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BIOSORPTION OF METAL IONS FROM AQUEOUS SOLUTIONS

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ABSTRACT

Copper biosorption from aqueous solutions by calcium alginate is reported in this paper. The experimental section includes potentiometric titrations of biosorbents, batch equilibrium and kinetic studies of copper biosorption, as well as fixed-bed biosorption experiments. The potentiometric titration results show that the surface charge increases with decreasing pH. The biosorption of copper strongly depends on solution pH; the metal ion binding increases from 0 to 90 percent in pH ranging from 1.5 to 5.0. In addition, a decrease in ionic strength results in an increase of copper ion removal. Kinetic studies indicate that mass transfer plays an important role in the biosorption rate. Furthermore, a fixed-bed biosorption experiment shows that calcium alginate has a significant capacity for copper ion removal. The two-pK Basic Stern model successfully represents the surface charge and equilibrium biosorption experimental data. The calculation results demonstrate that the copper removal may result from the binding of free copper and its hydroxide with surface functional groups of the biosorbents.

INTRODUCTION

It has been well documented that biosorbents possess a high potential to sequester and accumulate inorganic ions present in aqueous solutions. Biosorbents have a diverse chemical composition, depending on the material sources, preparation methods, etc. The

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potential binding sites of biosorbents are amino, carboxyl, phosphate, and sulphate groups. Because these active sites could exhibit different chemical properties, they display different affinities or specificity for various metals. The quantity and type of the active sites of biosorbents are a major factor in the binding behavior of metal ions at a given solution pH.

Numerous studies show that the biosorption of metal ions from aqueous solutions is strongly pH dependent. With an increase in solution pH, the metal ion binding increases. Rao et al. (1) studied Cu^{2+} biosorption by *G. lucidum* and *A. niger* at initial copper concentration of 0.5 mM and found that the metal ion binding had an increasing trend from pH 2 to 6, with the maximum occurring between pH 5 and 6. Hao et al. (2) studied the biosorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} at initial metal ion concentration of 5 ppm by using *C. prolitera, P. pavonica,* and *Z. marina.* The results showed that the binding of metal ions increased from pH 2 to 6, with the maximum occurring between pH 5 and 6. On the other hand, for some biosorbents, pH plays a different role in biosorption when the initial metal ion concentrations are different. Hao et al. (2) reported that when the initial concentrations of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} were 10 ppm and *U. lactuca* was used as biosorbent, the metal ion binding was independent of pH. However, when the concentrations of these metal ions were 100 ppm, metal ion removal increased as pH increased. Ke et al. (3) also reported similar results for the biosorption of Ag^{+} by using *Datura* cells. The binding was pH-independent when the initial concentration was 0.1 mM, but it became strongly pH-dependent when the initial concentration increased to 1 mM. These investigations suggest that at least two binding sites are involved (3): one site is pH-independent and displays a greater affinity and lower availability than the other site, which is pH-dependent. Ionic strength also plays an important role in the metal ion biosorption. Chang and Hong (4) reported that the mercury uptake by *P. aeruginosa* decreased with increasing ionic strength. Cho et al. (5) showed that there was no significant decrease in the binding of Cd^{2+} and Zn^{2+} up to the ionic strength of 10^{-3} M, but the biosorption extent diminished when ionic strength exceeded 10^{-2} M. These results indicate that the electrostatic attraction plays an important role in the removal of metal ions by biosorbents.

Even though many experimental studies have been published on metal ion biosorption, few models have appeared in the literature that can be used to predict metal ion biosorption. The most commonly used models in the assessment of biosorption performance are the Langmuir and Freundlich equations. In many cases, these models can give a good representation of the experimental data, however, they fail to predict the effect of pH and other important factors. Jang et al. (6) proposed an extended Langmuir model that takes into account the competition between hydrogen and copper ions for the sorption sites. This model is similar to solution reactions and does not consider the effect of pH and ionic strength on the surface properties of biosorbents. On the contrary, the surface complex formation model (SCFM) takes into account the effects of pH, ionic strength, concentration of metal ion, and other factors. It has been found that SCFM works well in the modeling of metal ion adsorption by hydrous oxides (7,8) and activated carbon (8,9).

