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CHARACTERIZATION OF A Ca-ALGINATE BASED ION-EXCHANGE RESIN AND ITS APPLICATIONS IN LEAD, COPPER, AND ZINC REMOVAL

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ABSTRACT

Characterization of a novel ca-alginate based ion-exchange resin and its application in metal removal were investigated. The metal removal percentages increased from almost 0 to nearly 100% for metal concentrations < 0.1 mmol/L at pH 1.2 to 4, and a plateau was established at pH > 4. The removal percentages were in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$ at pH < 4. Lower initial concentrations and ionic strengths slightly enhanced the removal percentage. The maximum metal removal capacities ($q_{\max}$) were 2.01 and 2.04 mmol/g for lead and copper, respectively, which are much higher than activated carbons and other reported biosorbents. Competitive effects were important for zinc removal, but less significant for lead and copper uptake. Organic chemical leaching from the resin was negligible.

The single- and multiple-species metal ions were removed completely within approximately 90 and 130 minutes, respec-

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tively. The lead removal became much faster when its concentration was decreased and in the absence of other metal ions. Presence of competitive metal ions significantly reduced the metal uptake rate. Removal process kinetics were controlled by the mass transfer, while the local equilibrium followed an ion-exchange relationship.

Key Words: Ca-alginate based ion-exchange resin; Metal removal; Equilibrium; Kinetics; Competitive effect

INTRODUCTION

Increasing levels of toxic heavy metal contamination in aqueous environments has become a common problem in many developing countries (1,2). Precipitation, ion exchange, activated carbon adsorption, membrane technologies, and electrodialysis are the existing treatment approaches for the removal of metal from aqueous solution of various strengths. Although they have been used for many years, these technologies have disadvantages.

Removal of heavy metal ions from waste streams by inexpensive recyclable biosorbents has emerged as an innovative technique since 1980 (3). The major advantage is the high removal efficiencies for metal ions. This process is normally termed as biosorption. Normally biodegradation is not involved in the process because most biosorbents are inactive. The term "biosorption" is used simply because the biosorbents are made from the organisms, such as bacteria and seaweed.

Parameters affecting the biosorption processes include pH, metal concentration, and ionic strength (3–7). Sag, Ozer, and Kutsal (7) reported that *Z. ramigera* and *R. arrhizus* exhibited the highest lead removal rate at pH 4.5–5.0. A study by Kapoor, Viraraghavan, and Cullimore (8) illustrated that the biosorption by *Aspergillus niger* increased sharply when pH was increased from 3 to 4. Uptake of lead and cadmium reached equilibria in 5 hours, while copper and nickel were completely removed in 6 hours. The biosorbent could be used for 5 cycles after elution with HNO_3. Seaweeds and their derivatives have been used to sequester copper, nickel, lead, zinc, and cadmium (9). The metal concentrations were decreased to less than 1 mg/L from their initial values of 10 mg/L. The final copper concentration was consistently reduced to as low as 0.2 mg/L after 11 cycles of batch operations.

As the organisms are cumbersome to obtain, application of biopolymers extracted from the organisms has attracted much attention (3). Alginate, commercially available in the form of sodium alginate, is one of the biopolymers for metal removal. It is a high molecular-weight biopolymer composed of chains of 1,4-linked β-D-mannuronic and α-L-guluronic acids (10). When the alginate is used for metal removal, it is usually prepared as calcium alginate beads that contain a huge amount of water (11,12). These beads reportedly had a relatively high capacity for copper removal. The alginate is also used to immobilize microorganisms for metal uptake. Fixed-bed columns packed with calcium alginate-immobilized biomass of *Pseudomonas aeruginosa* PU21 were used to treat the lead waste stream (13). The study showed that the metal removal capacities of the calcium alginate–and polyacrylamide-immobilized cells were 1.35 and 0.15 mmol Pb/g, respectively. The columns can be regenerated by elution with HCl solution at pH 2.0. In addition, several papers documented successful application of sodium alginate in metal removal (14,15).

The removal rate by the calcium alginate beads prepared by the conventional approach is lower than is that by activated carbons because the activated beads are normally larger (5). A new type of ca-alginate based ion-exchange resin with high metal removal was first prepared by a simple method (16). Copper and zinc removal capacities and the reaction kinetics were investigated (16); however, the detailed characterization of the resin and the application in lead and other metal removal were not completed. We investigated the removal capacity and kinetics under various conditions, such as pH and initial concentrations. A series of experiments aimed to characterize the resin were conducted. Competitive effects of various metals were also studied. Based on the data obtained, the mechanisms for the metal ion uptake were examined.

MATERIALS AND METHODS

The ca-alginate based ion-exchange resin was prepared by dispersing 10–20 g powdery sodium alginate (Fluka, Switzerland) into a stirred 1-L 0.1 mol/L $CaCl_2$ solution. Solid beads were immediately formed. The solution was normally stirred for 1 day to stabilize the resins, which subsequently were washed with deionized water 3 times to remove the $CaCl_2$ from the surfaces. After drying at 60°C for 2 days, the resins were cooled and stored in a desiccator for the experiments. The calcium chloride solution was recycled in the resin preparation in subsequent runs.

The light yellow resins had an averaged diameter of 0.385 mm (measured by an Olympus light microscope, Japan) and a density of 1500 kg/m^3. The diameter found was smaller than the one reported (16), possibly due to the longer stirring time (1 day) used in our study. Measurement by a total organic carbon analyzer (LabTOC2100, Zellweger Analytics, USA) showed that the total carbon (TC) of the resin was approximately 0.16 gTC/g resin.

