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Feasibility of Using Alginate to Absorb Dissolved Copper from Aqueous Media

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Alginate (a biopolymer from kelp and some bacterial strains) is known to absorb copper favorably in the presence of other cations. In this work, the feasibility of using a 2-liter batch three-phase (air/liquid/alginate gel) loop fluidized bed reactor to polish water containing 10-150 ppm dissolved copper was investigated. Three methods were tested: (1) Calcium alginate spheres, prepared by dispensing sodium alginate (3.2 wt. % in water) into a 0.05 M calcium nitrate solution, were used as the absorbent, (2) the alginate spheres were formed in situ *by dispensing the sodium alginate solution directly into the reactor fluid, and (3) same as (2) except that a trace amount of EDTA was added to the alginate solution. Batch absorption data showed that Method 3 yielded the best result; the concentration of dissolved copper was successfully reduced from 140 ppm to 10 ppm with 3.2 g sodium alginate and 0.2 g EDTA used. However, when the initial concentration was below 40 ppm, both Method 2 and Method 3 are not recommended because the concentration of dissolved copper was too low to allow* in situ *formation of alginate spheres. Method 1 was found to be useful for treating water containing 10 ppm dissolved copper. But the competition from calcium seriously affected the effective capacity of the alginate for copper. The application of the classical shell progressive model to describe the absorption kinetics was discussed.*

INTRODUCTION

Conventional methods for removing heavy metals include chemical precipitation, ion exchange, solvent extraction, and electrowinning. These methods can be effective in removing the bulk of metals from solutions at high or moderate metal concentrations. Other methods (used alone or in conjunction with conventional methods) are needed to "polish" the effluent water containing low to medium concentrations of hazardous metals to meet stringent regulations recently mandated by EPA [*1*].

Due to the superior metal-complexing capacity of many biopolymers and their selectivity for specific metals, the biochemical approach has been considered as a supplementary means or a potential alternative to existing methods of metal removal or recovery [2]. Polysaccharides as metal-binding biopolymers produced by several species of Gram-negative bacteria are known to function in the absorption of exogenous metals from wastewaters [3-6].

A laboratory-scale continuous-flow stirred-tank reactor was used to test the efficiency of Fe^{3+} removal by the crude biomass *Zoogloea ramigera* [*7*]. The fluidized bed reactor developed by Brierley *et al.* [*8*], represents a major breakthrough in the technology of biological recovery of metal; the proprietary bioabsorbent has proved to be effective in reducing the level of lead in wastewater.

There are several possible improvements which will make the biological or biochemical approach more technically feasible and efficient: (1) By using biopolymers purified from microbial cultures or plants instead of crude biomass, the binding capacity of the absorbent can

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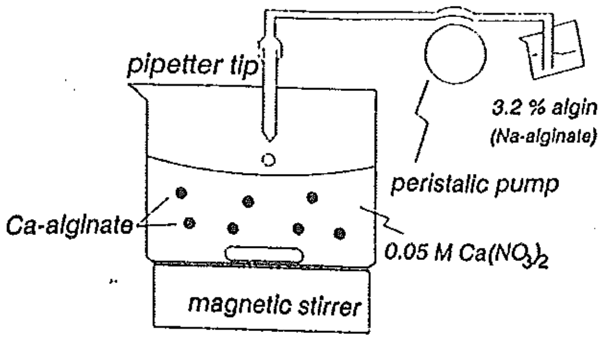

Figure 1. Schematic diagram of the apparatus used to prepare calcium alginate spheres in Runs 1-6.

be increased tremendously. The reactor volume may therefore be reduced for more efficient operation. This represents a lower equipment and operating cost in a commercial-scale water treatment plant; (2) By choosing a gel-forming biopolymer as the candidate absorbent for target heavy metals, the separation of metal-saturated biopolymer gels from aqueous medium can be done with great ease.

