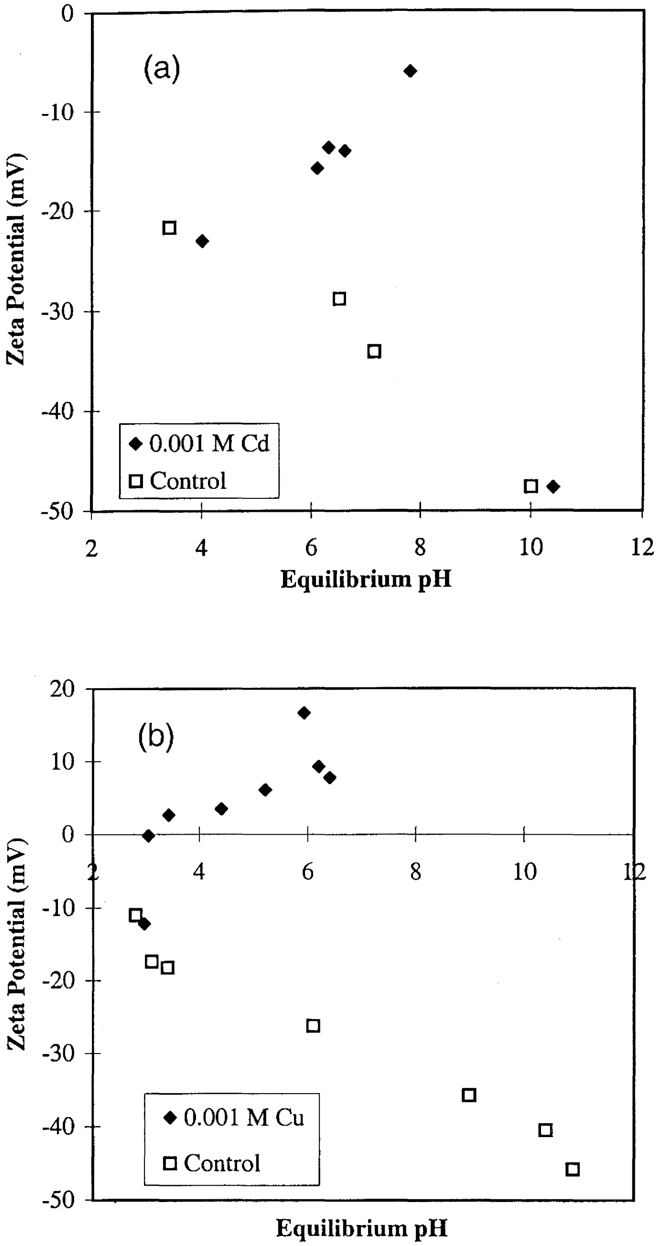


FIGURE 8. Changes in zeta potential due to equilibrium (a) cadmium and (b) copper sorption.

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 therefore, 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 h. Dzombak and Morel (10) reported that sorption kinetics might 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 as well as 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 (11,12,13).

Changes in 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 h. 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

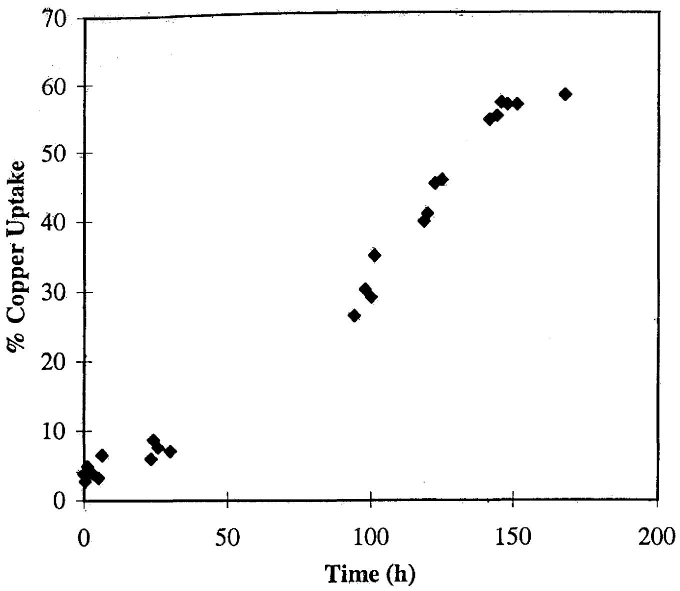
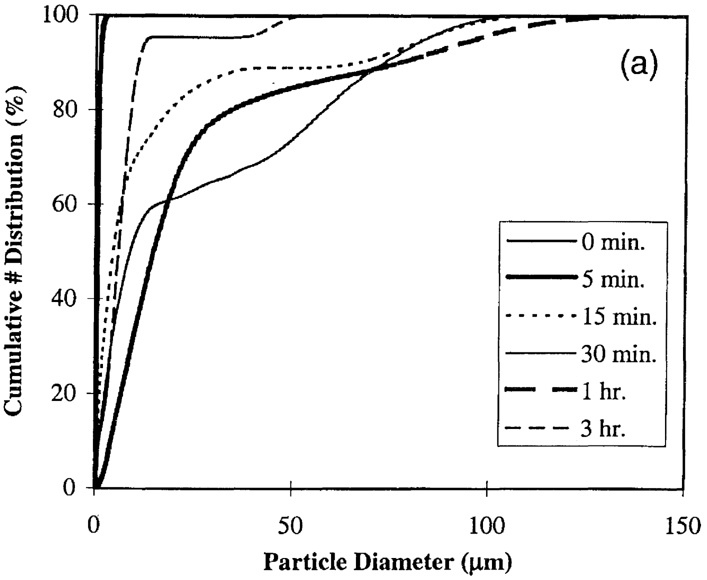


FIGURE 9. Sorption history of copper ion uptake by ferric oxide particles.

cadmium, where aggregates more than 200 times larger than the primary particles (0.3 to 0.8 μm) were formed. Some evidence for particle breakup was also observed in the cadmium uptake experiments. This may have been caused by the agitation in the reaction vessel. Changes in the suspension pH monitored over a period of 50 h for both cadmium and copper uptake are presented in Figures 11a and 11b. In the case of cadmium 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 copper 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 (14).