Digestion experiments were first conducted to determine the amount of total calcium in the resins and sodium alginate. Both of the resin and sodium alginate were dissolved by calcium- and sodium-free hydrogen peroxide and nitric acid on a heater until no solids were observed. The calcium concentrations of both samples were then measured by an inductively coupled plasma emission spectroscopy (ICP-ES) (Perkin Elmer Optima 3000, USA). Because the resins contained calcium ions, these cations could be exchanged with hydrogen ions in the solutions. The resins were placed into 100-mL solutions with various initial pH values. The final pH and calcium concentrations were measured.

In the equilibrium studies, we prepared copper, lead, and zinc solutions by dissolving the metal salts (J. T. Baker, Phillipsburg, NJ, USA) in deionized water. The resins were added into the conical flasks that contained the metals with different concentrations and pH values. The flasks were placed in a shaking water bath with temperature controlled at 25°C for 2 days. The final samples were acidified by HCl according to the instrumental requirement of the ICP-ES. They were subsequently filtered by Whatman Autovial syringeless 0.45 μm polytetrafluoroethylene filters (Clifton, NJ, USA) and analyzed by the ICP-ES. In addition, the organic contents of some samples were measured by a Shimadzu TOC analyzer (Model 5000a, Shimadzu, Japan).

A series of kinetic experiments with various metals and at $\mathrm{pH} > 4.0$ were carried out. The resins were added to the solutions while being stirred. The samples were taken at periodic time intervals, acidified, filtered, and analyzed by ICP-ES.

RESULTS AND DISCUSSION

Characterization of the Ca-Alginate Based Resin

The digestion experiments showed that the calcium contents in the ca-alginate resins and sodium alginate were 3×10^{-3} and 2×10^{-4} mol/g, respectively. The calcium content was slightly higher than that previously reported (16), probably due to the slight differences in calcium concentrations and amounts of sodium alginate used in the preparation and/or was the result of incomplete resin washing. In addition, the used calcium chloride solutions were sometimes recycled to save cost, which could have affected the outcome.

An increase in the pH was observed after the resins were placed in the solutions with various initial pH values for 48 hours (Fig. 1a). The leaching of calcium ions was observed; ionic strength decreased as the pH increased. This observation demonstrates that the ca-alginate resins have ion exchange properties. The decrease in activity of hydrogen was plotted against the increase in activity of calcium (Fig. 1b). The linear relationship in the diagram demonstrated that 1 mol of calcium in the resin could be exchanged with 2 mol of hydrogen in the solution.

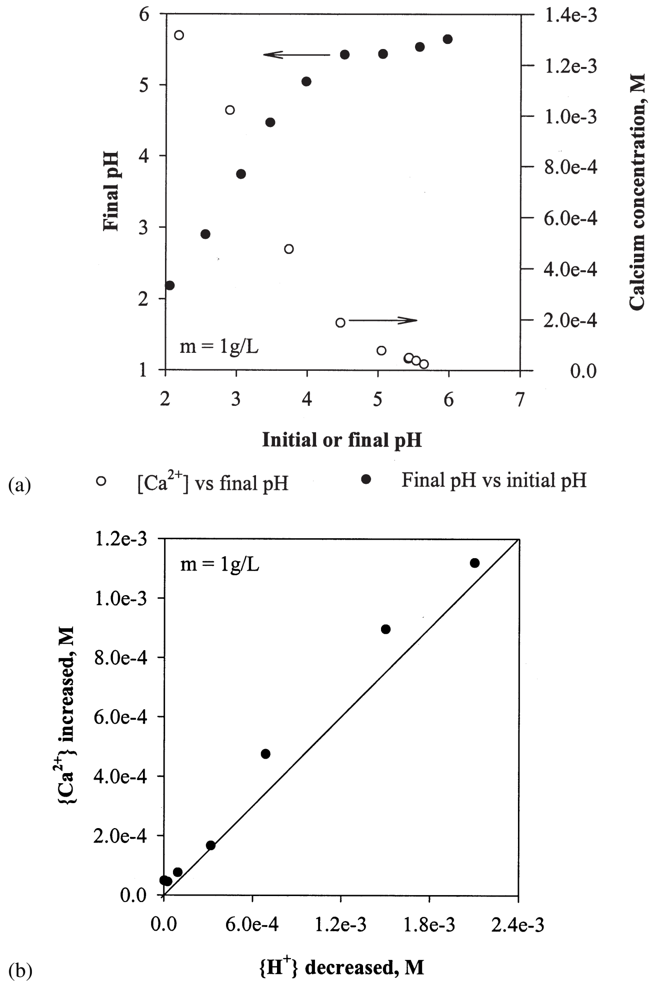


Figure 1. Characterization of the ca-alginate based resins: (a) effect of initial pH on final pH and release of calcium ions; (b) ion exchange reaction.

In other words, $\{H^+\}_{\text{decreased}} = 2\{Ca^{2+}\}_{\text{increased}}$. Thus, it can be proposed:

$$2H^+ + [Ca^{2+}R^{2-}] \rightarrow Ca^{2+} + [H_2R] \qquad (1)$$

where H^+ is the hydrogen ion in the aqueous solution and R symbolizes the negatively charged functional groups of the cation exchanger. The bracket ([ ]) represents the solid phase. According to this reaction, reduction of 1 mol hydrogen causes an increase of 2 mol calcium.