The gel-forming property of alginic acid (a biopolymer extracted from kelp and some microbial species) in the presence of bivalent metal ions such as calcium (magnesium and copper as well) has been utilized in recent years to produce spherical carriers for immobilized mammalian cell culture (Bellco Bioreactor). After extrusion from the tip of a dispenser, the drop of cell-containing, water-soluble Na-alginate immediately forms a semi-rigid spherical Ca-alginate gel upon contacting the surface of the $CaCl_2$ solution. The unique feature of this immobilized cell system has attracted great interest in the biotechnology industry.

An airlift, fluidized bed *loop* reactor (referred to as the reactor hereafter in this report) operated batchwise was used in this work. This type of reactor has exhibited an excellent external mass transfer efficiency due to the favorable flow pattern and constant circulation of spheres [9]. Since the absorption rate of copper at low concentrations could be limited by the film (external to the absorbent) resistance when other types of reactors are used, the high external mass transfer efficiency of the reactor could become an attractive feature for practical application.

Besides its gel-forming property, alginate (composed entirely of strong metal-binding uronates) is known to have a high metal-binding capacity and a favorable selectivity for copper in the presence of other cations [10-12]. Therefore, in the first phase of this work, the feasibility of using calcium alginate spheres to absorb dissolved copper from aqueous media was tested. In the second phase of this work, the procedure was modified such that alginate spheres did not need to be prepared separately prior to absorption experiments. By dispensing the sodium alginate solution directly into the reactor fluid containing a sufficiently high concentration of dissolved copper, semi-rigid alginate spheres (copper form) can be formed *in situ* and continually circulated in the reactor to absorb copper. It will be shown that the absorption capacity for copper can be further enhanced through innovative formulation of the alginate absorbent.

GOALS

The main goal of this work was to evaluate the rate of copper absorption by alginate as well as the capacity of alginate for copper under different operating and environmental conditions. Formulation of the alginate gel for enhancing the absorption capacity was also attempted.

EQUIPMENT, MATERIALS, AND METHODS

Preparation of Calcium Alginate Spheres

Figure 1 shows the device used to prepare calcium alginate spheres. One hundred milliliters of the aqueous solution containing 3.2 grams of *algin* (Kelton grade, composed primarily of sodium alginate, courtesy of Kelco Co.) was delivered by a peristaltic pump and extruded through a plastic pipette of 2 mm inner diameter. The drop of viscous algin solution became a translucent, semi-rigid sphere as soon as it came in contact with the surface of the calcium nitrate solution (concentration: 0.05 M, volume: 1000 ml). A magnetic stirrer at the bottom of the beaker provided a mild agitation of the solution. Each sphere contains an average of 1.654 mg algin (=3.2 g algin/1940 spheres dispensed). The spheres were soaked in the calcium nitrate solution and stored in the refrigerator for later experiments. The spheres became rigid and turned opaque white in color after storage in the calcium nitrate solution overnight, indicating complete penetration of calcium into the spheres.

The Reactor

The schematic diagram of the glass reactor is shown in Figure 2. Air was sparged through the bottom of the "riser" at a flow rate of 0.6 liters/minute causing the liquid to circulate clockwise. The liquid holdup in all experiments was 1.85 liters. The selective cupric ion electrode (Orion 94-29), reference electrode (Orion 90-02), were inserted through the top opening of the riser. Alginate was dispensed (either as spheres of the calcium form or as liquid in the water-soluble sodium form) through the top opening of the "downcomer." The spheres were collected at the end of experiments by dipping a Teflon screen through the top opening of the downcomer.

Instruments

A pH/Ion meter (Accumet 825 MP, Fisher Scientific) was used to display free cupric ion concentration in the solution. The calibrating standards were agitated gently and were adjusted to the ionic strength identical to that of the copper-containing solution used in absorption experiments. Since the copper electrode is sensitive to light, calibration and measurement of free cupric ion concentration were conducted under constant lighting conditions (by keeping the ceiling fluorescent lights on throughout the whole period of experiment).

