



EFFECT OF pH ON THE ABSORPTION OF Cu(II) BY ALGINATE GEL

L. K. JANG¹, D. NGUYEN¹ and G. G. GEESEY²

¹Department of Chemical Engineering, California State University, Long Beach, CA 90840 and

²Center for Biofilm Engineering and Department of Microbiology,
Montana State University, Bozeman, MT 59717, U.S.A.

(First received November 1993; accepted in revised form March 1994)

Abstract—The absorption of copper from synthetic solutions of cupric sulfate (initial Cu concentration: 200 ppm, initial pH: 2.4 or 3.4) in a batch loop fluidized bed reactor by alginate gels was investigated. Compared to the results obtained without addition of sulfuric acid [Jang L. K., Geesey G. G., Lopez S. L., Eastman S. L. and Wichlacz P. L., *Wat. Res.* **24**, 889–897 (1990)], the copper-binding efficiency of the alginate gels at pH 3.4 was affected mildly by the acidity of the solution; at pH 2.4, the percent copper recovered was reduced by roughly one-half. In this work, an extended Langmuir model that took into account the competition between monovalent hydrogen ions and divalent cupric ions for the carboxyl groups on the alginate molecules was derived. This model yielded the binding group density of the alginate gel and binding stability constants for cupric alginate and alginic acid simultaneously. The new model was shown to be superior to the simple Langmuir model that expressed the results as conditional copper binding stability constant and capacity at a given pH. Application of the extended Langmuir model to the prediction of copper binding at pH 2 is also illustrated.

Key words—alginate, copper, pH, Langmuir model, metal recovery

INTRODUCTION

Many acidic biopolymers have demonstrated superior metal-binding properties and have been tested for their abilities of recovering metals from aqueous media. Some aqueous media such as ore leachates and mine drainages are acidic (pH 2–4). If the biopolymer is to be used in such aqueous media to recover metals, the competition from hydrogen ions for the available metal-binding groups may reduce the overall metal-binding capability of the biopolymer. Our preliminary work has suggested the feasibility of using alginate gel to recover copper and cobalt from cobalt ore leachate (pH ~2.5) (Jang *et al.*, 1991). More work is needed to quantify the effect of pH on the metal binding properties of alginate.

Several published papers have reported the effect of pH on metal absorption by microbial biomass (Cotoras *et al.*, 1992), natural polyelectrolyte (Jellinek and Sangal, 1972), algal surface (Xue *et al.*, 1988), and hydrous oxides (Goncalves *et al.*, 1985). Metal loading on these absorbents decreased with decreasing pH, indicating a strong competition between hydrogen ions and metal ions for the available binding sites. Mathematical models of various forms have been proposed in these papers for the evaluation of metal binding constants at a given pH.

In this work, batch absorption experiments using Na-alginate to recover copper from acidic cupric sulfate solutions (initial pH: 2.4–3.4, initial Cu con-

centration: 200 ppm) in a 2-l loop fluidized bed reactor were performed. Since the copper concentration was sufficiently high, the drops of the viscous Na-alginate solution dispensed formed a rigid shell of Cu-alginate gel upon contact with the solution and continued to circulate in the reactor to absorb copper. No efforts were made to maintain the solution pH while copper was being absorbed. The change of pH in a batch experiment was used to compute the mol of hydrogen ions absorbed. A simple Langmuir model was used to obtain conditional copper binding capacity and stability constant at a given pH. An extended Langmuir model that takes into account the competition between monovalent hydrogen ions and divalent cupric ions for negatively-charged carboxyl groups was derived in this work. This new model yielded the effective binding group density and binding stability constants for copper and hydrogen ions simultaneously. The results obtained were used to predict copper binding capability of alginate gels at a pH of 2.

Possible improvements in the modelling by including the Donnon potentiation effect and the existence of unidentate copper-carboxyl group complex will also be discussed.