EQUILIBRIUM STUDY

Single-Species Metal Ion Removal

Equilibrium experimental studies at various pH values, initial concentrations, types of anions, and ionic strengths (NaCl) were conducted. As shown in Fig. 2, the sharp increase in the lead uptake from 5 to almost 100% from pH 1.2–4.0 was observed and a plateau was formed at pH > 4.0. Similar findings of metal removal by other biosorbents were reported (11,17). In addition, the diagram shows that the critical pH for the maximum metal uptake (pH_{cr}) shifted to the right when the initial concentration was increased. For example, the pH_{cr} values were 2.8 and 4.5 for the initial concentrations of 0.03 and 0.89 mmol/L, respectively. In addition, ionic strength seems to have little impact on the pH_{cr} value.

The pH-dependence for metal removal can be interpreted on the basis of ion exchange reactions. In the pH range employed in our study, lead exists as Pb^{2+} according to the metal speciation calculation by *MINEQL* (18). These ions can exchange with calcium ions (Ca^{2+}) in the solid matrix according to

$$Pb^{2+} + [Ca^{2+}R^{2-}] \rightarrow Ca^{2+} + [Pb^{2+}R^{2+}] \tag{2}$$

Because hydrogen ions are also positively charged, a similar ion exchange reaction occurs between hydrogen and calcium as shown in Eq. (1). Previous re-

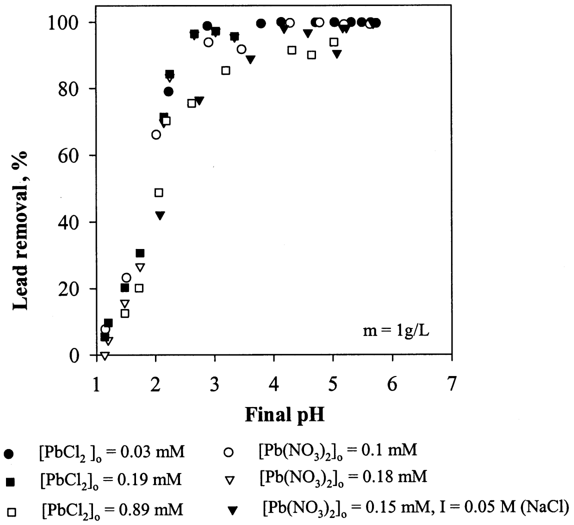


Figure 2. Effect of pH, initial concentration, presence of anions, and ionic strength on lead removal.

search shows that the pK values of guluronic and mannuronic acids are 3.65 and 3.38, respectively (19). Hydrogen ions would compete with lead ions for the exchangeable sites. As a result, less exchangeable sites are available at lower pH. We concluded that the optimum metal removal can be achieved at $\mathrm{pH} > 4.0$.

The presence ionic strength (NaCl) slightly lowered the metal ion removal. At $\mathrm{pH} > 3.5$, the removal for the initial concentration of 0.03–0.19 mmol/L was almost 100% in the absence of ionic strength, while the removal efficiency at an ionic strength of 0.05 mol/L and an initial concentration of 0.15 mmol/L was decreased to 95%. This result is contrary to the observations of metal ion adsorption by hydrous oxides (20) and activated carbons (21). In those cases, the removal increased with an increasing ionic strength as a result of the electrostatic double-layer compression (21). The competition between lead and sodium ions for the exchange sites in our case became important, resulting in the lower lead removal.

The initial lead concentration can affect the removal percentage as shown in Fig. 2. As the initial concentration was increased, the removal percentage reduced. In addition, the effect of anions on metal removal was found less important (see the cases of $Pb(NO_3)_2$ and $PbCl_2$). In these 2 solutions, the free lead ions were removed according to Eq. (2). In addition, $PbCl^+$ and $[Ca^{2+}R^{2-}]$ could have similar ion exchange reactions as that depicted in Eq. (1). As a result, no obvious difference in the removal was observed.

The solution pH increased slightly in the experiments; an example is shown in Fig. 3a. As discussed, the calcium inside the resins can exchange for some hydrogen in the solution, leading to the increase in pH. To determine the role of ion exchange in the lead uptake by the resins (Eqs. 1 and 2), we plotted the increase of $\{Ca^{2+}\}$ against the decrease of $(\{H^+\}/2 + \{Pb^{2+}\})$, as illustrated in Fig. 3b. All points were linearly fitted (1/1), indicating that ion exchange played a major role in the metal uptake process.

Equilibrium experiments of copper and zinc were performed, and the results are illustrated in Fig. 4 together with those of lead removal. As observed, higher solution pH resulted in the higher metal removal. For these 3 metal concentrations up to 0.1 mmol/L, the removal increased from 2–10% to almost 100 % in pH 1–5. The removal curves of lead, copper, and zinc ions shifted from left to right. The pH_{cr} values for lead, copper, and zinc were 4.0, 4.0, and 5.0, respectively. When the pH was between 1 and 3.5, the removal for these metals is in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$. For example, at pH 3 the removal percentages for lead, copper, and zinc were 95, 70, and 45%, respectively. The variation in metal removal efficiency for these metals could be caused by the different affinities between the metal and the functional groups on the resin. When the pH was increased to above 5.0, the removal for all the metal ions reached its maximum values (greater than 95%).