There are several studies reported on the kinetics of biosorption. For example, Corder and Reeves (10) demonstrated that no further uptake of nickel by *A. flos-aquae* was observed after 3 hours, which is assumed to be the equilibrium time. Konishi et al. (11) showed that the biosorption of neodymium and ytterbium reached equilibrium in two hours, while Chen et al. (12) reported that the equilibrium time for copper ion was ten hours. Reaction-controlled (11) and diffusion-controlled models (12) were used to describe the kinetics of biosorption.

Very few studies of dynamic continuous-flow biosorption have been reported. Volesky and Prasetyo (13) reported sorption of cadmium with reinforced *Ascophyllum nodosum* biosorbent in a continuous-flow fixed-bed column. The results showed that the exit concentration of cadmium was below 5 ppb when the flow concentration was 10 ppm. They presented an empirical model to describe the fixed-bed performance, but this model can not predict the effect of such important factors as pH.

Advantages of metal ion biosorption and the lack of understanding of its mechanism initiated this research. The research focuses on formulation of an equilibrium model, development of a kinetic model, and establishment of a fixed-bed model. These models will be able to predict the effect of such important factors as pH and ionic strength at given experimental conditions. The research around metal ion biosorption includes experimental and modeling work. Experimental work provides the basis for the development of models, while the models developed will be used to represent the experimental data. Here we report results from the first phase of our research, and subsequent investigation results will be published in the future.

In this study, calcium alginate, one type of biosorbent, was first prepared by polymerization. Titrations of biosorbents, batch equilibrium experiments, batch kinetic experiments, and fixed-bed biosorption experiments were carried out. Modeling of surface charge and equilibrium experiments were conducted by using one of the surface complex formation models, the two-pK Basic Stern (BS) model (8). The parameters of the model were found by using the sequential quadratic programming (SQP) optimization technique (14).

EXPERIMENTAL

Materials

1.5% sodium alginate was prepared by dissolving 1.5 g of sodium alginate (Janssen Chimica, NJ) in 98.5 mL distilled water. 1.0 M calcium chloride was prepared by dissolving 147 g of $CaCl_2 \cdot 2H_2O$ (Janssen Chimica, NJ) in distilled water and diluting to 1.0 L. Calcium alginate was prepared by dripping sodium alginate into calcium chloride solution. The solution was stirred by a magnetic stirrer at speed of 300 rpm for 24 hours in order to stabilize the biosorbent beads. By this procedure, 1.5% calcium alginate was prepared. Calcium alginate with other densities can be obtained by following a similar procedure. The average diameter of biosorbent beads, prepared by the above method, is 2.5 mm with a narrow size distribution. The shape of the biosorbent beads is almost spherical. In the kinetic experiments, biosorbents with smaller size were needed and prepared by introducing compressed air to the mouth of the tube where sodium alginate drips. Turbulence induced by the air reduces the diameter of the sodium alginate drop, and biosorbents with 1.5 mm average diameter were obtained.

Calcium alginate, the biosorbent used in this study, is formed by the complexation of alginate with calcium. In order to check whether calcium alginate is insoluble in water, the total organic carbon (TOC) was measured after stirring calcium alginate beads for 2 hours in distilled water or copper ion solution. The TOC of the solution was found to be very low, and therefore the dissolution of calcium alginate is neglected.

The copper perchlorate was purchased from Alfa (Ward Hill, MA), and the sodium perchlorate, sodium hydroxide, and perchloric acid from Fisher Scientific (Pittsburgh, PA). All chemicals were of reagent grade. The ionic strength of the solution was adjusted by adding appropriate amounts of sodium perchlorate. The titrations were carried out by using a Brinkman 716 DMS Titrino automatic titrator (Westbury, NY). The concentrations of copper were measured using a Varian SpectrAA-10 atomic absorption spectrometer (Palo Alto, CA). The relative error of the concentration measurements is less than 3 percent. The solution pH was measured by an Accumet pH meter 25 from FisherScientific (Pittsburgh, PA). All the samples were filtered using MSI (Westboro, MA) membrane filters (25 mm diameter and 0.45 µm pore size).

Potentiometric Titrations

A 2-mL volume of 1.5% calcium alginate beads was added to a volumetric flask containing 100 mL of 0.05 M sodium perchlorate. The biosorbent beads remained in the solution for 24 hours. The titrations were, then, carried out by using either 1 M sodium hydroxide to increase the pH or 0.01 M perchloric acid to lower the pH. An equilibrium time of two hours was used. During the titration, the flask was covered with parafilm in order to avoid dissolution of carbon dioxide in the solution, and the solution was stirred by a magnetic stirrer at speed of 300 rpm.