SUMMARY AND CONCLUSIONS

The results of an experimental investigation of metal ion sorption onto inorganic colloidal particles are reported in this work. The sorption of both copper and cadmium



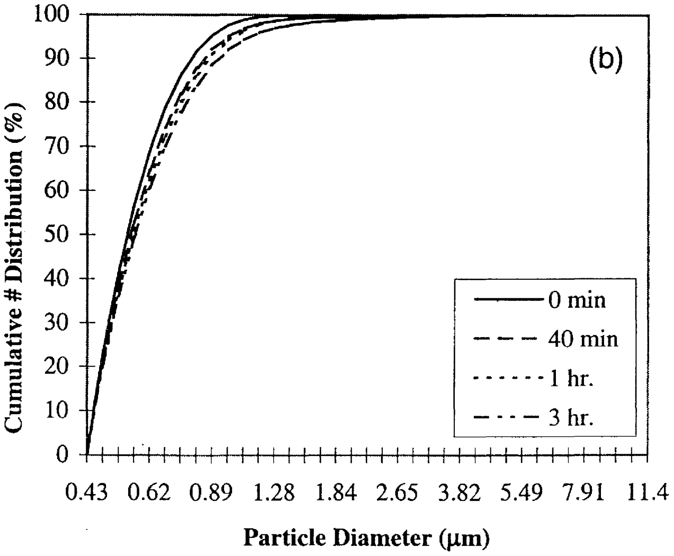
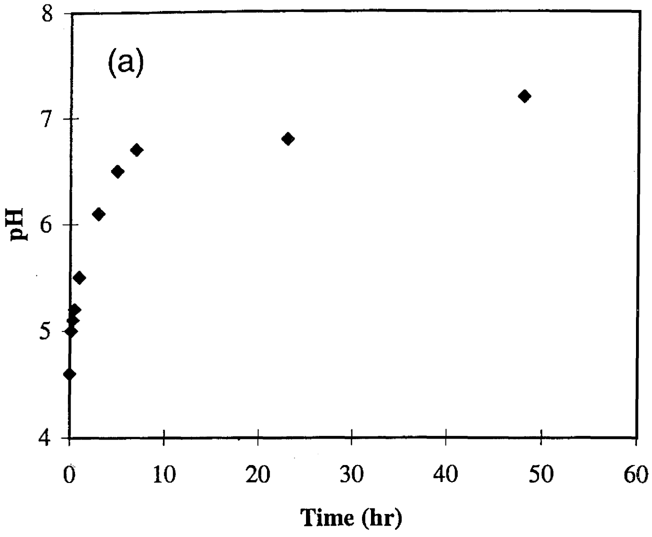


FIGURE 10. Size distribution changes during (a) cadmium and (b) copper kinetic experiments.



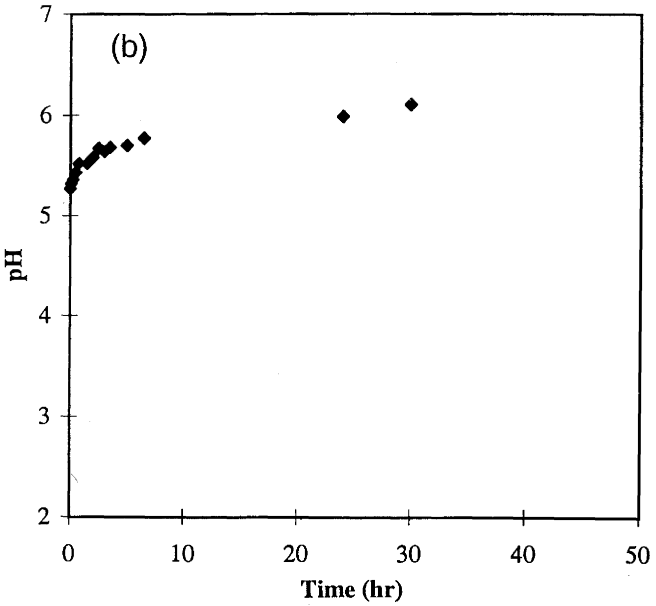


FIGURE 11. pH histories during (a) cadmium and (b) copper kinetic experiments.

appears to be pH dependent, with an increase in the extent of sorption at high pH ranges. Some competition between protons and metal ions for the same types of binding sites is evident. Further, it is clear that copper and cadmium ion sorption alters the surface potential of ferric oxide particles, as an increase in the zeta potential values well over the baseline was found in the equilibrium experiments. This surface charge neutralization observed during sorption equilibrium indicates that destabilization of the ferric oxide particles may occur in aqueous solutions during ion uptake. Size distribution measurements made during sorption dynamics studies indicate possible aggregate formation under conditions of solution pH and ionic strength commonly encountered in natural systems.

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