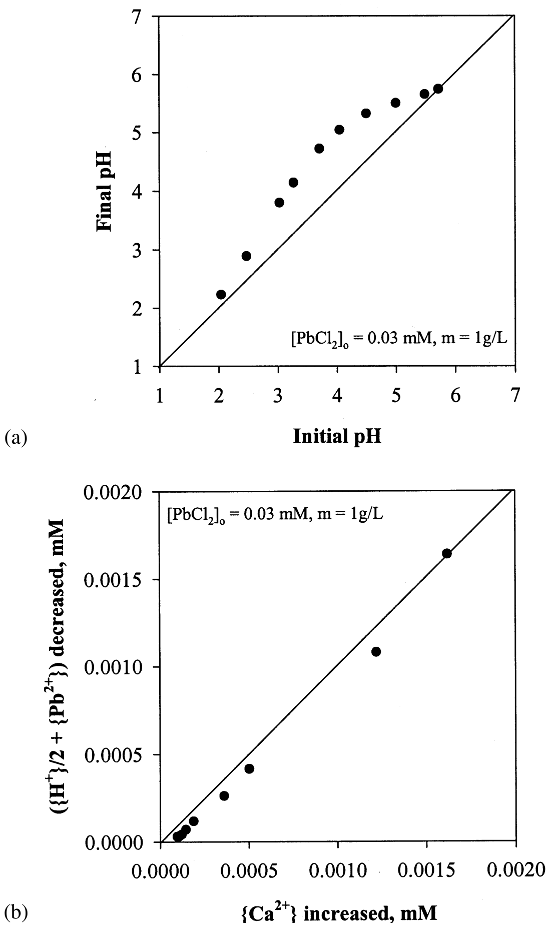


Figure 3. Lead removal as a function of pH: (a) pH variation, and (b) ion exchange reaction.

A series of experiments for determining the adsorption isotherm parameters for lead and copper removal were carried out at pH 4–5. Metal removal capacity (q, mg/g) is defined as amount of metal removed (mg) per mass of the resins (g), while C_e is the equilibrium metal concentration (mg/L). The Langmuir equation fitted the experimental data much better than did the Freundlich equation. The Langmuir equation can be expressed as

$$q = \frac{q_{\max} b C_e}{1 + b C_e} \tag{3}$$

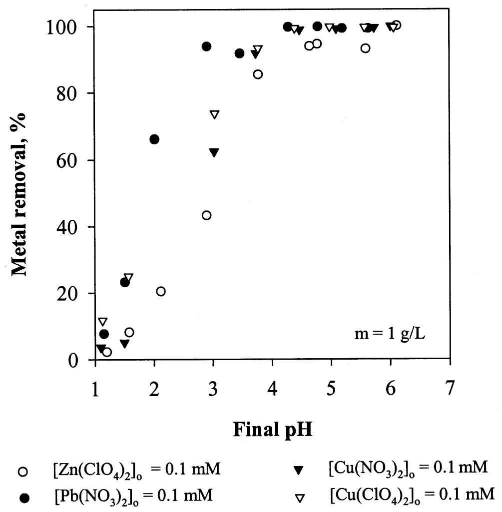


Figure 4. Effect of pH on single-species metal removal.

where $q_{\max}$ and b are the maximum metal removal capacity and the Langmuir constant, respectively. Equation (3) can be rewritten as:

$$\frac{C_e}{q} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \tag{4}$$

C_e/q was plotted against C_e for lead and copper removal as shown in Fig. 5.

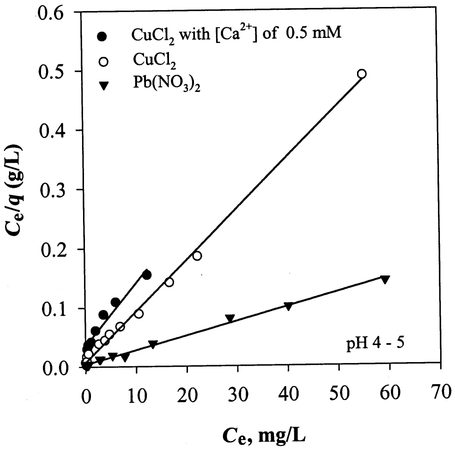


Figure 5. Determination of Langmuir equation constants: lead and copper removal.

q_{max} and b values for lead and copper were 416.7 mg Pb/g, 129.9 mg Cu/g (or 2.01 mmol Pb/g and 2.04 mmol Cu/g), and 0.7059 (mg Pb/L)$^{-1}$ and 0.8462 (mg Cu/L)$^{-1}$, respectively. q_{max} for copper was slightly higher than the 115.4 mgCu/g reported by (16), probably due to the difference in calcium content in the resins.

The existence of calcium ions had an effect on metal removal. Isotherm experiments for copper in the presence of calcium were conducted with the resins prepared in the same manner as those used in experiments depicted in Fig. 5. q_{max} and b were 112.4 mg Cu/g (or 1.76 mmol Cu/g) and 0.2312 (mg Cu/L)$^{-1}$, respectively, compared to q_{max} of 129.9 mg Cu/g (2.04 mmol Cu/g) and b of 0.8462 (mg Cu/L)$^{-1}$ in the absence of calcium. The presence of calcium slightly reduced the removal capacity, which is a result that can be explained through Eq. (2).

A series of experiments were carried out previously to determine the copper adsorption capacity by the carbons from Calgon. The solution pH was maintained slightly above 6 to avoid the negative pH effect. The q_{max} values for copper were approximately 1.5, 3.35, and 7.04 mg Cu/g (or 0.02, 0.05, and 0.11 mmol Cu/g) at the ionic strength (NaCl) values of 0, 0.005, and 0.05 mol/L, respectively. In addition, the q_{max} for lead was 15.04 mg Pb/g (or 0.07 mmol Pb/g) at ionic strength (NaCl) of 0. Filtrasorb 400 from Calgon can remove lead and copper with the q_{max} values of 0.15 and 0.03 mmol/g, respectively (22). A study conducted by Marshall et al. (23) on the enhanced metal adsorption by soybean hulls modified with citric acid showed that the q_{max} for copper was 1.7 mmol/g.