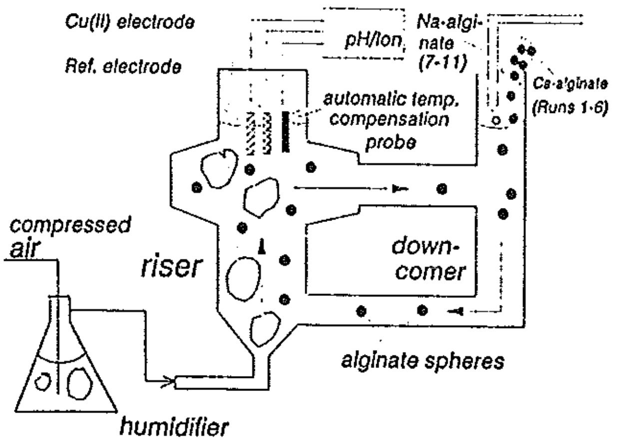

Figure 2. Schematic diagram of the loop fluidized bed reactor for testing the efficiency of copper absorption by alginate gels.

TABLE 1. SUMMARY OF EXPERIMENTAL CONDITIONS OF COPPER ABSORPTION USING CALCIUM ALGINATE

Run No.	No. spheres	Initial Conc. × 10^3, M	Final Conc. × 10^3, M	Initial Radius cm	Final Radius cm	% Cu absorbed	D_{eff} × 10^5 cm^2/s	Avg. Binding Density+ × 10^4 mole/cm^3	g Cu absorbed/ g algin dispensed	Final pH
1	150	1.28	0.98	0.179	0.183	23.4	1.44	1.49	0.142	4.90
2	300	1.01	0.623	0.183	0.192	38.9	1.06	0.884	0.092	5.00
3	600	1.17	0.657	0.183	0.182	47.8	1.38	0.687	0.061	5.05
4	1200	1.45	0.556	0.176	0.173	61.7	1.33	0.620	0.053	5.08
5	2400	1.47	0.329	0.169	0.171	77.6	1.77	0.426	0.034	5.20
6	150	0.084	0.060	0.179	0.254	30	0.55	0.060	0.011	5.85

+ Average Binding Density per unit volume of the sphere

$$= \frac{\text{(initial conc. − final conc.) (vol. reactor fluid)}}{\text{(No. Spheres) (Avg. final vol. of the spheres)}}$$

temperature = 20 ± 1°C

Bench-scale Batch Absorption Experiments

(a) Absorption of dissolved copper using calcium alginate: The ionic strength of the reactor fluid was adjusted by adding 0.1 M $NaNO_3$ in all experiments. An appropriate amount of cupric sulfate was added to the reactor fluid so that the approximate initial concentration was either 10^{-3} or 10^{-4} M (corresponding to 63.55 and 6.355 ppm dissolved copper, respectively). The accurate initial concentration of dissolved copper was determined using the cupric ion electrode. The concentration of dissolved copper was recorded continuously following the addition of calcium alginate spheres. A summary of the nominal experimental conditions is given in Table 1. The initial size and final size of the spheres were measured with a dial caliper for 30 spheres randomly picked.

The objective of Runs 1-5 using different number of spheres to treat water with an initial dissolved copper concentration of about 10^{-3} M was to determine whether an increase in the total amount of calcium present in the system could severely impede the efficiency of copper absorption. The objective of Run 6 using 150 spheres to treat water with an initial dissolved copper concentration about 10^{-4} M was to determine if the present technology was still feasible for polishing water containing less than 10 ppm dissolved copper.

(b) In situ formation of semi-rigid alginate spheres: In a separate trial, it was found that stable semi-rigid spheres could be formed if the concentration of dissolved copper was above 0.6 × 10^{-3} M (in the absence of calcium) using the device shown in Figure 1. Therefore, in Runs 7-9 the viscous algin solution was dispensed directly into the reactor fluid containing approximately 140 ppm (ca. 2.2 × 10^{-3} M) dissolved copper (sulfate form) and 0.1 M sodium nitrate. A semi-rigid, translucent sphere was formed immediately after the drop of algin solution came in contact with the surface of the reactor fluid. The sphere formed continually circulated in the reactor to absorb dissolved copper until final equilibrium was reached. The average pumping rate of the algin was 2 ml (40 drops) per minute. The concentration of dissolved copper was recorded until very little change in reading was observed. The conditions of Runs 7-9 with different amounts of alginate dispensed are given in Table 2.