Equilibrium Experiments

Copper solutions with different concentrations were prepared, the solution pH was adjusted by adding perchloric acid, and the ionic strength was adjusted at 0.005 M or 0.05 M by adding sodium perchlorate. 100 mL of copper solutions was added to 125 mL flasks. 2 mL of 1.5% calcium alginate beads was then added to the flasks. The flasks were placed in a shaking water bath with the temperature controlled at 25±1°C for 24 hours. The final samples were filtered, acidified, and analyzed by atomic absorption spectroscopy. The final pH was also measured.

Kinetic Experiments

In order to obtain information on the effects of pH and biosorbents' size on the kinetics of biosorption, two series of experiments around these objectives were carried out.

In series one, the experiments focused on the pH effect. 500 mL of 10^{-4} M copper solution was first prepared, the solution pH was adjusted by adding perchloric acid, and the ionic strength was kept at 0.05 M by adding sodium perchlorate. 2 mL of 2% calcium alginate beads was rapidly added to the solution. The solution was stirred by using a magnetic stirrer at speed of 300 rpm. 0.5 mL samples were taken at appropriate times during the experiments, acidified, and analyzed by atomic absorption spectroscopy.

In series two, the experiments concentrated on the mass transfer resistance, therefore biosorbents with different sizes were used. Biosorbent beads of two types, one of 1.5-mm diameter and another of 2.5-mm diameter, were prepared and used in these experiments. 100 mL of 10^{-4} M copper solution was prepared, and the ionic strength was adjusted to 0.05 M. 2 mL of 1.5% calcium alginate beads of one of the two sizes (i.e. 1.5-mm or 2.5-mm) was rapidly added to the solution. The solution was stirred by using a magnetic stirrer at speed of 300 rpm. Samples were taken at appropriate time intervals, acidified, and analyzed.

Fixed-bed Experiment

An up-flow fixed-bed reactor was employed in this study. A 160 mm in height and 28 mm inside diameter column was packed with 1.5% calcium alginate biosorbents. The copper concentration of the influent was 3.05 ppm, and the ionic strength was adjusted by adding sodium perchlorate. The influent pH was 4.3, and the flow rate was 1.25 mL/min. The samples from the effluent were taken at appropriate times, acidified, and analyzed; the pH of the effluent was measured as well.

THEORETICAL

It is assumed that the uptake of metal ions by biosorbents is affected by three processes occurring simultaneously: surface ionization, complex formation, and the formation of an electrostatic double layer adjacent to sorbent surfaces (8). Reaction of metal ions with functional groups on the surface of biosorbents results in the removal of metal ion. The functional groups are treated as analogs of complex ligands in the solution. Electrolyte, e.g. XY, is used to adjust the ionic strength and provide information on the formation of the electrostatic double layer.

The two-pK Basic Stern model is employed to describe the biosorption process here. The schematic representation of the BS model is shown in Figure 1. The two-pK refers to the surface ionization corresponding to three types of surface species (SO^-, SOH, and SOH_2^+) and is associated with two equilibrium constants, K_{H1} and K_{H2}. There are several possibilities to represent the removal of copper ion. The removal may result from the sorption of free metal ion (M^{m+}) or metal ion hydroxide $\left(M(OH)_l^{(m-l)+}\right)$, which forms the surface complex SO^-M^{m+} or $SO^-M(OH)_l^{(m-l)+}$, or a combination of both. In addition, complexation of metal ions by multidentate surface sites, i.e. formation of $\left(SO^-\right)_n M(OH)_l^{(m-l)+}$, may contribute to the binding of metal ion.

The surface protolysis and metal ion sorption reactions are listed in Table 1. Based on the equilibrium expressions derived from the reactions, the electrostatic relations, and the mass balances, the distributions of ions in both solid and liquid phases can be easily obtained by using KINEQL (8) which is similar to MINEQL (15) for equilibrium calculations.