Metal biosorption by marine macro algae had the capacity to remove lead, copper, and cadmium in the ranges of 1.0–1.6, 1.0–1.2, and 0.8–1.2 mmol/g, respectively (6). Comparison of several biosorbents for lead removal reported by Suh and Kim (24) shows that the maximum uptake capacities of activated sludge, *Saccharomyces cerevisiae,* and *Aureobasidium pullulans* were 0.14, 0.46, and 0.82 mmol Pb/g. The resin used here had higher metal uptake capacities than reported activated carbons and other biosorbents.

The q_{max} values for lead and copper ions in our study were almost the same, and they were higher than the q_{max} for zinc (1.08 mmol/g) in the previous studies (16). Matheickal and Yu (17) indicated that the removal of lead was slightly higher than that of copper when several microorganisms were employed. Brady and Tobin (25) reported that metal ion removed by *R arrhizus* decreased in the order of Pb $>$ Cu $>$ Cd $>$ Zn $>$ Mn $>$ Sr. Comparisons of the results of various biosorbents show that the metal uptake for various metal ions follows a certain trend due to the affinities between metals and organic sorbents.

Based on the adsorption isotherm experimental data, we plotted the concentration of decreased against that of calcium ions increased (Fig. 6). All the points were linearly fitted for a slope of 1, demonstrating that lead ions were exchanged with calcium ions to an identical extent. According to Eq. (2), the amount of lead ions removed is equal to that of calcium ions released into the solution. As the calcium content was 3.0 mmol/g, the theoretical maximum metal-removal ca-

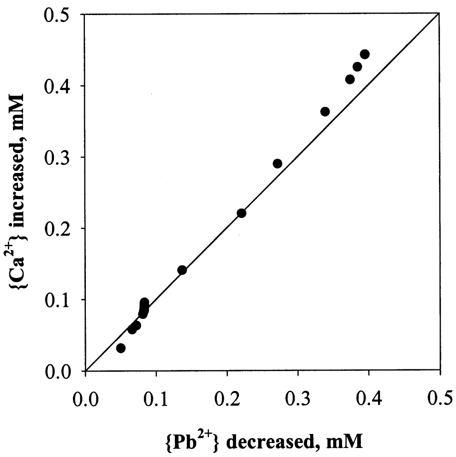


Figure 6. Role of ion exchange in lead removal.

pacity could be 3.0 mmol metal/g. However, the maximum capacities for different metal ions are various due to the difference in metal affinities for functional groups. In addition, some calcium ions may form solid complexes. As a result, these calcium ions could not be exchanged by other cations.

Because alginate is a biopolymer with a higher molecular weight, some organic compounds could be released after the resins remain in contact with the metal wastewater for a longer time. To find out such possibility, we used a total organic carbon (TOC) analyzer to measure organic strength resulting from solubilization of organic compounds from the resins. The samples for TOC analysis were obtained by placing the resins in deionized water for 48 hours under complete mixing conditions. The organic leaching of 10–20 mg TOC/L was observed when 10 g/L resins were used at pH values ranging from 2 to 7. Or the leaching was 1–2 mg TOC/g resin. These values were lower than those reported in the literature (17). The resin TC was approximately 0.16 g TC/g resin, which means that 0.6–1.3% of the organic compounds were leaked. As the resins had undergone heat treatment at 60°C, they were quite stable and caused less dissolution in the water solutions. The result will be of practical significance when these resins are applied to remove the metal ions in waste streams.

Multiple-Species Metal Ion Removal

Effect of pH on multiple-species metal ion removal was investigated. As illustrated in Fig. 7, the removal for these three metal ions reached the maximum

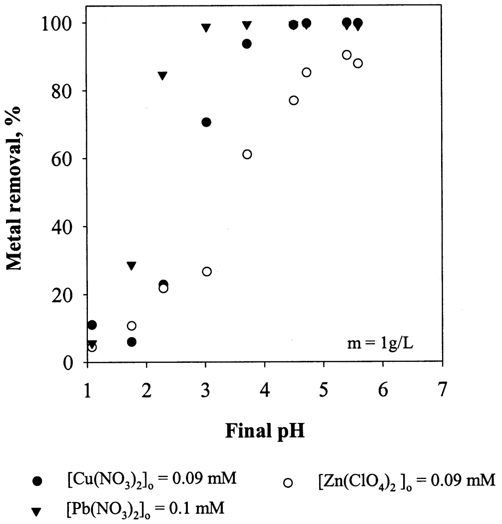


Figure 7. Effect of pH on multiple-species metal removal.

values and no significant change was observed when pH was above 5. The removal was almost 100% for both lead and copper, while that for zinc was approximately 90%. When the pH was below 5, the metal ion removal followed the order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$, which is consistent with that of the single-species metal removal. From Figs. 4 and 7, one can see that the pH_{cr} values for the single-species metals were slightly higher than those for the multiple-species metals. For example, lead and zinc removal in the single- and tri-species systems achieved their maximum at pH 4 and 5, and 5 and 5, respectively.