Effect of chemical additives on the absorption capacity: To further enhance the capacity (and speed, if possible) of copper absorption, the algin solution with a trace amount of EDTA, a chelating compound, added was directly dispensed into the reactor fluid. The rationale behind this innovative approach was that the alginate gel formed in the reactor fluid could provide a matrix for holding the water-soluble EDTA. The uronate residuals (repeating monomer units of alginate) and EDTA could then collaborate to bind copper more efficiently. Conditions of Runs 10-12 with different amounts of EDTA added are summarized in Table 2.

Estimation of Effective Diffusivity of Cupric Ions

Since the absorption of copper by alginate can be described qualitatively by a reactive ion exchange process

TABLE 2. SUMMARY OF ABSORPTION EXPERIMENTS USING ALGINATE SPHERES FORMED *IN SITU*

Run No.	No. Spheres Dispensed	Wt. Algin Dispensed, g	Initial Conc. × 10^3, M	Final Conc. × 10^3, M	Avg. Final Radius, cm	Avg. Binding Density × 10^4 mole/cm^3	g Cu absorbed/ g algin dispensed	Final pH
Without EDTA Added to Algin								
7	150	0.24	0.869	0.634	0.222	0.632	0.115	5.12
8	1000	1.6	1.82	0.545	0.224	0.501	0.094	5.30
9	2000	3.2	2.20	0.305	0.236	0.318	0.070	5.45
With 0.1 g EDTA Added to Algin								
10	2000	3.2	2.25	0.25	0.234	0.345	0.074	5.56
With 0.2 g EDTA Added to Algin								
11	2000	3.2	2.27	0.16	0.230	0.365	0.078	5.77

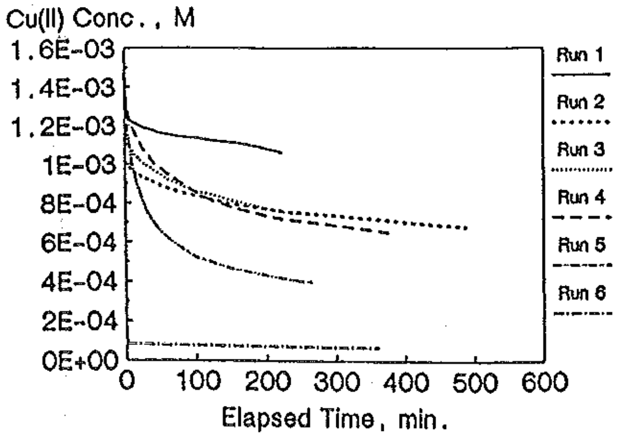

Figure 3. The time courses of free copper concentration in Runs 1-6 using Ca-alginate spheres.

(between copper and sodium or between copper and calcium), the classical (reacted) shell progressive model (SPM) or shrinking (unreacted) core model (SCM) [*13, 14*] of absorption kinetics could provide a means for revealing the controlling mechanism(s) of absorption as well as the essential rate parameters. By assuming that (1) the arithmetic mean radius between the initial and final states of each absorption experiment can be used to express the average total volume and surface area of the spheres, (2) the binding site density in the reacted outer shell at any instant of time can be represented by the average binding site density over the whole sphere at the end of each run, (3) copper penetrated completely into the spheres at final equilibrium, (4) the external film resistance was absent, and (5) the quasi-steady state of diffusion existed in the outer shell at any instant of time, the effective diffusivity D_{eff} can be calculated from the slope of the best-fit straight line on the plot of $F(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X)$ versus $\int_0^t C_t\, dt$ as $D_{eff} = [slope] \cdot [C° R^2/6]$; where X is the fractional attainment of equilibrium $[= (C_{initial} - C_t) \div (C_{initial} - C_{final})$, C_t is the free copper concentration in the reactor fluid at any instant of time $t]$, R is the average radius of the spheres, and $C°$ is the average copper-binding site density (in mole/cm^3) of the alginate gels.