THEORY

Model 1: the simple Langmuir model

In this model, the effective copper binding capacity and stability constant at a certain pH were obtained

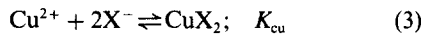
from batch absorption data using the familiar Langmuir model

$$\frac{(\text{Cu}^{2+})}{Q_{\text{Cu}}} = \frac{1}{kK'_{\text{Cu}}} + \frac{(\text{Cu}^{2+})}{k} \quad (1)$$

where (Cu^{2+}) is the equilibrium copper concentration in solution (mol/l), Q_{Cu} is the density of copper absorbed in the alginate gel (g or mol Cu/g Na-alginate), k is conditional binding capacity (g or mol Cu/g Na-alginate) available for copper at a given pH, and K'_{Cu} is the conditional stability constant (l/mol) of Cu-alginate complex at a given pH. The original definition of the stability constant requires k and Q_{Cu} be expressed on the unit gel-volume basis. Since the gel volume can be canceled from both sides of equation (1), the basis can be changed to the dry weight of the Na-alginate for convenience. In this simple model, the actual total binding sites for H^+ and Cu^{2+} and the stability constant of alginic acid are not calculated. The conditional binding capacity k is a model-fitted value whose biochemical nature needs not to be specified.

Model 2: the extended Langmuir model for competition between Cu^{2+} and H^+ for binding functional 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 cavity (or "site") formed by the neighboring uronate residues has two carboxyl groups. At low pH, H^+ and Cu^{2+} compete for the carboxyl groups (X^-). Therefore, the following model is proposed



where X^- is the free carboxyl groups available for binding which can be expressed by

$$(\overline{\text{X}^-}) = \overline{k_x} - \overline{Q}_{\text{H}} - 2\overline{Q}_{\text{Cu}} \quad (4)$$

and the stability constants K_{Cu} and K_{H} are defined by

$$K_{\text{Cu}} = \frac{\overline{Q}_{\text{Cu}}}{(\text{Cu}^{2+})(\overline{\text{X}^-})^2} \quad (5)$$

and

$$K_{\text{H}} = \frac{\overline{Q}_{\text{H}}}{(\text{H}^+)(\overline{\text{X}^-})} \quad (6)$$

In equations (4)–(6), the over bar denotes the alginate gel phase and all terms with an over bar have units of (mol/l gel). $\overline{k_x}$ is the mol of carboxyl groups per l gel volume, \overline{Q}_{H} is the mol of H^+ absorbed (i.e. HX) per l gel volume, and \overline{Q}_{Cu} is the mol of Cu^{2+} absorbed (i.e. CuX_2) per l gel volume. The coefficient 2 in equation (4) means each mol of copper bound occupies 2 mol of carboxyl groups.

By substituting equation (4) into equation (5), followed by inverting and taking the square root on both sides of the resultant equation, the following linear form of the Langmuir model based on

the copper concentration is obtained after some rearrangement

$$\sqrt{\frac{(\text{Cu}^{2+})}{\overline{Q}_{\text{Cu}}}} = \frac{1}{\overline{k_x}} \sqrt{\frac{1}{K_{\text{Cu}}}} + \frac{\sqrt{(\text{Cu}^{2+})}}{\overline{k_x}} \left(\frac{\overline{Q}_{\text{H}}}{\sqrt{\overline{Q}_{\text{Cu}}}} + 2\sqrt{\overline{Q}_{\text{Cu}}} \right) \quad (7)$$

Similarly, substituting equation (4) into equation (6) followed by inverting the resultant equation yields a parallel Langmuir model based on the hydrogen ion concentration after some rearrangement

$$\frac{(\text{H}^+)}{\overline{Q}_{\text{H}}} = \frac{1}{\overline{k_x} K_{\text{H}}} + \frac{(\text{H}^+)}{\overline{k_x}} \left(1 + \frac{2\overline{Q}_{\text{Cu}}}{\overline{Q}_{\text{H}}} \right) \quad (8)$$

Therefore, the values of $\overline{k_x}$, K_{H} , and K_{Cu} can be obtained from the slopes and the intercepts of $\{(\text{Cu}^{2+})/\overline{Q}_{\text{Cu}}\}^{1/2}$ vs $(\text{Cu}^{2+})^{1/2}\{(\overline{Q}_{\text{H}}/\overline{Q}_{\text{Cu}})^{1/2} + 2\overline{Q}_{\text{Cu}}^{1/2}\}$ and $(\text{H}^+)/\overline{Q}_{\text{H}}$ vs $(\text{H}^+)\{1 + (2\overline{Q}_{\text{Cu}}/\overline{Q}_{\text{H}})\}$ of batch data of simultaneous absorption of cupric ions and hydrogen ions. If the proposed model is correct, the $\overline{k_x}$ values from equations (7) and (8) should be very close. This treatment is similar to our recent work [Jang *et al.*, 1995] in which two different kinds of divalent cations (copper and cobalt) compete for the same type of binding sites. In the present work the above model was derived that describes the competition between divalent cations (cupric ions) and monovalent cations (hydrogen ions) for the same type of negatively-charged functional groups.

