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USE OF A GEL-FORMING BIOPOLYMER DIRECTLY DISPENSED INTO A LOOP FLUIDIZED BED REACTOR TO RECOVER DISSOLVED COPPER

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Abstract—A novel technique for the recovery of copper from synthetic aqueous solutions containing 60–200 ppm dissolved copper was developed in this work. A viscous solution of sodium alginate (a kelp-derived biopolymer known to bind copper) was dispensed dropwise by using a multi-tip dispenser into the synthetic solution circulating in an air-lift glass loop fluidized bed reactor. Upon contact with the copper-containing solution, the alginate gelled into stable spheres which continued to circulate in the reactor to absorb copper. The percent of copper recovered at the lower ionic strength (0.01 M $NaNO_3$) was found to be greater than that at the higher ionic strength (0.1 M $NaNO_3$) of the solution. (Consequently, the conditional copper-binding stability constant for the former case was greater.) An intrinsic copper-binding stability constant, independent of the ionic strength of the solution, was obtained by using a two-phase model modified from our recent work (Jang *et al.*, *J. Polymer Sci., Part B* **27**, 1301–1315, 1989; *J. phys. Chem.* **94**, 482–488, 1990c).

Key words—alginate gel, copper binding, fluidized bed reactor

INTRODUCTION

The earliest reference of ion exchange probably dates back to Biblical times. Moses succeeded in preparing drinking water from brackish water on an industrial scale using wood (Exodus 15: 23–25). Many polymers of biological origin are known to bind metals [e.g. alginic acid and polysaccharides (Smidsrod and Haug, 1968, 1972; Haug and Smidsrod, 1970; Kohn, 1975), humic acid (Zunino and Martin, 1977) and microbial exopolymers (Mittelman and Geesey, 1985; Geesey and Jang, 1989)]. The capability of biomaterials, especially biopolymers derived from microorganisms (Friedman and Dugan, 1968) and plants, to chelate heavy metals has been applied to the recovery or removal of heavy metals from mine drainages and industrial wastewaters (Patterson, 1987).

In our laboratories, a technique for the recovery of dissolved copper by using gel-forming biopolymers (such as sodium alginate, a kelp-derived biopolymer known to bind copper) and an innovative reactor was developed. We will show that the biopolymer solution can be directly dispensed into a copper-containing solution circulating in a loop fluidized bed reactor to form stable gels *in situ*; no separate step is needed to prepare biopolymer or biomass gels prior to absorption experiments.

When a drop of concentrated sodium alginate solution hits the surface of an aqueous solution containing Cu^{2+} at a sufficiently high concentration, a spherical bead is formed as a result of bridging reaction between Cu^{2+} and the uronate residues of the alginate molecules. According to the egg-box model (Rees and Welsh, 1977) describing the mechanism of gelation of alginate in the presence of Cu^{2+}, each binding site (or cavity) for Cu^{2+} consists of two carboxyl groups and two hydroxyl groups on interacting uronate residues (repeating monomeric units of alginate, each unit carrying a carboxyl group) (Fig. 1).

The initial concentrations of dissolved copper (sulfate salt) in the synthetic aqueous solutions used in this work ranged in 60–200 ppm, which were representative of the copper concentration in some wastewater sources. The final copper concentrations were varied in a wide range (from 10 to 180 ppm) by varying the amounts of sodium alginate dispensed. We also investigated the sensitivity of the apparent copper-binding affinity of the biopolymer to the ionic strength in the solution.

The Cu^{2+} absorbed by the alginate gel exists in two states: bound covalently (to binding sites) and migrating freely (in the gel domain while held electrostatically by unoccupied charged groups). Conventional Langmuir's model [equations (A2) and (A3)] is customarily used to determine the conditional copper-binding stability constant that describes the binding equilibrium between all Cu^{2+} absorbed in

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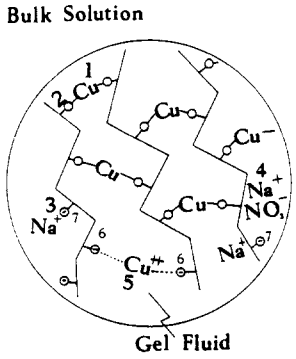

Fig. 1. A conceptual picture showing the gelation of alginate in the presence of Cu^{2+}. The surface of the gel serves as a semi-permeable membrane. Each section on the polymer chain represents a uronate residue. The role played by hydroxyl groups in stabilizing copper bound is not shown. 1, Copper bound covalently of which the activity is denoted by $(\overline{Cu^{2+}\text{-}BS})$; 2, carboxyl groups binding copper covalently; 3, Na^+ that remains in the gel to balance the unbound charged carboxyl groups; 4, $Na^+NO_3^-$ that invades the gel phase; 5, Cu^{2+} held electrostatically in the gel fluid of which the activity is denoted by $(\overline{Cu^{2+}})$; 6, charged carboxyl groups holding Cu^{2+} electrostatically; 7, charged carboxyl groups holding Na^+ electrostatically. The dashed lines indicate the electrostatic interactions between Cu^{2+} and unbound carboxyl groups.

