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SELECTIVITY OF ALGINATE GEL FOR Cu vs Co

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Abstract—The selectivity of the kelp alginate gel for copper compared to cobalt was investigated. When copper and cobalt existed at relatively high concentrations (100 ppm each), Na–alginate solution was directly dispensed into the mixed solution circulating in a loop fluidized bed reactor to produce Cu/Co–alginate gels *in situ*. Two extended Langmuir models were derived and tested against experimental data in this work: Model 1 was a general Langmuir model for two absorbates competing for the same type of binding site. Model 2 was based on the "egg-box" model for gelation of sodium alginate in the presence of divalent metal ions with the assumption that each metal ion would bind two carboxyl groups on neighboring uronate residues that formed the "site". It was found that Model 1 data better and parameters obtained from Model 1 were used to predict the amount of Na-alginate needed to "polish" a cobalt solution containing a trace amount of copper.

Key words—copper, cobalt, alginate, selectivity, metal recovery

INTRODUCTION

The selectivity of alginate from different sources for divalent metals has been reported in the literature (Huag and Smidsrod, 1970; Geesey and Jang, 1989) and equilibrium dialysis across a semi-permeable membrane has been a widely accepted method of investigation. In the equilibrium dialysis method, the alginate solution in the dialysis cell may exist in the sol state or the gel state, depending on the alginate concentration and the metal concentration. It was reported that the ion-exchange properties were affected by the gel-sol state of the alginate (Smidrod and Haug, 1972).

In recent years, workers in the field of biohydrometallurgy have used biomass or biopolymer in the gel form or the "immobilized" form to recover dissolved heavy metals from aqueous media (Torma *et al.*, 1993). One of the most frequently discussed questions is the selectivity of the biosorbent for a specific metal in a consortium of dissolved metals. To revisit this problem from the standpoint of resource recovery and waste minimization, it is essential to design experiments under conditions (metal concentrations, pH, composition of the aqueous media, and temperature) close to those in field applications. Furthermore, efforts should be devoted to the production of gels in an economic and technically-feasible manner to facilitate metal recovery or removal under different conditions.

Rigid fully-calcified alginate beads have been used by us (Jang *et al.*, 1990d) and other workers (Chen *et al.*, 1993) to absorb copper at relatively high concentrations (several hundred ppm). An alternative method of producing semi-rigid, partially calcified beads as the absorbent for copper at low concentrations was reported (Jang *et al.*, 1990b).

One focus of investigation in our laboratories is the recovery of strategic metals from mine drainage or ore leachate. Since the cobalt ore leachate contained fairly high concentrations of dissolved metals, the approach of directly dispensing the Na–alginate solution into the leachate media to form gels *in situ* was successful (Jang *et al.*, 1991). To focus on the relative selectivity of Na–alginate for Cu and Co in the absence of interference from other species, synthetic solutions containing only cupric sulfate and cobalt sulfate at concentrations of 100 ppm for each metal was used in this work. Two extended Langmuir models were derived to treat experimental data. Model 1 was the general Langmuir model for two absorbates (Cu and Co) competing for the same type of binding site. Model 2 was based on the biochemical picture, the "egg-box" model, for the gelation of Na–alginate in the presence of divalent metal ions. Experimental data were used to test against these two models. We will also demonstrate how the parameters obtained from Model 1 (i.e. binding capacity and binding affinity constants for Cu and Co) can be used to predict the amount of polymer needed to "polish" a mixed solution containing a trace amount of Cu^{2+} in the presence of predominant Co^{2+}. Experimental results and theoretical predictions will be compared.