The concentration effect on multiple-species metal removal was investigated. In the first experiment, the initial concentration of copper was 0.09 mmol/L while that of zinc was 2.5–29 mg/L (0.04 to 0.45 mmol/L). As the concentration of zinc was increased 11-fold, the final concentrations of copper and zinc were 0–0.5 mg/L and 0.2–6.8 mg/L, respectively (Fig. 8a). Because copper was easier to remove than was zinc, the addition of zinc did not affect copper removal. Figure 8b shows the results of the second experiment conducted with the same copper concentration of 0.11 mmol/L and varied lead concentrations (5 to 105 mg/L, or 0.02 to 0.51 mmol/L). As the initial lead concentration was increased 21 times, the lead and copper removal percentages were almost unchanged, ranging from 96 to 99%, and 94 to 97%, respectively. As both metal ions can be easily removed, the removal percentages for the metals were quite high and no significant competitive effect on other metal removal was observed.

An experiment with the mixture of lead, copper, and zinc was also performed, and the results are presented in Fig. 8c. The final lead concentration was very low in all the cases (not shown here). The final copper concentration was as low as 0.1–0.2 mg/L in the initial lead concentrations that ranged from 5 to 100 mg/L (0.02 to 0.48 mmol/L). The final zinc concentration increased from 0.5 to 1.6 mg/L or the removal decreased from 92 to 75%. Similarly, Loaec, Olier, and Guezennec (4) reported that cadmium and zinc uptake was significantly reduced in the presence of lead when a novel bacterial exopolysaccharide was used. These

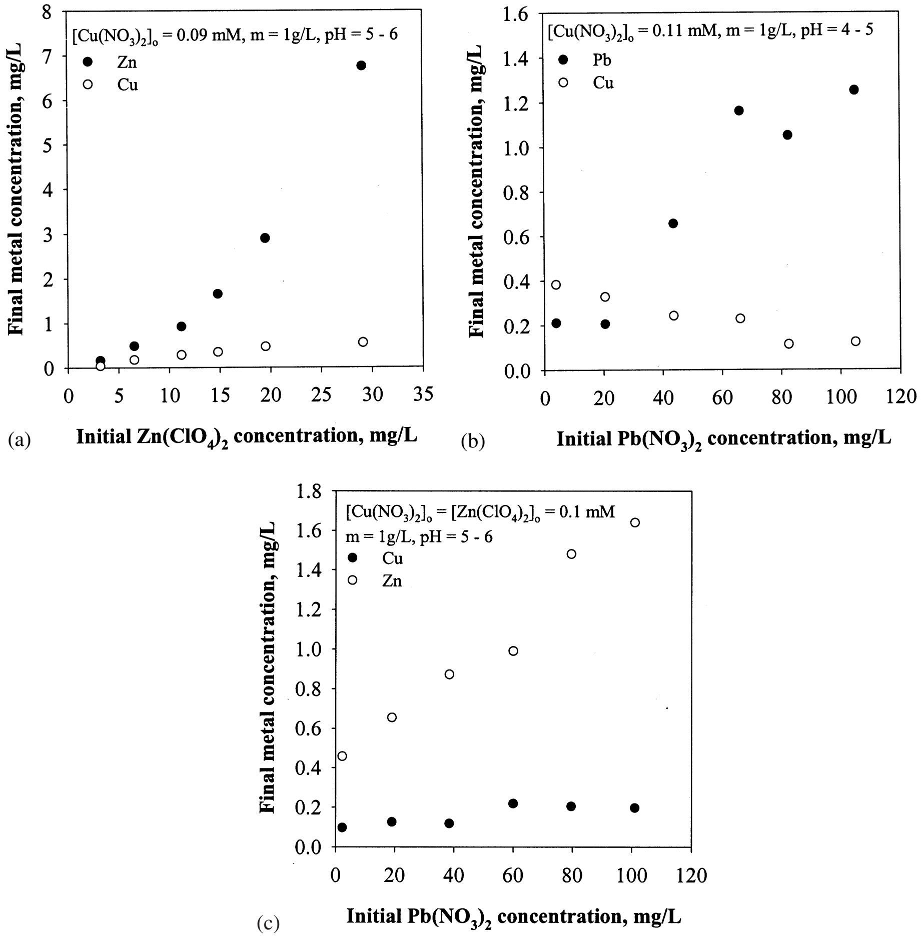


Figure 8. Effect of metal concentration in competitive removal: (a) Zn in Cu—Zn, (b) Pb in Cu—Pb, and (c) Pb in Cu—Pb—Zn.

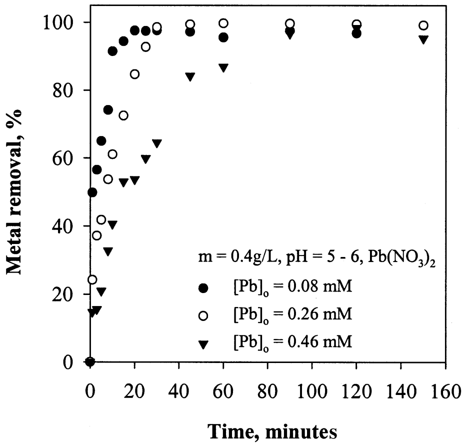


Figure 9. Effect of initial lead concentration on removal kinetics.

findings are consistent with findings regarding the single- and bi-species metal removal. In addition, both bi- and tri-species metal removal experiments showed that calcium concentration and solution pH were increased.

KINETIC STUDY

Single-Species Metal Ions

Lead removal experiments with 3 different initial concentrations were carried out, and the results are shown in Fig. 9. The removal of lead ions increased dramatically in the first 20 minutes of the experiment. No further removal was observed after 90 minutes. The equilibrium time was much shorter than that of activated carbons (5,21,26), the regular calcium alginate beads (11,27,28), and most biosorbents (3,17).