In order to carry out calculations, the values of model parameters have to be known. These parameters include the surface area of biosorbents (in m^2/L), the concentration of functional groups (in M), the equilibrium constants of surface protolysis and biosorption reactions, as well as the capacitance of the electrostatic double layer (C_1). These values are obtained by comparing experimental data to model calculations and using optimization techniques. All estimations of the parameters were carried out by a computer program that includes both KINEQL and SQP and minimizes the following objective function:

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

where $y_{j,measured}$ and $y_{j,calcalated}$ correspond to the experimental data points and calculated results, respectively. NP is the number of experimental data, and NPAR is the number of parameters to be found.

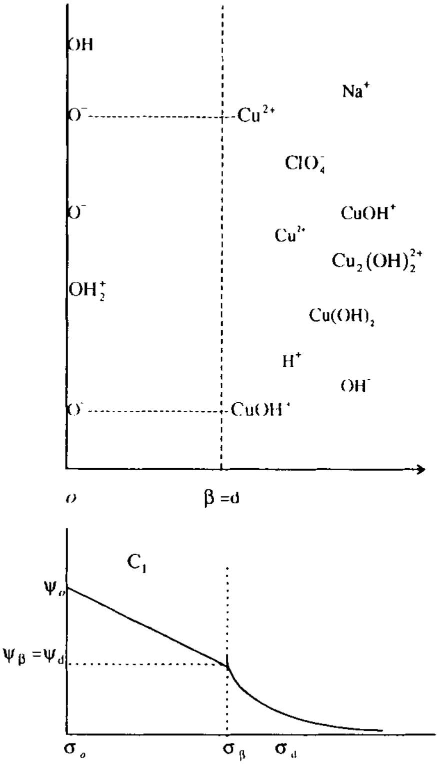

FIGURE 1. Schematic presentation of the Basic Stern model.

The titration of biosorbents provided the information to determine the surface area of biosorbents, the concentration of functional groups, the equilibrium constants of the surface protolysis reactions, and the capacitance of the electrostatic double layer C_1 (see Figure 1). These five parameters were obtained by using the objective function defined by Equation [1] with y_j as the surface charge of biosorbent. Then, based on the equilibrium biosorption experiments and the model parameters determined previously, the equilibrium constants of metal ion biosorption reactions were found by using the objective function defined above, with y_j as the metal ion concentration in solution. As soon as the parameters are obtained, the speciation of ions at equilibrium is well-defined.

Table 1 Two-pK Basic Stern Model for Metal Ion Adsorption

Reactions	Equilibrium Expressions**
Surface protolysis reactions $SOH + H^+ \Leftrightarrow SOH_2^+$	$\frac{[SOH_2^+]}{[SOH]\{H^+\}} = K_{H1}\exp\left(-\frac{e\psi_o}{kT}\right)$
$SOH \Leftrightarrow SO^+ + H^+$	$\frac{[SO^-]\{H^+\}}{[SOH]} = K_{H2}\exp\left(\frac{e\psi_o}{kT}\right)$
Metal ion $\left(M^{m+}\right)$ adsorption* $nSOH + M^{m+} + lH_2O \Leftrightarrow \left(SO^-\right)_n M(OH)_l^{(m-l)+} + (n+l)H^+$	$\frac{\left[\left(SO^-\right)_n M(OH)_l^{(m-l)+}\right]\{H^+\}^{(n+l)}}{[SOH]^n\{M^{m+}\}} = K_{M(OH)_l}^n \times \exp\left(\frac{e\left(n\psi_o - (m-l)\psi_\beta\right)}{kT}\right)$

* n is the number of surface sites in mols/L, which reacts with one mol/L of M^{m+} in solution; n = 1, 2, ..., N. *l* defines the *l*-th hydrolysis product of M^{m+}; *l* = 0, 1, 2,..., L; *l* = 0 corresponds to the simple ion.

**Expressions include electrostatic interactions; if electrostatic interactions are neglected, exponential terms equal to one.

RESULTS AND DISCUSSION

Surface Charge of Biosorbent

The titration of biosorbent at 0.05 M ionic strength was carried out. The surface charge (in C/L) was determined by:

$$\sigma_o = \left(c_A - c_B + \left[OH^-\right] - \left[H^+\right]\right)F \qquad [2]$$

where c_A and c_B are the concentration of acid or base needed to reach a point on the titration curve, in mol/L, $\left[H^+\right]$ and $\left[OH^-\right]$ are the concentrations of H^+ and OH^-

(mol/L) converted from pH and adjusted by Davis equation (16), and F is the Faraday constant (96490 C/mol).