The values of \overline{Q}_{Cu} and \overline{Q}_{H} can be calculated from material balance equations for batch absorption processes

$$\overline{Q}_{\text{Cu}} = \frac{V_{\text{R}}[(\text{Cu}^{2+})_0 - (\text{Cu}^{2+})]}{V_{\text{g}}} \quad (9)$$

and

$$\overline{Q}_{\text{H}} = \frac{V_{\text{R}}[(\text{H}^+)_0 - (\text{H}^+)]}{V_{\text{g}}} \quad (10)$$

where the subscript "0" denotes the initial condition, V_{R} is the volume of the reactor fluid (l), V_{g} is the volume of the gels at final equilibrium (l), and (H^+) is the hydrogen ion concentration (mol/l) calculated by

$$(\text{H}^+) \cong 10^{-\text{pH}} \quad (11)$$

EXPERIMENTAL

The schematic diagram of the air-lift loop fluidized bed reactor used to hold aqueous media is given in our previous publication (Fig. 2 in Jang *et al.*, 1990b). The procedure is similar to our previous work (Jang *et al.*, 1990b) except that a sulfuric acid solution was added dropwise to the reactor holding a cupric sulfate solution (200 ppm Cu; 0.01 M NaNO_3) until pH dropped to a desired value (2.4 and 3.4 in this work). (The reason for using sulfuric acid to adjust pH was because it is non-volatile thus preventing the loss of acidity due to aeration. The reason for using salt and nitrate salt was because these are two of the main anions found in the ore leachates). Then the viscous solution containing 3.2 wt% Na-alginate (Algin, Kelton grade, Kelco) was

Table 1. Results of batch copper absorption experiments at initial pH of 3.4 (the main experimental condition that was varied among different runs was the amount of Na-alginate dispensed)

| Run No. | 1 | 2 | 3 | 4 |
|---|-------|-------|-------|-------|
| Initial Cu ²⁺ concentration (ppm) | 202.5 | 204.0 | 200.0 | 199.5 |
| Final Cu ²⁺ concentration (ppm) | 167.1 | 144.8 | 118.6 | 90.4 |
| % copper absorbed | 18.2 | 29.3 | 41.0 | 54.9 |
| Dry Na-alginate dispensed (g) ^a | 0.638 | 0.984 | 1.413 | 2.001 |
| Q _{Cu} (g Cu/g Na-alginate) | 0.102 | 0.111 | 0.107 | 0.101 |
| C _{Cu,2+} /Q _{Cu} [(mol/l)/(mol/g Na-alginate)] | 1.632 | 1.301 | 1.114 | 0.890 |
| Initial pH | 3.382 | 3.410 | 3.372 | 3.350 |
| Final pH | 3.591 | 3.574 | 3.564 | 3.720 |

^aCalculated from the actual weight of the 3.2% Na-alginate solution dispensed.

Temperature: 20 ± 1°C; cupric salt added: CuSO₄ · 5H₂O; concentration of inert NaNO₃ added: 0.01 M; volume of reactor fluid: 1.85 l.

dispensed with a multi-tip dispenser into the acidic copper-containing solution through the top opening of the downcomer. From our previous studies, the drops of the Na-alginate solution formed stable spherical gels of Cu-alginate upon contact with the reactor fluid. The results of batch absorption with different amounts of the Na-alginate dispensed were used to obtain parameters in both the simple and the extended Langmuir model.

The gels at the end of each experiment were retrieved from the reactor with a nylon net inserted through the top opening of the downcomer of the loop reactor. The gel volume V_g was determined by the liquid volume displaced by the gels in a graduated cylinder. The pH was measured with a calibrated combination glass membrane electrode and meter and the copper concentration was measured by atomic absorption spectroscopy.