The equilibrium time of metal adsorption by activated carbons normally ranges from several hours to days. Reed and Matsumoto (26) reported that the cadmium adsorption was completed in 6 hours. The copper removal by Filtrasorb 200 and 400 from Calgon achieved the maximum in 3 and 4 hours, respectively (21,29). In metal biosorption, the equilibrium time varies depending upon types of biosorbents used. Konishi et al. (27) showed that uptake of neodymium and ytterbium by alginate beads reaches equilibrium in 2 hours. Chen et al. (11) reported that the removal of copper by the "regular" calcium alginate beads reached equilibrium in 15 hours.

As the resins used in this study were relatively small, the external mass transfer resistance was low, leading to a high metal uptake rate. The rapid kinetic rate is of practical importance as the biosorption using this resin may require smaller reactor volume. Because the sizes of the resin are quite small, the head loss can be significantly increased when they are used in packed-bed reactors. Therefore, we recommended that batch reactors, continuous stirred tank reactors, and fluidized beds be used.

Figure 9 shows that high initial concentration increased the equilibrium time. The removal was complete in 30, 30, and 90 minutes for the initial concentrations of 0.08, 0.26, and 0.46 mmol/L, respectively. This is in agreement with the observations in the literatures (13,30). Matheickal and Yu (30) reported that the equilibrium time increased with increasing initial lead concentrations. Chang et al. (13) demonstrated that the lead uptake became slower when the particle sizes of calcium alginate–immobilized cells were increased. A series of experiments showed that the removal kinetics increased as the stirring speeds were increased (data not shown). Hence, we hypothesized that the mass transfer controlled this process. A diffusion-controlled model is being developed to describe this kinetics process.

Experiments on copper removal kinetics in the absence and presence of calcium ions were completed. As shown in Fig. 10, the removal reached a maximum value of approximately 50 minutes in the absence of calcium ions. However, the equilibrium time was increased to 90 minutes in the presence of calcium ions; this result could be due to the higher mass resistance.

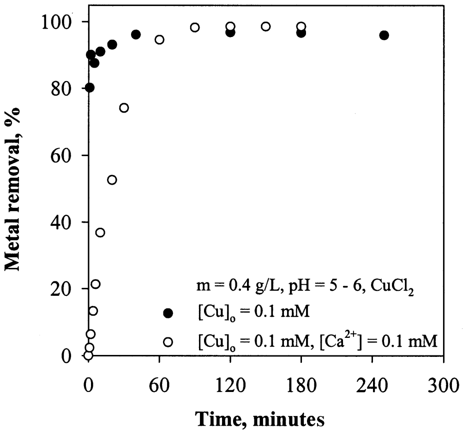
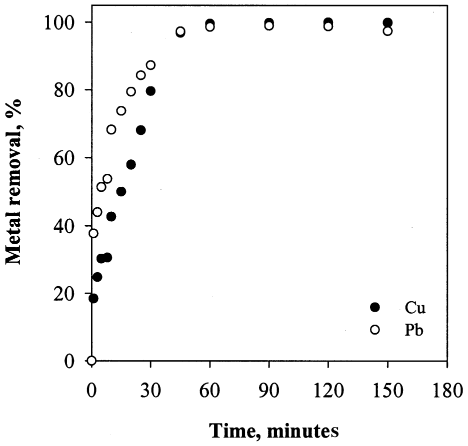


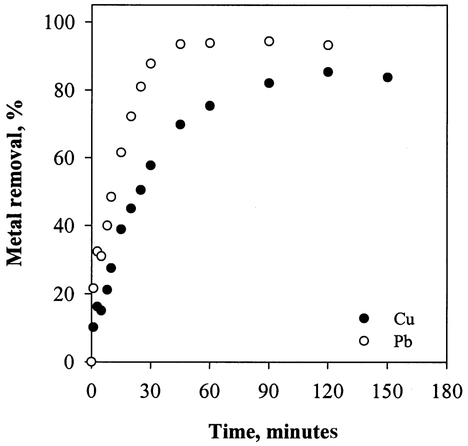
Figure 10. Effect of calcium ions on copper removal kinetics.

Multiple-Species Metal Ions

The effect of competitive metal ions was investigated, and the results are shown in Figs. 11a–c. Figure 11a shows that the removal for both copper and lead ([Cu]:[Pb] = 1.1:1.0) was completed (100%) after 60 minutes. Before the equilibrium was reached, the lead was removed at a faster rate than was copper. The

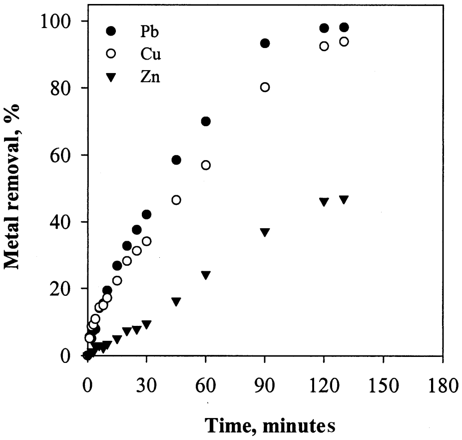


(a) m = 0.4g/L, pH = 5 - 6, $[CuCl_2]_o$ = 0.11 mM, $[Pb(NO_3)_2]_o$ = 0.1 mM



(b) n = 0.4g/L, pH = 5 - 6, $[CuCl_2]_o$ = 0.54 mM, $[Pb(NO_3)_2]_o$ = 0.1 mM

Figure 11. Multiple-species metal removal kinetics: (a) copper of 0.11 mmol/L and lead of 0.1 mmol/L; (b) copper of 0.54 mmol/L and lead of 0.1 mmol/L; (c) copper of 0.13 mmol/L, zinc of 0.1 mmol/L, and lead of 0.09 mmol/L.