THEORY

Model 1: the extended Langmuir model for two absorbates competing for the same type of binding sites

Assuming that there exists n dissolved metal species competing for the same type of binding site in the gel, the extended Langmuir model can be written as

$$\mathrm{M}_i + \mathrm{A} \rightleftharpoons \mathrm{M}_i\mathrm{A}; \quad K_i' \quad (i = 1, 2, \ldots, n) \tag{1}$$

where M_i is the free, unbound ith metal species in the aqueous phase, A is the available unoccupied binding sites in the gel, $\mathrm{M}_i\mathrm{A}$ is the metal bound in the gel phase or the binding sites occupied by the bound metal, and K_i' is the binding stability (equilibrium) constant for the ith metal–polymer complex defined by

$$K_i' = \frac{Q_i}{(\mathrm{M}_i)(\mathrm{A})} \quad (i = 1, 2, \ldots n) \tag{2}$$

where (M_i) is the concentration of the ith metal species (mol/l) in the aqueous phase, (A) is the concentration of the unoccupied binding sites in the gel (mol/g dry polymer), and Q_i is the concentration of the occupied binding sites (mol/g polymer). Let k be the maximum binding site density in the gel phase (mol/g polymer), we have

$$(\mathrm{A}) = k - \sum_{j=1}^{n} Q_j. \tag{3}$$

By substituting equation (3) into equation (2) and inverting the resultant equation, the following extended Langmuir model is obtained after some rearrangement

$$\frac{(\mathrm{M}_i)}{Q_i} = \frac{1}{kK_i'} + \frac{(\mathrm{M}_i)}{k}\left(1 + \sum_{j=1}^{n} \frac{Q_j}{Q_i}\right) \quad (i \neq j). \tag{4}$$

When $n = 2$, equation (4) can be simplified to

$$\frac{(\mathrm{M}_1)}{Q_1} = \frac{1}{kK_1'} + \frac{(\mathrm{M}_1)}{k}\left(1 + \frac{Q_2}{Q_1}\right) \tag{5}$$

and

$$\frac{(\mathrm{M}_2)}{Q_2} = \frac{1}{kK_2'} + \frac{(\mathrm{M}_2)}{k}\left(1 + \frac{Q_1}{Q_2}\right). \tag{6}$$

Therefore, the values of k, K_1', and K_2' can be obtained from the slopes and the intercepts of the best-fit lines of $(\mathrm{M}_1)/Q_1$ vs $(\mathrm{M}_1)[1 + (Q_2/Q_1)]$ and $(\mathrm{M}_2)/Q_2$ vs $(\mathrm{M}_2)[1 + (Q_1/Q_2)]$. If the above model is correct, the k values obtained from equations (5) and (6) should agree very well.

The selectivity of the polymer gel for M_i compared to M_j can be defined as

$$S_{i/j}' = \frac{K_i'}{K_j'}. \tag{7}$$

Model 2: the extended Langmuir model for competition among divalent metal species for negatively-charged binding groups

According to the "egg-box" model for the gelation of alginic acid in the presence of divalent metal ions at sufficiently high concentrations, each site formed by the neighboring uronate residues contains two carboxyl groups (binding groups). Equations (1)–(7) would take the following alternative form

$$\mathrm{M}_i + 2\mathrm{X} \rightleftharpoons \mathrm{M}_i\mathrm{X}_2; \quad K_i \quad (i = 1, 2, \ldots, n) \tag{8}$$

$$K_i = \frac{\bar{Q}_i}{(\mathrm{M}_i)(\bar{\mathrm{X}})^2} \quad (i = 1, 2, \ldots n) \tag{9}$$

$$(\bar{\mathrm{X}}) = \bar{k}_{\mathrm{X}} - 2\sum_{j=1}^{n} \bar{Q}_j \tag{10}$$

$$\sqrt{\frac{(\mathrm{M}_i)}{\bar{Q}_i}} = \frac{1}{\bar{k}_{\mathrm{X}}}\sqrt{\frac{1}{K_i}} + \frac{2\sqrt{(\mathrm{M}_i)\bar{Q}_i}}{\bar{k}_{\mathrm{X}}} \times \left(1 + \sum_{j=1}^{n} \frac{\bar{Q}_j}{\bar{Q}_i}\right) \quad (i \neq j) \tag{11}$$

when $n = 2$

$$\sqrt{\frac{(\mathrm{M}_1)}{\bar{Q}_1}} = \frac{1}{\bar{k}_{\mathrm{X}}}\sqrt{\frac{1}{K_1}} + \frac{2\sqrt{(\mathrm{M}_1)\bar{Q}_1}}{\bar{k}_{\mathrm{X}}}\left(1 + \frac{\bar{Q}_2}{\bar{Q}_1}\right) \tag{12}$$