It has to be pointed out that the surface charge is expressed in C/L. For most cases, such as the titration of oxides, the surface charge is expressed in density units (C/m^2) and obtained by (16):

$$\sigma_o = \frac{(c_A - c_B + [OH^-] - [H^+])F}{Sa} \qquad [3]$$

where S is the specific surface area (m^2/kg), and a is the concentration of biosorbent in solution (kg/L). Sa in Equation [3] represents the total surface area of sorbent per volume of solution (m^2/L). Calcium alginate beads contain 98.5% of water, and therefore it is difficult to measure their surface area with conventional methods. For this reason, in this study, we express surface charge in C/L instead of surface charge density units (C/m^2).

The surface charge vs. solution pH is shown in Figure 2. (Points represent experimental data, while the line represents modeling results.) With increasing pH, the surface charge decreases and becomes less positive, implying that at higher pH, the biosorption of metal ion will be higher.

The modeling of surface charge was carried out based on the two-pK BS model which is described by the reactions 1 and 2 of Table 2. A computer program combining both KINEQL and SQP was used to search for the surface area of biosorbents, the concentration of functional groups, the equilibrium constants of the reactions, as well as the capacitance C_1. The representation of surface charge is given in Figure 2, and the parameters found are listed in Table 3. The quality of the fit is judged from the value of SHAT; the parameter optimization gave a SHAT value of 0.08. The model gives a good representation, indicating that SCFM can successfully represent the surface charge of biosorbent.

Equilibrium Biosorption

Equilibrium experiments with initial pH ranging from 1.5 to 6.0, initial copper ion concentration (Co) of 1×10^{-4} M, and ionic strengths of 0.005 M and 0.05 M, were carried out with the results shown in Figures 3a and 3b. (Points represent experimental data, while line represents modeling results.) The removal efficiency increased from

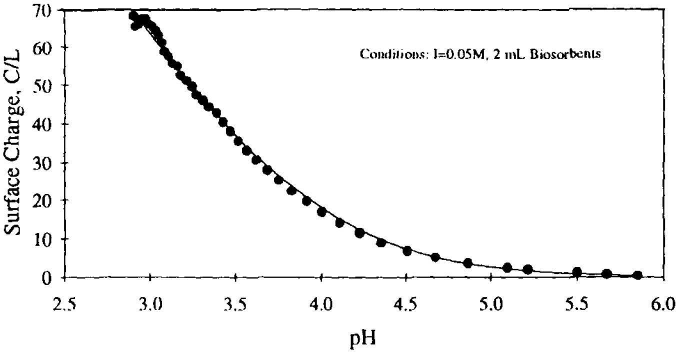

FIGURE 2. Effect of pH on surface charge.

Table 2 Surface and Solution Reactions

Surface Reactions:

1. $SOH + H^+ + \exp(-y_o) \overset{K_{H1}}{\Leftrightarrow} SOH_2^+$
2. $SOH - H^+ - \exp(-y_o) \overset{K_{H2}}{\Leftrightarrow} SO^-$
3. $SOH + Cu^{2+} - H^+ + 2\exp(-y_\beta) - \exp(-y_o) \overset{K_{Cu}}{\Leftrightarrow} SO^-Cu^{2+}$
4. $SOH + Cu^{2+} - 2H^+ + \exp(-y_\beta) - \exp(-y_o) \overset{K_{CuOH}}{\Leftrightarrow} SO^-CuOH^+$

Solution Reactions:

5. $Cu^{2+} - H^+ \Leftrightarrow CuOH^+$
6. $Cu^{2+} - 2H^+ \Leftrightarrow Cu(OH)_2$
7. $2Cu^{2+} - 2H^+ \Leftrightarrow Cu_2(OH)_2^{2+}$

$y_o = e\psi_o / kT$, $y_\beta = e\psi_\beta / kT$

ψ_o and ψ_β are potentials at o-layer and β–layer, respectively.