RESULTS

A summary of experimental conditions and results is given in Table 1 (initial pH ~ 3.4) and Table 2 (initial pH ~ 2.4). Stable alginate gels were formed *in situ* in all runs. Percentage of copper absorbed and the variable (C_{Cu2+}/Q_{Cu}) for fitting the simple Langmuir model [equation (1)] were also calculated and listed in Tables 1 and 2. When the percent copper absorbed was plotted against the amount of Na-alginate dispensed (Fig. 1), it was found that copper absorption

Table 2. Results of batch copper absorption experiments at initial pH of 2.4

| Run No. | 5 | 6 | 7 | 8 |
|--|--------|--------|--------|--------|
| Initial Cu ²⁺ concentration (ppm) | 201.2 | 203.8 | 204.3 | 204.1 |
| Final Cu ²⁺ concentration (ppm) | 177.1 | 169.1 | 154.0 | 131.5 |
| % copper absorbed | 12.6 | 17.5 | 25.1 | 36.0 |
| Dry Na-alginate dispensed (g) | 0.634 | 1.007 | 1.412 | 2.020 |
| Q _{Cu} (g Cu/g Na-alginate) | 0.0702 | 0.0638 | 0.0660 | 0.0664 |
| C _{Cu2+} /Q _{Cu} [(mol/l)/(mol/g Na-alginate)] | 2.523 | 2.653 | 2.335 | 1.981 |
| Initial pH | 2.426 | 2.445 | 2.460 | 2.421 |
| Final pH | 2.510 | 2.592 | 2.677 | 2.700 |

Temperature: 20 ± 1°C; cupric salt added: CuSO₄ · 5H₂O; concentration of inert NaNO₃ added: 0.01 M; volume of reactor fluid: 1.85 l.

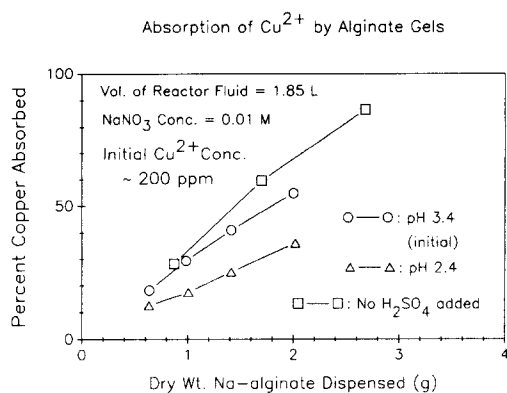


Fig. 1. Comparison of the percent copper recovery from synthetic solutions of cupric sulfate at different pH. The data points (□) are from our previous work (Jang *et al.*, 1990b).

efficiency at final pH ~ 3.6 was reduced mildly as compared to that obtained in our previous work (without sulfuric acid added) (Jang *et al.*, 1990b). At final pH ~ 2.6, the percentage copper absorbed was reduced to about one-half that in our previous work.

When data in Table 1 and Table 2 were treated separately with the simple Langmuir model, satisfactory fits were obtained giving $k = 1.148 \times 10^{-3}$ mol or 0.0730 g Cu per g dry Na-alginate and $K'_{Cu} = 4.182 \times 10^3$ l/mol at final pH ~ 2.6 and $k = 1.685 \times 10^{-3}$ mol or 0.107 g Cu per g Na-alginate and $K'_{Cu} = 3.30 \times 10^4$ l/mol at final pH ~ 3.6.

It is obvious from Tables 1 and 2 that at low pH Na-alginate not only absorbed Cu²⁺ but was protonated by the hydrogen ions from solution causing an increase in solution pH. Variables needed for the extended Langmuir model that takes into account the competition between cupric ions and hydrogen ions for the binding groups [equations (7) and (8)] were also calculated

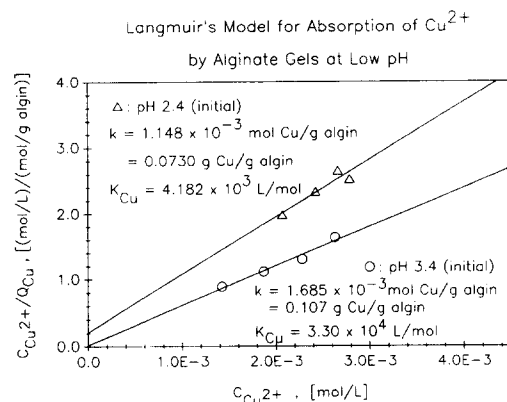


Fig. 2. Treatment of batch absorption data by the simple Langmuir model, giving "effective" copper binding capacity and stability constants at different pH. The symbol C in all figures means molar concentration.