$$\sqrt{\frac{(\mathrm{M}_2)}{\bar{Q}_2}} = \frac{1}{\bar{k}_{\mathrm{X}}}\sqrt{\frac{1}{K_2}} + \frac{2\sqrt{(\mathrm{M}_2)\bar{Q}_2}}{\bar{k}_{\mathrm{X}}}\left(1 + \frac{\bar{Q}_1}{\bar{Q}_2}\right) \tag{13}$$

$$S_{i/j} = \frac{K_i}{K_j}. \tag{14}$$

In the above equations, the over bar denotes the gel phase, $(\bar{\mathrm{X}})$ is concentration of the (binding) carboxyl groups (mol/l gel), $\bar{Q}_i$ is the concentration of ith metal bound in the gel phase (mol/l gel) which can be easily calculated from material balance between the initial and the final metal concentrations and the measured total gel volume at final equilibrium, and $\bar{k}_{\mathrm{X}}$ is the binding group density (mol/l gel). Equation (11) was obtained by substituting equation (10) into equation (9), followed by inverting and taking the square root of the resultant equation and some mathematical manipulation. Therefore, the values of $\bar{k}_{\mathrm{X}}$, K_1, and K_2 can be obtained from the slopes and the intercepts of the best-fit lines of $[(\mathrm{M}_1)/\bar{Q}_1]^{1/2}$ vs $2[(\mathrm{M}_1)\bar{Q}_1]^{1/2}[1 + (\bar{Q}_2/\bar{Q}_1)]$ and $[(\mathrm{M}_2)/\bar{Q}_2]^{1/2}$ vs $2[(\mathrm{M}_2)\bar{Q}_1]^{1/2}[1 + (\bar{Q}_1/\bar{Q}_2)]$. If the above model is correct, the $\bar{k}_{\mathrm{X}}$ values obtained from equations (5) and (6) should agree very well.

EXPERIMENTAL

Simultaneous absorption of Cu^{2+} and Co^{2+}

To evaluate the selectivity of Na-alginate (Algin, Kelco) for copper compared to cobalt, 1.85 l of synthetic aqueous medium containing cupric sulfate and cobalt sulfate at concentrations of 100 ppm for each metal were prepared and transferred to the 2-l loop fluidized bed reactor (Fig. 1). The concentration of the inert salt $NaNO_3$ added was 0.01 M. Different amounts of the viscous solution

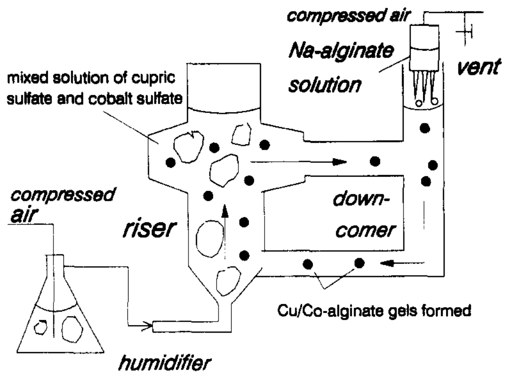

Fig. 1. Schematic diagram of the reactor for absorbing cupric ions and cobalt ions at relatively high concentrations by directly dispensing a 3.2 wt% Na–alginate solution.

containing 3.2 wt% of Na–alginate were dispensed into the reactor fluid by the multi-tip dispenser. The drops of Na–alginate solution formed stable spheres of Cu/Co–alginate upon contact with the reactor fluid. The initial, intermediate, and final copper and cobalt concentrations were determined by atomic absorption spectroscopy (AA). Experimental conditions are listed in Table 1. The gel volumes at final equilibrium are listed in Table 2.

Selective absorption of Cu^{2+} from a solution containing predominantly Co^{2+}

To explore the possibility of selectively "polishing" a solution containing a trace amount of Cu in the presence of predominant Co, the viscous solution of Na–alginate was dispensed into 1.85 l of reactor fluid containing 321 ppm Co and 18 ppm Cu. The experimental conditions are listed in Table 3.