Table 3 Parameters of Two-pK Basic Stern Model

Name of Parameter	Value of Parameter
C_1	$25.3\mu F / cm^2$
K_{H1}	$10^{0.49} M^{-1}$
K_{H2}	$10^{-13.00} M$
Surface Area	$10^4\ m^2/L$
Concentration of Functional Groups	0.924 M

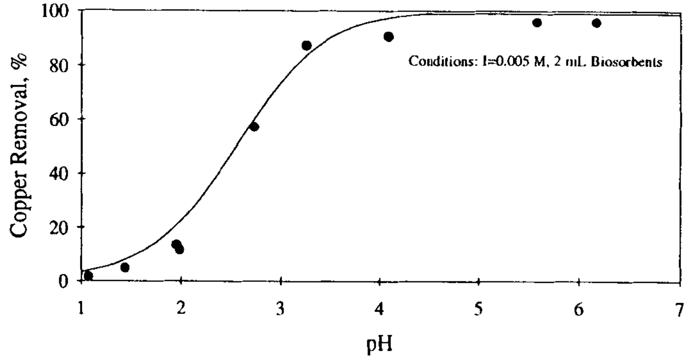

FIGURE 3a. Copper ion biosorption at I=0.005 M.

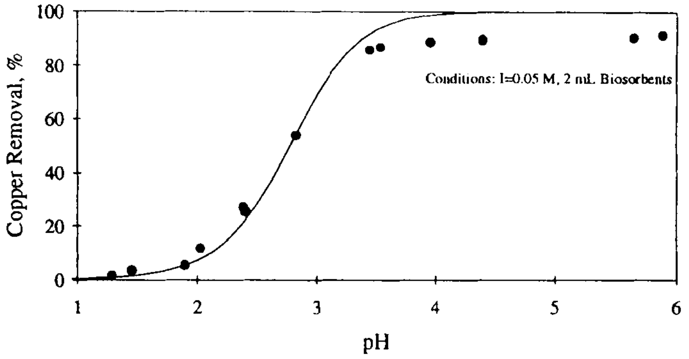

FIGURE 3b. Copper ion biosorption at I=0.05 M.

zero to 90 percent in a narrow pH range, and the sorption edge was between pH 1.5 and 5.0. The titration and equilibrium biosorption experiments clearly showed that the surface groups of biosorbents are analogous to weak acids. As pH becomes higher, more negatively charged sites become available, and therefore the metal ion removal efficiency is higher. At the same time, higher pH may result in metal ion removal by the so-called surface precipitation suggested by Farley et al. (17). Furthermore, by decreasing the ionic strength, the copper removal increases. This is contrary to what was observed in the adsorption of metal ions by activated carbon and hydrous oxides (8,9). One explanation is that some of the functional groups may be compressed due to some unknown reactions occurring at the higher ionic strength. Another explanation is the competition for the functional groups between copper ion and other ions. When more ions, other than copper, are brought to the solution (in other words, when ionic strength is higher), they may compete with copper for the functional groups, which results in less availability of the functional groups for the copper ion. Therefore, as ionic strength becomes higher, uptake of copper ion decreases. Similar results have been reported by Chang and Hong (4) and Cho et al. (5). During the biosorption, the solution pH did not change dramatically as shown in Figure 4, compared to the dramatic change of pH in the copper ion adsorption by activated carbon (9).

The two-pK BS model was employed to model equilibrium biosorption. Surface reactions 1 to 4 and solution reactions 5 to 7 of Table 2 were included in the calculations. The equilibrium constants of reactions 1 and 2, the capacitance C_1, the surface area of biosorbents, as well as the concentration of functional groups, were obtained previously from the modeling results of surface charge, and the equilibrium constants of reaction 5 to 7 are easily found from the literature (8). KINEQL and SQP were used in the modeling of equilibrium biosorption, with the results shown in Figures 3a and 3b, and Table 4. The model gives a good representation of experimental data. The calculation results indicate that copper biosorption results from the sorption of free copper ion and its hydroxide.

The model presented here successfully predicts the effect of pH on metal ion biosorption. It has to be pointed out, however, that two sets of equilibrium constants of metal ion biosorption reactions were used for the two different ionic strengths. In other words, the model presented here can not predict the effect of ionic strength with a unique set of parameters. There may be some other reactions different from those presented in this work that contribute to metal ion removal, and in future work, a research towards finding those reactions will be carried out.