(c) m = 0.4g/L, pH = 5 - 6, $[CuCl_2]_o$ = 0.13 mM
$[Zn(NO_3)_2]_o$ = 0.1 mM, $[Pb(NO_3)_2]_o$ = 0.09 mM

Figure 11. Continued.

equilibrium time for lead and copper removal was reached after a longer period than it was in the single-species metal removal (see Figs. 9 and 10). For instance, the equilibrium time for single-species lead removal (0.08 mmol/L) was 30 minutes, while it was 60 minutes in the presence of copper. When the copper and lead concentration ratio was increased to 5.4:1.0, the equilibrium time for lead removal was 50 minutes, while the complete copper removal was observed in 110 minutes (Fig. 11b). From these 2 figures, one can see that the lead removal kinetics was not changed when the competitive copper concentration was increased. The prolonged equilibrium time for copper was due to the concentration effect (Fig. 9). The slight slowdown in approaching the equilibration was probably due to the increased mass transfer resistance that was caused by the presence of more metal ions in the solutions.

An experiment for removing metals in tri-species metal solutions with various initial concentrations was conducted. Figure 11c shows that the removal rate followed the order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$ when the lead, copper, and zinc concentration ratio was approximately 1:1:1. However, the complete removal was reached in 130 minutes. Obviously, the removal rate was reduced due to the presence of competing metal ions.

To compare the competitive effects on lead removal, the removal histories under various conditions were plotted in Fig. 12. The lead-removal kinetics were clearly reduced in the presence of other metal ions. This trend intensifies with an increase in the concentrations and type of metal ion. For example, at 15 minutes the

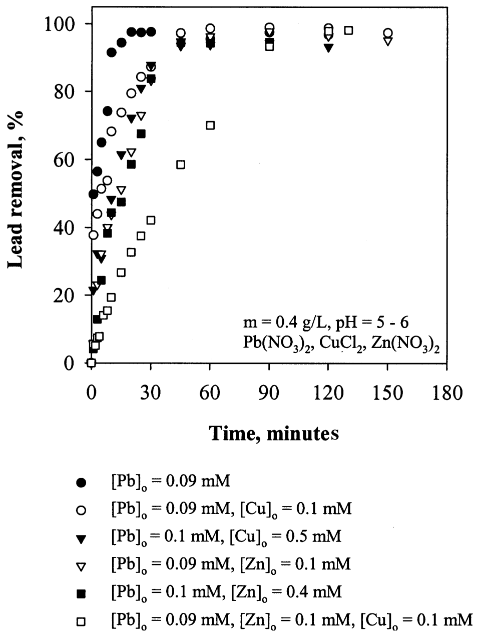


Figure 12. Effect of concentration and presence of competitive metal ions on lead removal kinetics.

lead removal percentage (in the presence of $[Cu]_o$ of 0.1 mmol/L) was 75%, compared to 94% in the absence of copper. When the copper concentration was increased from 0.1 to 0.5 mmol/L, the removal was further decreased to 62%. Similar effect from the addition of zinc ions was observed in the figure. In addition, the effect from zinc was higher than that from copper. With the same concentration of 0.1 mmol/L, the lead removal percentages in the presence of zinc and copper were 51 and 75%, respectively. When zinc and copper were added into the solution at the same time, the removal reduced appreciably to 26%. Comparison of zinc and copper showed that zinc was more effective at reducing the removal rate than was copper; however, it was less important in the final removal. The reduction in metal uptake speed caused by either higher initial concentration or the presence of other metal ions could be due to the increase in mass transfer resistance.

CONCLUSIONS

Digestion of the novel ca-alginate based ion-exchange resin by the strong acids showed that the resin contained 3×10^{-3} mol/g of calcium. The metal uptake was dependent on pH, initial concentration, ionic strength, and the presence of competitive metals. The metal removal percentage increased from almost 0 to nearly 100% at the metal concentration < 0.1 mmol/L in a pH range of 1.2 to 4, and a plateau was observed at pH > 4. When the solution pH was lower than 4, the single-species metal removal percentages were in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$. The removal obeyed the same rule in the multiple-species metal solutions at pH < 5. Lower initial concentration and ionic strength could slightly enhance the removal percentage. The maximum removal capacities (q_{max}) for lead and copper were 2.01 mmol Pb/g and 2.04 mmol Cu/g, which are much higher than they are for activated carbons and other reported biosorbents. In the multiple-species metal solutions, an increase in the zinc concentration did not affect the copper removal. However, higher concentrations of lead reduced zinc removal. Amounts of organic compound leaching from the resin were negligible.

Kinetic studies illustrated that the single- and multiple-species metal ions were removed completely within approximately 90 and 130 minutes, respectively. The lead removal became much faster at relatively low concentration and in the absence of other competing metal ions. Presence of multiple-species metal ions could lower the metal uptake rate. Among these 3 metals, zinc was found to have some influences in reducing other metal removal kinetics. The removal process may be described by a diffusion-controlled model where the equilibrium can be represented by an ion exchange relationship.

NOMENCLATURE

b	Langmuir constant $(mg/L)^{-1}$
C_e	equilibrium metal concentration (mg/L)
pH_{cr}	critical pH for the maximum metal uptake
q	metal removal capacity (mg/g)
q_{max}	maximum metal removal capacity (mg/g)
TC	total carbon
TOC	total organic carbon

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