The concentration of the carboxyl groups (7) divided by two is denoted by C_{BS}. The concentration of the unbound sites (each consisting of two carboxyl groups) used in the iterative procedure is the sum of carboxyl groups (6) and (7) divided by two and is denoted by $(\overline{BS})$. The concentration of copper absorbed [copper bound covalently (1) plus copper held electrostatically (5)] is denoted by $C_{Cu^{2+}\text{-}BS}$.

the gel domain (without distinguishing Cu^{2+} bound covalently from Cu^{2+} held electrostatically) and the Cu^{2+} in the bulk solution. However, actual copper-binding reactions take place in the gel domain and a more rigorous definition of the binding equilibrium should be based on the interactions between Cu^{2+} bound covalently and Cu^{2+} held electrostatically in the gel domain (instead of Cu^{2+} in the bulk solution). The concentration (or activity) of electrostatically-held Cu^{2+} in the gel domain cannot be measured directly.

Since the surface of the gel serves as a semi-permeable membrane allowing only simple electrolytes to permeate through (Fig. 1), the distribution of free cations between the bulk solution and the gel fluid (which is under the influence of negatively-charged carboxyl groups on the alginate molecule) should obey Gibbs–Donnan equilibrium [equation (A9)] (Jang *et al.*, 1989). The theory used to estimate the activities of cations (Na^+ and Cu^{2+}) in the gel domain from the known or measured concentrations of cations in the bulk solution is modified from our recent work (Jang *et al.*, 1989, 1990c) based on the two-phase model (Marinsky *et al.*, 1982, 1985, 1990) and is given in the Appendix.

We will demonstrate that when the conditions in the biopolymer gel domain are used to describe the affinity of the biopolymer gel for copper, a thermodynamic intrinsic copper-binding stability constant independent of the ionic strength in the solution can be obtained by using a modified Langmuir's model (Appendix).

EXPERIMENTAL

Biopolymer

Algin (Keltone grade sodium alginate, courtesy of Kelco Co.) was used in this study. To determine the exact uronate content of the algin received, a colorimetric method described by Blumenkrantz and Asboe-Hansen (1973) was used. In this method, the polymeric alginate may not be completely decomposed and hydrolyzed into monomeric uronic acid by the sulfuric acid/sodium tetraborate reagent. To determine the recovery of uronate residues during the assay, two parallel sample treatments were conducted, one using alginic acid (Sigma) containing 4.5×10^{-3} mol titratable uronic acid residues per gram of sample (Jang *et al.*, 1989) and the other using algin. Ten mg of each sample were dissolved in 10 ml water and sonicated with a Bransonic sonifier intermittently for 15, 30 and 60 s and then diluted to 100 ml prior to the assay. Preparations of glucuronic acid standards, alginic acid sample and algin sample were all duplicated. It is reasonable to assume that the recovery of uronate was the same for both samples. The percent recovery of uronate determined for alginic acid sample (with the exact number of moles of uronate residues known) was used to estimate the unknown uronate content of algin. The formulae for alginic acid, sodium alginate and uronic acid are $(C_6H_8O_6)_n$, $(C_6H_7O_6Na)_n$ and $C_6H_{10}O_7$, respectively. Since each copper binding site involves two uronate residues, the maximum possible binding sites were estimated to be half the total uronate residues in a given amount of algin dispensed in each experiment.

An algin solution prepared by mixing 3.2 g algin with 100 ml deionized water (NANOpure System) was used as the absorbent in this work. Since the algin powder was not readily dissolved in water, a plastic spoon was used to grind the clumps of algin in the beaker. The final homogeneous product was a viscous brownish liquid.