No attempts were made to maintain pH in this work. The metal sulfate salts are weakly acidic giving solution pH ranging in 4.8–5.5, depending on the concentrations of the metal salts. The pH level was at least two order of magnitude greater than the pK_{HA} value of alginic acid [= 3.0 (Jang *et al.*, 1990a)]. Therefore, the solution pH should not have affected the metal absorption by Na–alginate.

RESULTS

Selectivity of Na–alginate for Cu^{2+} vs Co^{2+}

The results of simultaneous absorption of Cu and Co from mixed solutions containing initial concentrations of 100 ppm for each metal are summarized in Table 1. Stable spherical gels were formed under the conditions listed in Table 1. From the initial and final concentrations of Cu and Co, it is evident that Na–alginate was much more selective for Cu than for Co.

By treating data with the extended Langmuir Model 1 [equations (5) and (6) where 1 denotes Co and 2 denotes Cu], it is found that the data fit the model very well (Figs 2 and 3). The values of the maximum binding capacity k from Figs 2 and 3 were very close (2.1145×10^{-3} mol metal/g Na–alginate and 2.082×10^{-3} mol/g, respectively). An average k value of 2.098×10^{-3} mol/g may be taken to be the binding capacity of the Na–alginate gel. The copper-binding stability constant was calculated to be 1.363×10^4 l/mol (Fig. 2), which was much greater than that of cobalt (653.5 l/mol, Fig. 3). The selectivity $S'_{Cu/Co}$ was calculated to be 20.86 or $S'_{Co/Cu} = 0.04794$ according to equation (7).

When the data were treated with Model 2 [Table 2 and equations (12) and (13)], it was found that only data points for Run No. 1–3 described a linear relationship (Figs 4 and 5). By inspecting the gel volume V_g at equilibrium (Table 2), it was found that there was a dramatic increase in the gel volume per unit mass of Na–alginate dispensed in Run No. 4 and 5, indicating a significant swelling of the gel. The average gel volume for Run No. 1–3 (30.96 ml/g Na–alginate) was very close to the original formulation of 31.3 ml/(g Na–alginate). The results of calculation from Run No. 1–3 are $\bar{k}_X = 0.1286$ (mol carboxyl group)/(l gel) and $K_{Co} = 1.324 \times 10^5$ [(l soln./mol)(l gel/mol)] (Fig. 4) and $\bar{k}_X = 0.1335$ mol/l gel and $K_{Cu} = 6.511 \times 10^5$ [(l soln./mol)(l gel/mol)] (Fig. 5). The average $\bar{k}_X$ value 0.1311 mol/l may be taken to be the density of the carboxyl groups in the alginate gel for Run No. 1–3. The selectivity $S_{Cu/Co}$ was calculated to be 4.92 according to equation (14).

Selective absorption of Cu from a solution containing predominantly Co

The results of "polishing" a mixed solution containing Cu (initial concentration: 18 ppm) and Co (initial concentration: 300 ppm) using different amounts of Na–alginate are summarized in Table 3. Again, stable spherical gels were formed in the reactor fluid. The experimental values of percent absorption of Cu and Co are presented as the solid

Table 1. Summary of experiments of simultaneous absorption of copper and cobalt and calculations based on Model 1

Run No.	1	2	3	4	5
Initial Cu^{2+} concentration (ppm)	104.0	102.2	101.8	101.5	102.3
Final Cu^{2+} concentration (ppm)	60.1	44.6	32.9	14.2	7.7
Initial Co^{2+} concentration (ppm)	95.6	97.3	96.8	96.5	98.2
Final Co^{2+} concentration (ppm)	93.5	90.2	86.3	74.5	63.6
Dry Na–alginate dispensed (g)	0.726	1.029	1.301	1.967	2.578
% Cu absorbed	43.1	57.1	68.2	86.1	92.3
% Co absorbed	3.7	8.8	12.2	23.4	33.8
Q_{Cu} (g Cu/g Na–alginate)	0.114	0.105	0.0987	0.0822	0.0678
$Q_{Cu} \times 10^3$ (mol Cu/g Na–alginate)	1.79	1.65	1.55	1.29	1.07
Q_{Co} (g Co/g Na–alginate)	0.00900	0.0154	0.0169	0.0212	0.0238
$Q_{Co} \times 10^3$ (mol Co/g Na–alginate)	0.153	0.261	0.287	0.360	0.404

Temperature: 20 ± 1°C; metal salts: sulfate form; concentration of inert $NaNO_3$ added: 0.01 M; pH ≈ 5; volume of reactor fluid: 1.85 l.