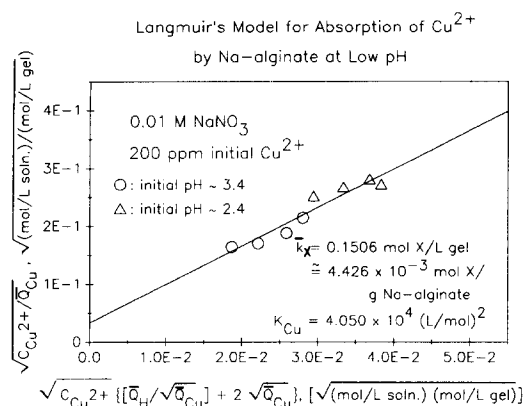


Fig. 3. Treatment of batch absorption data by the extended Langmuir model [equation (7)] which gives total density of binding groups and stability constant for copper-polymer complex.

and listed in Table 3 (initial pH ~ 3.4) and Table 4 (initial pH ~ 2.4).

Combined data from Tables 3 and 4 were found to fit equations (7) and (8) very well (Figs 3 and 4). The total binding group density \bar{k}_X was calculated to be 0.1506 mol X per l gel volume according to equation (7) (Fig. 3), which was very close to the value 0.1461 according to equation (8) (Fig. 4). The gel volume per unit mass of Na-alginate dispensed were found to vary slightly among all runs. By dividing the above \bar{k}_X values by the average Na-alginate density of 34.02 g per l gel volume, corresponding \bar{k}_X values 4.426×10^{-3} (Fig. 3) and 4.294×10^{-3} mol X per g Na-alginate (Fig. 4) were obtained. K_{Cu} was calculated to be 4.050×10^4 [(l soln./mol)(l gel/mol)] [equation (7), Fig. 3] and K_H was calculated to be 1.639×10^3 (l soln./mol) [equation (8), Fig. 4].

DISCUSSION

The results using the simple Langmuir model show that both the conditional copper binding capacity

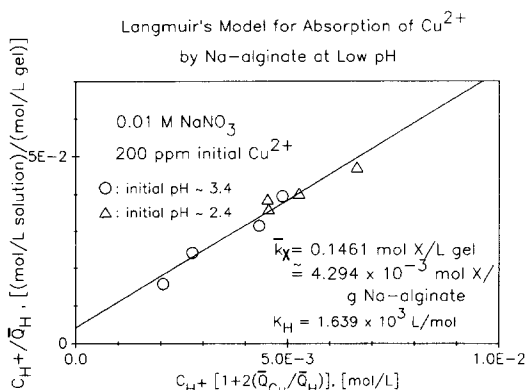


Fig. 4. Treatment of batch absorption data by the extended Langmuir model [equation (8)] which gives total density of binding functional groups and stability constant for alginic acid.

and stability constant of the alginate gel decreased with increasing hydrogen ion concentration (decreasing pH) (Table 5). This trend was consistent with our prediction that the effect of the competition from hydrogen ions for the binding groups would become significant as pH decreased, especially as pH dropped below the pK_{HA} value of 3.0 for alginic acid (Jang *et al.*, 1989, 1990a). This treatment is simple but has its drawbacks. It would be difficult to make predictions on the copper binding efficiency of alginate gels if the solution pH was not within the range tested.

An extended Langmuir model was derived in this work that described the competition between the divalent metal ions and the monovalent hydrogen ions for carboxyl groups on the uronate residues of the alginate molecules. The derivation procedure developed in this work transformed a non-linear equation [equation (5)] into a linear form [equation (7)] to facilitate data treatment. Such a treatment of data to yield binding group density and binding stability constants for copper and hydrogen ions simultaneously has not been seen in the literature, to the best of our knowledge. [The expression for B_2 in equation (1) by Jellinek and Sangal (1972) is equivalent to $K_{Cu}/(K_H)^2$ in this work. But individual values were not reported by these authors.] The binding group density obtained from Figs 3 and 4 was also listed in Table 5 for comparison. In the absence of competition from hydrogen ions at pH ~ 5 , the binding site density for copper would be 2.180×10^{-3} mol or 0.1385 g Cu/g Na-alginate ($=\bar{k}_X/2$, since each Cu^{2+} would occupy $2X^-$), which agreed extremely well with the theoretical maximum binding capacity 0.1383 g Cu/g Na-alginate (Jang *et al.*, 1990b) based on the uronate assay of the Na-alginate used and was greater than the conditional capacity of 0.0730 g/g at pH 2.6 and 0.107 g/g at pH 3.6. From the results and the above discussions, the extended Langmuir model has the following advantages over the simple model [equation (1)]:

(1) batch absorption data from different initial pH's and final pH's can be combined and treated according to equations (7) and (8);

(2) precise control of initial solution pH is not needed. The pH was also allowed to vary as absorption proceeded; and

(3) total density of binding groups instead of the conditional capacity was obtained. By comparing the results from Figs 3 and 4, almost identical \bar{k}_X values were obtained and the average \bar{k}_X agreed with that from biochemical assay.

The performance of alginate gel in copper recovery at any pH < 6 can be predicted. The following calculation procedure illustrates how the relative "loading" of HX and CuX_2 under a given condition [pH = 2, (Cu^{2+}) = 3×10^{-3} M] can be predicted. Assuming that the volume of the aqueous medium was so large that absorption of cupric ions and hydrogen

Table 3. Summary of calculations according to the extended Langmuir's model for H⁺ and Cu²⁺ competing for the same binding groups on the Na-alginate molecules

| Run No. | 1 | 2 | 3 | 4 |
|--|--------|--------|--------|--------|
| V_g , (l gel)* | 0.018 | 0.0267 | 0.0406 | 0.06 |
| $C_{H^+} \times 10^4$ (mol/l soln.) | 2.564 | 2.667 | 2.729 | 1.905 |
| $C_{H^+0} \times 10^4$ (mol/l soln.) | 4.150 | 3.890 | 4.246 | 4.467 |
| $\bar{Q}_{Cu} \times 10^2$ (mol/l gel) | 5.716 | 6.450 | 5.834 | 5.295 |
| $\bar{Q}_H \times 10^2$ (mol/l gel) | 1.629 | 0.8478 | 0.6913 | 0.7898 |
| $\sqrt{C_{Cu^{2+}}[(\bar{Q}_H/\sqrt{\bar{Q}_{Cu}})]}$ $+ 2\sqrt{\bar{Q}_{Cu}} \times 10^2$ [$\sqrt{(\text{mol/l soln.})(\text{mol/l gel})}$] | 2.802 | 2.584 | 2.211 | 1.865 |
| $\sqrt{C_{Cu^{2+}}/\bar{Q}_{Cu}}$ [$\sqrt{(\text{mol/l soln.})/(\text{mol/l gel})}$] | 0.2145 | 0.1880 | 0.1701 | 0.1639 |
| $(C_{H^+})[1 + 2(\bar{Q}_{Cu}/\bar{Q}_H)]$ $\times 10^3$ (mol/l soln.) | 2.056 | 4.325 | 4.879 | 2.745 |
| $C_{H^+}/\bar{Q}_H \times 10^2$ [(mol/l soln.)/(mol/l gel)] | 1.574 | 3.146 | 3.947 | 2.413 |

Note: the symbol C means molar concentration.
*Average Na-alginate content = 35.115 g/l gel(final).
Initial pH ~ 3.4; volume of reactor fluid: 1.85 l.

ions does not disturb the condition of the liquid, eliminating (X⁻) from equations (5) and (6) we have

$$\bar{Q}_{Cu} = \left[\frac{K_{Cu}(Cu^{2+})}{K_H^2(H^+)^2} \right] \bar{Q}_H^2 = \alpha \bar{Q}_H^2 \quad (12)$$

From equation (6), we have

$$(\bar{X}^-) = \frac{\bar{Q}_H}{(K_H)(H^+)} = \beta \bar{Q}_H \quad (13)$$

Substituting equations (11)–(13) and the parameters obtained in this work into equation (4) yields $\alpha = 0.4521$ and $\beta = 0.0610$ and the following quadratic equation

$$0.9042\bar{Q}_H^2 + 1.0610\bar{Q}_H - 0.1484 = 0 \quad (14)$$

which gives

$$\bar{Q}_H = 0.1262 \frac{\text{mol}}{\text{l gel}} \quad (15)$$

$$\bar{Q}_{Cu} = 0.00721 \frac{\text{mol}}{\text{l gel}} \quad (16)$$

and

$$(\bar{X}^-) = 0.00770 \frac{\text{mol}}{\text{l gel}} \quad (17)$$

From equations (15)–(17), it is predicted that at pH 2.0, about 85.1% ($= \bar{Q}_H/\bar{k}_x$) of all carboxyl groups are protonated and only 9.7% ($= 2\bar{Q}_{Cu}/\bar{k}_x$) are used to bind copper; and 5.2% carboxyl groups remain ionized.