RESULTS

Absorption of Dissolved Copper Using Calcium Alginate

The amount of metal bound per unit mass of biopolymer dispensed is an important index of the economics of biosorption methods. In Run 2, the mass of copper bound per unit mass of algin is calculated to be 0.092 g/g [=(0.00101 − 0.000623 mole/l) × 1.85 1 × 63.55 g copper/mole ÷ (300 spheres × 1.654 mg algin/sphere)]; the mass of copper bound decreased to 0.061 g copper/g algin when 600 spheres were added. The amount of copper absorbed per unit mass of algin used in Run 6 was significantly lower (0.0114 g/g) compared to Runs 1-5. (In fact, the color of the spheres in Run 6 only changed slightly, indicating a low effective binding capacity for copper.)

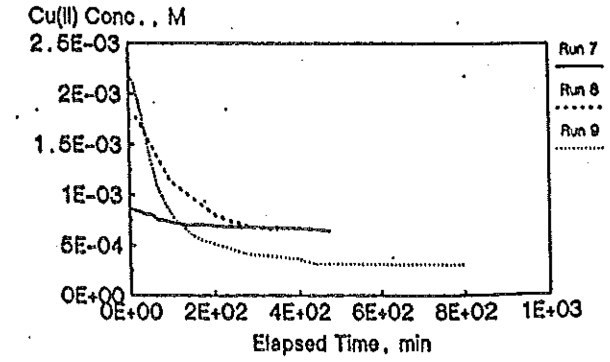

Figure 4. The time courses of free copper concentration in Runs 7-9 by dispensing algin directly into the reactor fluid.

The average radii of the spheres in Runs 1-5 remained essentially unchanged. However, in Run 6 which had a much lower initial concentration of dissolved copper the spheres swelled significantly.

The time courses of free cupric ion concentration for Runs 1-6 are presented in Figure 3.

Absorption of Dissolved Copper Using Alginate Spheres Formed *In Situ*

In Runs 7-9, stable semi-rigid alginate spheres were formed throughout the whole period of dispensing. (Since the rate of dispensing sodium alginate solution was properly controlled, the concentration of dissolved copper toward the end of dispensing was still sufficiently high for the *in situ* formation of semi-rigid spheres.) The final concentration of cupric ion decreased with increasing amount of algin dispensed. However, the mass of copper bound per unit mass of algin dispensed had the opposite trend. When Runs 1-5 (Table 1) and 7-9 (Table 2) are compared, it is evident that the calcium present in Runs 1-5 reduced the amount of copper bound to unit mass of algin.

Since the duration of dispensing the algin solution was 25 and 50 minutes in Runs 8 and 9, respectively, each sphere in these two runs should absorb dissolved copper at a different rate at any instant of time. However, comparing the time courses of free cupric ion concentration between corresponding experiments using calcium alginate spheres (Runs 1-5, Figure 3) and those with algin dispensed directly into the reactor fluid (Runs 7-9, Figure 4), it may be roughly concluded that the rate of absorption in the latter was slightly improved over the former.

Effects of Addition of EDTA

When 0.4-1.0 g EDTA (disodium form) was added to 3.2 g of the algin solution (Run 12), loose flocs of alginate were formed and the solution turned light blue. The EDTA that was originally added to the algin very likely escaped the "confinement" of the algin and instead bound dissolved copper in the reactor fluid. The chelated cupric ions in the solution could not be readily absorbed by the alginate. Since the original goal—absorption of copper by the alginate phase—was not achieved under this condition, the amount of EDTA added was decreased.