Table 2. Summary of calculations for simultaneous absorption of Cu and Co based on Model 2

Run No.	1	2	3	4	5
Gel volume, V_g (ml)	22.8	32.0	34.5	77.0	150
Gel volume per mass Na–alginate dispensed (ml/g)	31.4	31.1	30.4	39.1	57.9
$\bar{Q}_{Cu} \times 10^3$ (mol/l gel)	57.0	53.1	51.1	33.0	18.4
$\bar{Q}_{Co} \times 10^4$ (mol/l gel)	48.7	83.9	94.5	92.0	69.4
$\bar{Q}_{Cu}/\bar{Q}_{Co}$	11.7	6.33	5.41	3.59	2.65
$\bar{Q}_{Co}/\bar{Q}_{Cu}$	0.0854	0.158	0.185	0.279	0.377
$2\sqrt{(Cu)\bar{Q}_{Cu}} \cdot [1 + (\bar{Q}_{Co}/\bar{Q}_{Cu})] \times 10^3$ $[\sqrt{(mol/l\ soln.)(mol/l\ gel)}]$	15.9	14.1	12.2	6.95	4.11
$\sqrt{(Cu)/\bar{Q}_{Cu}}$ $[\sqrt{(mol/l\ soln.)/(mol/l\ gel)}]$	0.129	0.115	0.101	0.0823	0.0812
$2\sqrt{(Co)\bar{Q}_{Co}} \cdot [1 + (\bar{Q}_{Cu}/\bar{Q}_{Co})] \times 10^3$ $[\sqrt{(mol/l\ soln.)(mol/l\ gel)}]$	70.6	52.5	47.8	31.3	20.0
$\sqrt{(Co)/\bar{Q}_{Co}}$ $[\sqrt{(mol/l\ soln.)/(mol/l\ gel)}]$	0.571	0.427	0.394	0.371	0.394

lines in Fig. 6. Although Cu was in a trace amount, the percent recovery of Cu was far greater than that of Co.

DISCUSSION

The reason why Model 1 fit experimental data better than Model 2 may be explained as follows: in model 1, Q_i and (A) can be expressed in either (mol/g Na–alginate) or (mol/l gel volume) and the Na–alginate mass or the gel volume term can be cancelled from equation (2). Therefore, swelling of the gel should not have affected the validity of the model (as long as the morphology of the binding sites were not significantly altered by the swelling) and the resultant binding site density can be conveniently expressed in terms of [mol metal/g Na–alginate]. In the case of Model 2, the gel volume term cannot be canceled between $\bar{Q}_i$ and $(\bar{X})^2$ from equation (9). Since swelling of the gel essentially changed the density of the binding group $\bar{k}_X$ [(mol binding group)/l gel], it was not surprising to see the deviation of data points of Run No. 4 and 5 from the best-fit line passing through those of Run No. 1–3.

Since Model 1 fit batch absorption data better, the parameters obtained may be used to predict the amount of the polymer W needed for a specific goal of treatment. For example, an aqueous medium of volume V containing M_1 at an initial concentration of (M_{10}) and trace amount of M_2 at an initial concentration of (M_{20}) is to be "polished" by the polymer to lower the concentration of M_2 to (M_2) by a batch absorption process. From a material balance, we have

$$Q_i = \frac{V[(M_{i0}) - (M_i)]}{W} \quad (i = 1, 2) \qquad (15)$$

where the unknowns are W and (M_1). Substituting equation (15) into equation (2) (with $i = 1$ and 2) and eliminating A by dividing K_1' by K_2', we have

$$(M_1) = (M_{10})\left[1 + \frac{K_1'}{K_2'}\left(\frac{(M_{20})}{(M_2)} - 1\right)\right]^{-1}. \qquad (16)$$