Kinetic Biosorption Experiments

In order to obtain the information of relative importance of mass transfer and sorption reaction, kinetic experiments were carried out, with the results shown in Figures 5 and 6. In Figure 5, one can see that at low pH, there is minimal biosorption occurring,

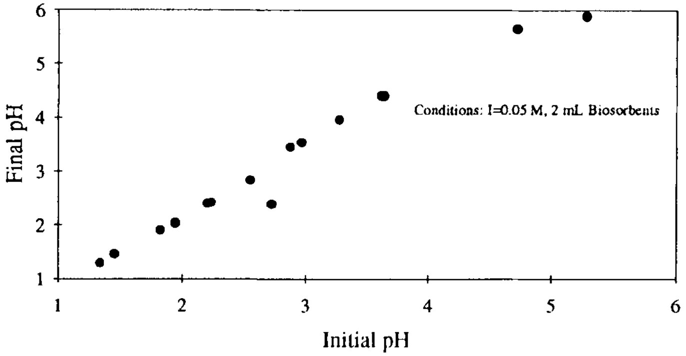

FIGURE 4. pH variation in the copper biosorption.

Table 4 Equilibrium Constants of Copper Biosorption Reactions

No	Ionic Strength	Parameters	SHAT
1	0.005 M	$K_{Cu} = 10^{-2.26}$, $K_{CuOH} = 10^{-9.01}$ M	0.66
2	0.05 M	$K_{Cu} = 10^{-4.41}$, $K_{CuOH} = 10^{-6.02}$ M	0.69

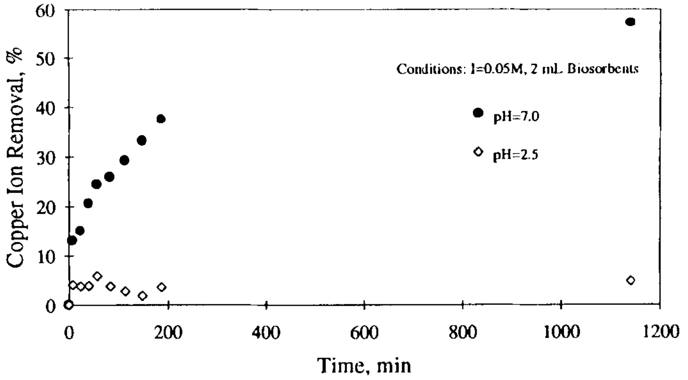

FIGURE 5. pH effect on biosorption history.

while at high pH, the biosorption increases. After several hours, most of copper ion is removed. Furthermore, the biosorbent size plays an important role. As shown in Figure 6, with increasing size, the biosorption rate decreases, indicating that mass transfer plays an important role in the biosorption rate. The biosorption begins with a rapid phase followed by a slow phase, which is similar to the copper adsorption by activated carbon (9). Some of the experimental data in Figure 6 seem to be very close; however, it has to be pointed out that the removal percentage difference between these two cases is relatively larger than the experimental error.

There are limited studies reported in the literature on modeling of the biosorption kinetics. The reaction-controlled and diffusion-controlled models were employed to describe the kinetics of biosorption. Tanaka et al. (18) found that the diffusion coefficients of substrates, such as glucose, into and out of the Ca-alginate gel agreed with those in water. Based on this result, Konishi et al. (11) assumed that resistances to both external mass transfer and intraparticle diffusion were insignificant and found that the biosorption kinetics was reaction-controlled. On the other hand, by assuming that chemical reactions were much faster than mass transfer, Chen et al. (12) employed a linear absorption model to describe the copper biosorption and found that the model fitted the experimental data well. These two models may be correct under their particular experimental conditions, however, they can not predict the effect of pH and ionic strength. Furthermore, both models cannot be extended to reactive multicomponent systems, i.e. systems with more than one metal ion and several reactions. As a result, such models are system specific and can not be used to predict the effect of various environmental variables, such as pH, ionic strength, metal ion concentration, as well as sorbent concentration. An algorithm named KINEQL has been developed by Yiacoumi and Tien (8,19,20) to calculate the rates of metal ion uptake when the uptake rate is controlled by either mass transfer or adsorption reaction. KINEQL is a general algorithm for solving kinetic problems encountered in aqueous systems. It has been showed that this model gives a good representation of metal ion adsorption kinetics by hydrous oxides (8,19,20) and activated carbon (9). Based on the above considerations, modeling of biosorption kinetics is being carried out by using KINEQL.