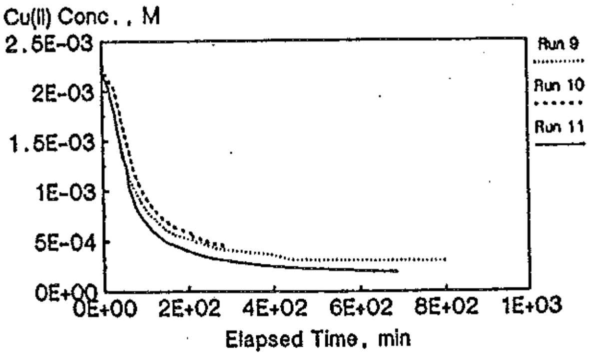

Figure 5. The time courses of dissolved copper concentration in Runs 9-11 by dispensing algin (with EDTA added in Runs 10 and 11) directly into the reactor fluid.

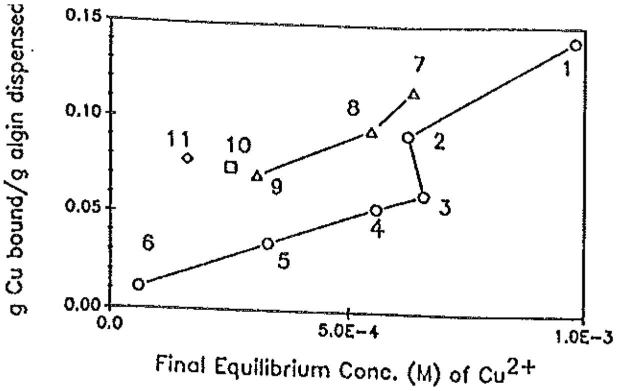

Figure 6. The mass of copper absorbed per unit mass of algin used versus the final concentration of dissolved copper.

When the algin solution containing 0.1 g or 0.2 g EDTA per 3.2 g algin was dispensed directly to the reactor fluid, stable semi-rigid spheres were formed and the solution did not turn light blue. The concentration of free dissolved copper was successfully reduced from 140 ppm to 10 ppm in Run 11. The effective capacity of algin was improved by 5.5% in Run 10 (0.1 g EDTA added) and 11% in Run 11 (0.2 g EDTA added), respectively, as compared with Run 9 (without EDTA added). The time courses of free cupric ion concentration of Runs 10 and 11 (Figure 5) also indicated a slightly improved absorption rate as compared with Run 9 (Figure 4).

Effective Diffusivity of Cupric Ions in the Alginate Matrix

The values of the effective diffusivity obtained under aforementioned assumptions are given in Table 2. The effective diffusivity of cupric ion ranged from 1.0×10^{-5} to 1.4×10^{-5} cm^2/s for Runs 1-5. The effective diffusivity of cupric ion in experiments of lower concentration (Run 6) are lower compared to Runs 1-5. In Runs 1-6, the satisfactory data fit justifies the use of SPM in describing the rate of absorption. In Runs 7-11, the batch absorption data were not treated with the classical SPM because each sphere was in contact with the reactor fluid for a different length of time (and, therefore, the rate of copper absorption by each sphere was different).

DISCUSSION

When the reactor fluid contained dissolved copper at an initial concentration of 140 ppm, an optimal absorption efficiency was obtained by dispensing directly 100 ml of the algin solution containing 0.2 g EDTA and 3.2 g algin. This approach offered several advantages: (1) The spheres could be formed *in situ* and continually absorb dissolved copper, thus eliminating the need for preparing biopolymer gels separately (as done in the absorption experiments using calcium alginate spheres); (2) The final copper concentration could be effectively reduced below 10 ppm, which was very difficult, if not impossible, to achieve using calcium alginate spheres. Theoretically, by adding more calcium alginate spheres more dissolved copper could be absorbed. However, as absorption of copper proceeded and more calcium was exchanged, the increasing amount of calcium in the reactor fluid could in turn compete for the available binding sites. This would seriously decrease the overall binding efficiency. If the mass of copper bound to unit mass of algin is plotted against the final equilibrium copper concentration (Figure 6), it is evident that the presence of calcium (Runs 1-6) reduced the effective copper-binding capacity as compared to the cases in the absence of calcium (Runs 7-9); and (3) The rate of absorption was somewhat improved compared with batch absorptions using calcium alginate spheres.