By substituting equation (15) (with $i = 1$ and 2) and the value of (M_1) from equation (16) into equation

Table 3. Selective absorption of copper from synthetic solutions containing predominantly cobalt by Na–alginate

Run No.	6	7	8	9
Initial Cu^{2+} concentration (ppm)	18.1	18.1	19.0	18.4
Final Cu^{2+} concentration (ppm)	5.3	2.7	2.5	1.2
Initial Co^{2+} concentration (ppm)	325.0	322.9	318.1	316.0
Final Co^{2+} concentration (exp.) (ppm)	307.2	290.4	275.9	243.5
Dry Na–alginate dispensed (exp.) (g)	0.629	1.009	1.360	2.135
% copper absorbed (exp.)	70.8	85.3	86.7	93.6
% cobalt absorbed (exp.)	6.35	10.1	12.2	20.4
Estimated final Co^{2+} concentration (equation 16) (ppm)[a]	291.6	252.5	241.6	183.6
Est. dry Na–alginate needed (equation (17)] (g)	0.838	1.428	1.805	3.216
Estimated % cobalt absorbed	10.3	21.8	24.0	41.9

[a] Assuming the final Cu^{2+} concentration to be identical to the experimental value. (exp.).

Temperature: 20 ± 1°C; metal salts: sulfate form; concentration of inert $NaNO_3$: 0.01 M; pH ≈ 5; volume of reactor fluid: 1.85 l.

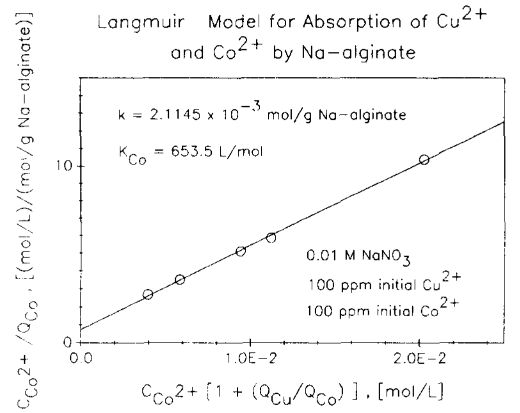

Fig. 2. Treating data of simultaneous absorption of cupric ions and cobalt ions by directly dispensing the Na-alginate solution according to equation (5) [1: Co; 2: Cu; (M_1): $C_{Co^{2+}}$].

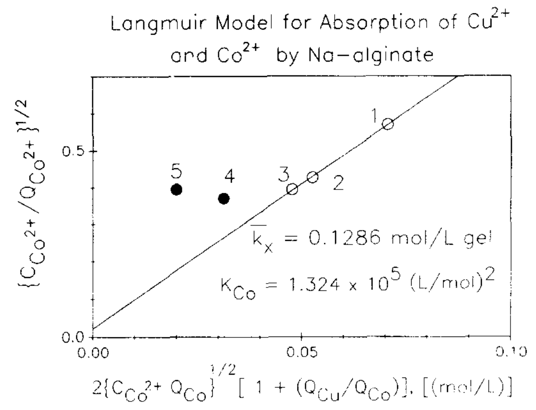

Fig. 4. Treating data of simultaneous absorption of cupric ions and cobalt ions by directly dispensing the Na-alginate solution according to equation (12) [1: Co; 2: Cu; (M_1): $C_{Co^{2+}}$].