The above sample calculation also suggests that if an acidic copper-containing (or divalent metal-containing) aqueous media is to be treated with biopolymer gel, the K_H value of the polymer has to be as low as possible. In other words, the acid dissociation constant K_{HA} (for $HX = H^+ + X^-$), which is the inverse of K_H , has to be as high as possible. (The pK_{HA} value of the alginate gel under the experimental conditions used was $3.215 [= -\log_{10}(1.693 \times 10^3)^{-1}]$ in this work, which differs slightly from the intrinsic value 2.96 of the colloidal alginic acid determined in our previous work [Jang *et al.*, 1989].) From the above experimental evidence and theoretical

Table 4. Summary of calculations according to the extended Langmuir's model for H⁺ and Cu²⁺ competing for the same binding functional groups on the Na-alginate molecules

| Run No. | 5 | 6 | 7 | 8 |
|--|--------|--------|--------|--------|
| V_g , (l gel)* | 0.0186 | 0.0300 | 0.0432 | 0.0645 |
| $C_{H^+} \times 10^3$ (mol/l soln.) | 3.090 | 2.559 | 2.104 | 1.995 |
| $C_{H^+0} \times 10^3$ (mol/l soln.) | 3.750 | 3.589 | 3.467 | 3.793 |
| $\bar{Q}_{Cu} \times 10^2$ (mol/l gel) | 3.766 | 3.367 | 3.392 | 3.271 |
| $\bar{Q}_H \times 10^2$ (mol/l gel) | 6.559 | 6.356 | 5.839 | 5.157 |
| $\sqrt{C_{Cu^{2+}}[(\bar{Q}_H/\sqrt{\bar{Q}_{Cu}})]}$ $+ 2\sqrt{\bar{Q}_{Cu}} \times 10^2$ [$\sqrt{(\text{mol/l soln.})(\text{mol/l gel})}$] | 3.833 | 3.680 | 3.337 | 2.943 |
| $\sqrt{C_{Cu^{2+}}/\bar{Q}_{Cu}}$ [$\sqrt{(\text{mol/l soln.})/(\text{mol/l gel})}$] | 0.2720 | 0.2811 | 0.2673 | 0.2415 |
| $(C_{H^+})[1 + 2(\bar{Q}_{Cu}/\bar{Q}_H)]$ $\times 10^3$ (mol/l soln.) | 6.639 | 5.270 | 4.548 | 4.527 |
| $C_{H^+}/\bar{Q}_H \times 10^2$ [(mol/l soln.)/(mol/l gel)] | 4.712 | 4.026 | 3.603 | 3.869 |

Note: the symbol C means molar concentration.
*Average Na-alginate content = 32.92 g/l gel(final).
Initial pH ~ 2.4; volume of reactor fluid: 1.85 l.

Table 5. Comparison of copper binding capacity and stability constant at different pH

| pH | k (g Cu/g Na-alginate) [equation (1)] | K'_{Cu} (l/mol) [equation (1)] | K_H (l/mol) |
|---------------------|--|--|------------------------------|
| ~2.6 | 0.0730 | 4.182×10^3 | — ^(b) |
| ~3.6 | 0.1070 | 3.300×10^4 | — |
| ~5.0 ^(a) | 0.1247 | $\geq 10^5$ (estimated) | — |
| | \bar{K}_X (mol X/g Na-alginate) [equation (7) and (8)] | K_{Cu} (l/mol) ² [equation (7)] | K_H (l/mol) [equation (8)] |
| 2.4–3.6 | 4.360×10^{-3} | 4.050×10^4 | 1.639×10^3 |

^aReference: Jang *et al.* (1990b)

^bCannot be obtained.

prediction, we may conclude that alginate gel is an effective copper absorbent even at pH somewhat lower than the pK_{HA} due to the superior complex reaction between the alginate and cupric ions. However, at low pH the acidic condition is undesirable because most of the carboxyl groups are protonated leaving few ionized groups for binding copper.