To absorb copper from an extremely dilute solution (Run 6), the approach of dispensing algin solution directly into the reactor fluid was not valid (because the concentration of dissolved copper was too low to allow formation of semi-rigid spheres). By adding 150 calcium alginate spheres, the level of dissolved copper was reduced by 30% and could be reduced to a greater extent if more spheres were added. In this sense, the present technology could still be useful for treating water containing less than 10 ppm dissolved copper. However, the effective copper binding density will be reduced as more calcium alginate spheres are added due to the increased competition from calcium for metal-binding sites and the decreased concentration of copper in the reactor fluid.

In our recent work, the copper-binding and the calcium-binding constants of algin were obtained by using the Langmuir's isotherm model [*15*]. The selectivity of alginate for copper versus calcium, defined as the ratio of the copper-binding constant to the calcium-binding constant, was found to be 3. With the selectivity known, the lowest achievable copper concentration can be estimated. To minimize the potential competition from calcium as evidenced in the present work, partially coagulated calcium alginate spheres instead of the fully coagulated spheres were prepared and used to absorb copper from a dilute solution [*15*].

The absorption of copper by either calcium alginate spheres or semi-rigid algin spheres (formed *in situ*) should belong to Type IV of ion exchange according to Helfferich [*14*]. In the case of copper absorption by calcium alginate spheres, some of the covalent bonds between calcium and uronate have to be broken to accommodate the incoming cupric ions. In the case of absorption by sodium alginate, the sodium ions, which were bound to uronates through electrostatic attraction, could be replaced by cupric ions with more ease as compared to the case of absorption by calcium alginate. Nernst-Planck equation predicts that the effective diffusivity of the incoming species (Cu^{2+}) is greatly influenced by the mobility of the counter-diffusing species (Na^+ in Runs 7-9 has a greater mobility than Ca^{2+} in Runs 1-5) [*14*]. These two factors (*i.e.*, the ease of forming covalent bonds between cupric ion and uronate groups as well as a higher effective diffusivity of cupric ions) could qualitatively explain why the rate of copper absorption was greater when algin was directly dispensed into the reactor fluid.

In our laboratory, the preliminary approach developed in this work has been modified and extended beyond the treatment of synthetic aqueous media: (1) A multi-tip dispenser has been fabricated which greatly shortens the length of time needed to dispense the algin solution [*16*]; (2) Metal-saturated alginate gels were treated with mineral acids of medium strengths or sodium bicarbonate to elute metals absorbed. Electrolytic methods have also been attempted to recover metals (directly from metal-saturated gels) in the elemental form [unpublished results]; (3) Besides EDTA, biopolymers or biomass that do not form gels in the presence of copper or calcium were blended with algin and subsequently dispensed directly into copper-containing aqueous media or into calcium nitrate solution to produce calcified spheres [*17*]. In this way, the biopolymer absorbent can be tailored to recover target metals; and (4) a two-step approach (dispensing of the sodium alginate solution followed by calcium alginate spheres) was found to be effective in recovering a consortium of metals, including copper and cobalt (a strategic metal), from acidic cobalt ore leachates [*17*].

CONCLUSIONS

(1) The calcium alginate spheres were effective in treating water containing 10-100 ppm of dissolved copper. However, the effective copper binding density was reduced with increasing amounts of calcium introduced (with the spheres) or with decreasing initial dissolved copper concentration;

(2) The absorption efficiency and absorption rate can be enhanced by dispensing algin solution directly into the reactor fluid with an initial concentration of dissolved copper at 140 ppm. Not only was the competition from calcium absent but a separate step of preparing biopolymer gel was not needed;

(3) When a trace amount of EDTA was added to the algin which was later directly dispensed to the reactor fluid, the absorption capacity for copper was increased by 11%. The concentration of dissolved copper was successfully reduced from 140 ppm to 10 ppm.

(4) The rate of absorption can roughly be described by shell progressive model of reactive ion exchange.

ACKNOWLEDGMENT

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