(5), the amount of the polymer W needed can be estimated

$$W = \frac{V[(M_{10})-(M_1)]}{k} \times \left[\frac{1}{(M_1)K_1'} + 1 + \frac{(M_{20})-(M_2)}{(M_{10})-(M_1)}\right]. \quad (17)$$

The results of theoretical prediction are summarized in Table 3 and plotted as the dash line in Fig. 6. From Table 3 and Fig. 6, it is evident that Na-alginate was able to preferentially absorb the trace Cu when Co was the predominant species, although as much as 30% Co was "sacrificed" in this process. There was fair agreement between the experimental results and the theoretical predictions (Fig. 6). Theoretical calculations predicted that the amount of Na-alginate needed was increased by a factor >2 when the final copper concentration was lowered from 2.7 ppm (Run 7, Table 3) to 1.2 ppm (Run 9, Table 3). To achieve a very low final copper concentration, the single batch treatment illustrated in this work has to be revised. A possible alternative is the successive multi-batch process with each batch using only a fraction of the total alginate.

The binding group density $\bar{k}_X$ from Model 2 in this work {0.1311 mol X/l gel or 4.057×10^{-3} mol X/g Na-alginate [=(0.1311 mol/l)(30.96 ml/g)]} was very close to that from our recent work [4.360×10^{-3} mol/g for absorption of copper from acidic aqueous media (Jang *et al.*, 1995)] and our previous work [4.353×10^{-3} mol/g, based on biochemical assay of the Na-alginate (Jang *et al.*, 1990c)]. This comparison suggests that Model 2 can still yield good results provided swelling of the gel can be prevented.

One possible improvement for Model 2 is to consider the existence of unidentate complex

$$M_i + X \rightleftharpoons M_iX; \quad \beta_i \qquad (18)$$

where β_i is the stability constant of the unidentate ith-metal-alginate complex. The graphical procedure

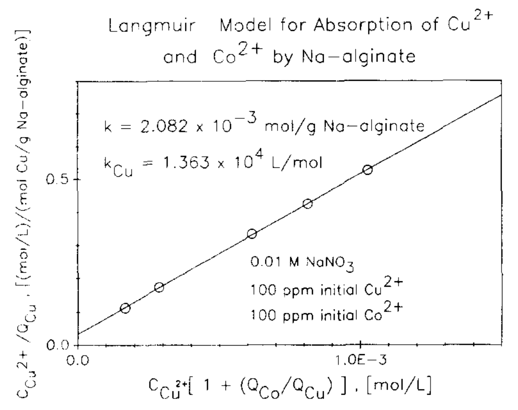

Fig. 3. Treating data of simultaneous absorption of cupric ions and cobalt ions by directly dispensing the Na-alginate solution according to equation (6) [1: Co; 2: Cu; (M_2): $C_{Cu^{2+}}$].

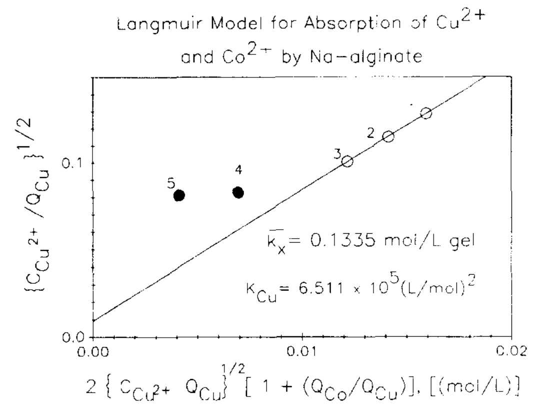

Fig. 5. Treating data of simultaneous absorption of cupric ions and cobalt ions by directly dispensing the Na-alginate solution according to equation (13) [1: Co; 2: Cu; (M_2): $C_{Cu^{2+}}$].

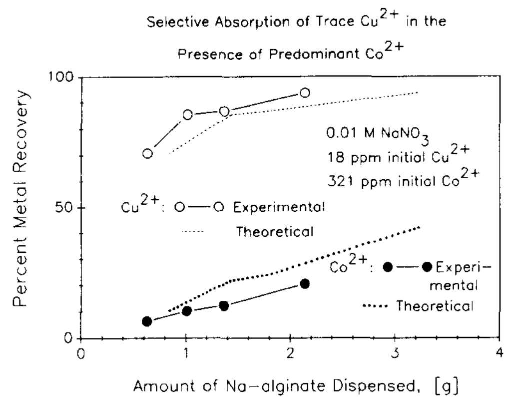

Fig. 6. Results of experiments and theoretical predictions for the selective removal of cupric ions from a synthetic solution of cobalt sulfate (321 ppm Co) containing a trace amount of cupric sulfate (18 ppm Cu).