The biosorbents contain 98.5 percent of water, which indicates that the diffusivity of copper ion in the biosorbents is expected to be close to that in water. In addition, since

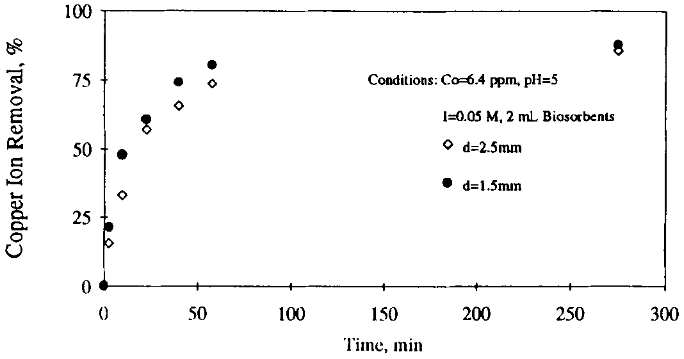

FIGURE 6. Effect of biosorbent size on biosorption history.

calcium alginate contains a significant amount of water, it is an exceptionally hydrophilic polymer and should display very rapid rates of biosorption reactions. Therefore, it is suspected that external mass transfer will be the rate-limiting step in sorption. Based on these observations, a mass transfer model will first be considered in our modeling. This work is part of our research to describe the kinetics of metal ion sorption by calcium alginate. Modeling the kinetics of metal ion biosorption from aqueous solutions is the objective of future work.

Fixed-bed Experiment

A fixed-bed biosorption experiment was carried out, and the ratio of the concentration of effluent to that of influent (C/Co) vs. time is shown in Figure 7. The breakthrough occurred in the beginning of the experiment, and the column reached saturation in 300 hours. The effluent pH was 4.3, compared to the influent pH of 4.4. The fixed-bed result indicates the high capacity of the biosorbent for the removal of copper ion. In this experiment, a column with height of 160 mm and diameter of 28 mm was used, and the average diameter of biosorbents was 2.5 mm. The observed breakthrough curve has a gradual shape. If the dispersion in the column is small, the spreading of the breakthrough curve may be caused by the mass-transfer limitations discussed in the Kinetic Biosorption Experiments section.

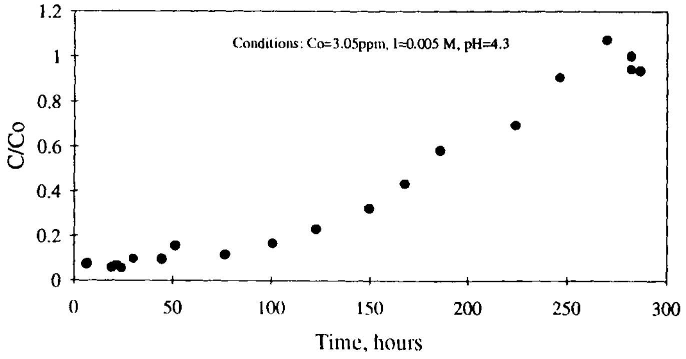

FIGURE 7. Breakthrough curve from the fixed-bed biosorption experiment.

Fixed-bed experiments under different pH, ionic strength, and concentration of metal ion will be carried out in the future to provide the basis for the development of a fixed-bed biosorption model. This fixed-bed model will also consider effects of pH, ionic strength, metal ion concentration, and biosorbent concentration, and will be developed based on the surface complex formation model discussed previously and applied to the modeling of biosorption equilibrium data.

SUMMARY

Calcium alginate, a biosorbent, was prepared by polymerization. Potentiometric titrations of biosorbents, batch equilibrium and kinetic experiments, as well as fixed-bed biosorption experiments of copper ion, were carried out with the objective to obtain sufficient information for the development of a predictive model. The results show that with increasing solution pH, surface charge decreases. Both pH and ionic strength play an important role in the copper ion biosorption. The copper removal increases from 0 to 90% in the pH range of 1.5 to 5.0. In addition, high ionic strength is found to decrease the extent of biosorption. The effect of pH on surface charge and equilibrium biosorption is successfully predicted by using the surface complex formation model.

Kinetic experiments show that the biosorption rate is enhanced when biosorbents of smaller size are used, indicating that mass transfer plays an important role in the biosorption kinetics. Fixed-bed experiments show that the biosorbent used in this work has a high capacity for copper ion removal.

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