Cotoras *et al.* (1992) have shown that *Azotobacter vinelandii* biomass loaded with metals can be treated with HCl at pH < 2 to elute metals. The model developed in this work can also be used to predict the pH required to elute metals from alginate gels or other biomass.

The *operational* pH standards consisting of low concentrations of phosphates and phthalates were used in this work. Therefore, for low ionic-strength aqueous media, definition equation (11) should be accurate to ± 0.02 in pH or $\pm 3.5\%$ in concentration in the pH range of 2–12 following IUPAC recommendations (1985) and Levine (1988). If the glass-membrane pH electrode is calibrated by the same operational standards and used to measure pH of high ionic-strength solutions, the right side of equation (11) has to be divided by the activity coefficient of hydrogen ions, the values of which have been reported in the literature (Kieland, 1937; Jang *et al.*, 1989).

An important refinement of the extended Langmuir model is necessary when considering the Donnan potential effect. In our previous work (Jang *et al.*, 1990b), it has been shown that by considering the Donnan potential term the Langmuir plots for the absorption of copper from cupric sulfate solution (pH ~ 5) by Na-alginate at two different ionic strengths merged into one plot, although only minor improvement of the data was achieved. Our laboratories are conducting experiments using aqueous media containing a higher concentration of added inert salt. Intrinsic capacity and stability constants will be obtained using a similar mathematical procedure outlined in the Appendix of Jang *et al.* (1990b).

A further improvement in the modelling is necessary if the possible existence of the unidentate complex CuX^+ is considered. In the derivation of the extended Langmuir model such possibility was tentatively ig-

nored on the basis of the egg-box model for gelation of alginate in the presence of divalent cupric ions. Our previous work (Jang *et al.*, 1990b) has yielded the binding capacity of 0.1247 g Cu/g Na-alginate at pH ~ 5 and 0.01 M sodium nitrate. This "effective" capacity was somewhat lower than the theoretical maximum binding capacity of 0.1383 g/g based on the biochemical assay of the sample with the assumption that each cupric ion would bind to two carboxyl groups. Marinsky (1982) reported that the stability constant for the unidentate complex CuX^+ was greater than that for the bidentate complex CuX_2 in the case of complexation of Cu(II) by a cross-linked poly methacrylic gel due to the restricted accessibility of the repeating ligands in the gel. By comparing the effective binding capacity with the theoretical maximum binding capacity, it is possible that a small fraction of copper absorbed by alginate gel existed in the form of unidentate complex. The graphical procedure by Marinsky (1982) and Jang *et al.* (1990a) should be followed to assess the extent of the formation of unidentate complex.

CONCLUSIONS

(1) Stable alginate gels can be formed inside the acidic cupric solution at pH 2.4–3.4 and 200 ppm Cu by using the air-lift fluidized bed reactor and a multi-tip dispenser.

(2) The simple Langmuir model gave conditional copper binding capacity and stability constant that decreased with decreasing pH.

(3) Alginate gel was a good copper absorbent for pH > 2.5. At pH 3.5, the copper binding efficiency was affected mildly by the acidity of the solution.

(4) The extended Langmuir model that describes the competition between the divalent metal ions and the monovalent hydrogen ions for the negatively-charged binding groups fit batch absorption data very well.

(5) The parameters obtained by using the extended Langmuir model (density of binding groups and stability constants for copper and hydrogen ions) can be used to predict the copper absorption efficiency of alginate gels at any pH < 6. Theoretical predication indicated that at pH 2.0 only 9.7% of the carboxyl

groups were bound to copper and 85.1% were protonated. To treat acidic metal-containing solutions, synthetic polymers or biopolymers with low pK_{HA} and high metal-binding stability constant should be used.

Acknowledgements—This work was supported by a cooperative agreement between the U.S. National Science Foundation, Montana State University and California State University, Long Beach. (Grant No. ECD-8907039). Comments and suggestions from Dr J. Marinsky, State University of New York at Buffalo and Dr D. Cotoras, Universidad de Chile are most appreciated.

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