Table 4. Comparison of K'_{Cu} values from various phases of our work

Presence of species competing for available binding sites or groups	K'_{Cu} (l/mol)
H^+ (pH ~ 2.6)	4.182×10^3 [(a)]
H^+ (pH ~ 3.6)	3.30×10^4 [(a)]
—	$> 10^5$ [(b)]
Co^{2+}	1.363×10^4 [(c)]
Ca^{2+}	7.96×10^3 [(d)]

[(a)] Jang *et al.* (1995).
[(b)] Jang *et al.* (1990c).
[(c)] This work.
[(d)] Jang *et al.* (1990b).

by Marinsky (1982) and Jang *et al.* (1990a) was employed to obtain binding stability constants for unidentate and bidentate copper–polymer complexes. This approach is especially advantageous when the gel volume varies significantly. In our future work, the graphical procedure developed previously will be expanded to accommodate a consortium of metals. A multi-variate regression algorithm needs to be developed for this purpose.

In this work the pH of the mixed solution of cupric sulfate and cobalt was in the neighborhood of 5. Since the typical pH range of cobalt ore leachate was 1.5–2.5 (Jang *et al.*, 1991), more work on the Cu/Co selectivity under the acidic condition is needed. By combining Model 2 developed in this work and Model 2 developed in our recent work (Jang *et al.*, 1995] (for competition between cupric ions and hydrogen ions for binding carboxyl groups on Na–alginate), it is possible to yield a further extended model that describes the competition among a consortium of divalent metals and hydrogen ions for binding carboxyl groups. However, the binding stability constant of a metal species may not be totally independent of the composition of the liquid. If we tentatively accept K_{Cu} value of 6.51×10^5 [(l soln./mol)(l gel/mol)] from the partial fit of experimental data to Model 2 in this work, it is found that this value is significantly greater than the corresponding value 4.050×10^4 [(l soln./mol)/(l gel/mol)] in the presence of hydrogen ions (Jang *et al.*, 1994). The existence of other metal species, hydrogen ions, inorganic or organic colloids, and anions may very likely affect the speciation of the target metal, which in turn may affect the free energy associated with the process of binding to sites or functional groups. The issue of metal speciation needs to be explored.

If K'_{Cu} values (Model 1) from various phases of our work are compared (Table 4), it is found that the presence of other divalent metals and hydrogen ions competing for available sites or groups affected the stability of the copper–alginate complex. One possible explanation is that the morphology of the binding sites in the alginate gel depends on the type and the amount of cations bound. Another possibility is that Model 1 is based on the concentration of cupric ions in the bulk solution. By considering the Donnan potential effect and using the activity of cupric ions in the gel phase rather than concentration in the bulk solution, the results are expected to be improved as have been demonstrated by Jang *et al.* (1990c).

The alginate used in this work showed an excellent Cu/Co selectivity of 21:1. The alginate used in this study contained 31% guluronate residue and 69% mannuronate residue according to the supplier. Since the selectivity of alginate for the divalent ions is mainly due to the guluronate residue (Smidsrod and Huag, 1968), greater Cu/Co selectivity may be achieved by using guluronate-rich alginate from different sources.

CONCLUSIONS

(1) The Langmuir model for two absorbates competing for the same type of binding sites (Model 1) was successfully used to describe simultaneous absorption of Cu^{2+} and Co^{2+} by the alginate gel formed *in situ*.

(2) The Langmuir model for divalent metals competing for binding carboxyl groups (Model 2) partially fitted experimental data. Data points obtained under conditions causing significant gel swelling deviated from the model.

(3) The Cu/Co selectivity was 20.9 based on the results of batch absorption experiments and Model 1.

(4) Alginate was able to selectively remove dissolved copper in the presence of predominant cobalt. There was fair agreement between the theoretical prediction of the amount of alginate needed to achieve a specific goal of treatment using Model 1 with the experimental results.

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