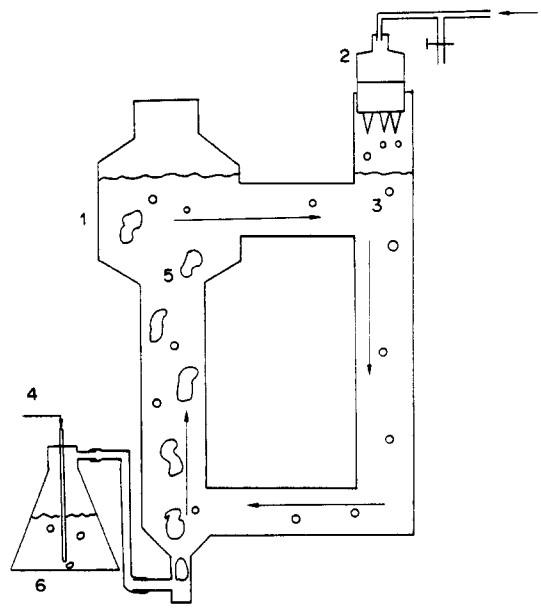

Fig. 2. A schematic diagram of the loop fluidized bed reactor used to study the absorption of copper by alginate gels. 1, 2.0-l. glass reactor; 2, dispenser of algin solution (see Fig. 3 for details); 3, newly-formed Cu-alginate beads; 4, compressed air; 5, air bubbles; 6, humidifier of the incoming air.

Reactor

The schematic diagram of the 2.0-l. glass reactor is shown in Fig. 2. Air was sparged from the bottom of the left side (the riser) of the reactor loop causing the fluid to circulate in the direction shown. Air flow rate was maintained at 0.4–0.5 l/min. A dispenser (Fig. 3) fabricated from a plastic bottle and twelve 200 μl pipetter tips was used to dispense the viscous algin solution directly into the reactor fluid through the top opening of the right side (the downcomer) of the reactor loop. Upon contact with the reactor fluid, the algin gelled into 4 mm-diameter spheres. The dispensing rate was controlled by a clamp on the vent tube of the compressed air line connected to the dispenser. The total volume of the algin solution dispensed varied in the range of 10–120 ml. The initial concentration of $CuSO_4$ was in the range of 60–200 ppm (copper) and the amount of inert neutral salt $NaNO_3$ added was 0.1 or 0.01 mol/l. The initial volume of the solution was 1.7–1.85 l.

The experimental conditions of various runs are summarized in Table 1. In runs 1–7, the amount of algin added was roughly proportional to the initial concentration of Cu^{2+}. In runs 8–15, different amounts of algin were added to the reactor fluid containing 200 ppm Cu^{2+} initially. With the exception of runs 14 and 15, the amount of initial total Cu^{2+} was greater than or equal to the maximum possible copper binding sites, thus ensuring a complete penetration of Cu^{2+} throughout the gel.

Procedure

Before the start of each run, two 0.4 ml samples of reactor fluid were withdrawn from the reactor. At the time of initiation of addition of the algin solution and 2 min intervals thereafter for 30 min, 0.4-ml reactor fluid was withdrawn from the top of the riser. (The time spent to dispense the algin solution was also recorded.) Afterwards the period of sampling was gradually increased. Each run lasted for 8–16 h. All the samples were diluted by 5 to 10-fold with deionized water and the concentrations of dissolved copper were determined by atomic absorption (AA) spectrometry (Perkin–Elmer Zeeman 5100). The initial and final concentrations were used to calculate copper-binding capacity and stability constant in this work. At the end of each run, the alginate spheres were collected by a nylon net inserted through the opening of the downcomer. The spheres were briefly dried by rolling over a clean tissue paper. The total volume of the alginate spheres was determined by the volume of the final solution displaced by the spheres in a graduated cylinder. A fraction of the beads were counted (N) and weighed (W). The total number of beads in each run was estimated as [total wet weight of beads $\times$ (N/W)]. The final diameters of 20–50 beads from each experiment were measured by a dial caliper.

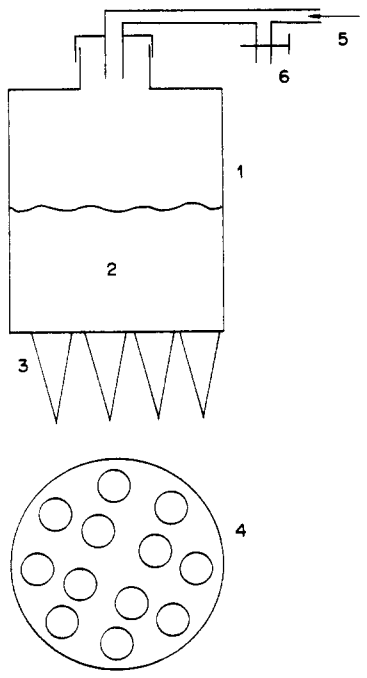

Fig. 3. A schematic diagram of the dispenser. 1, Side view of a 200-ml plastic bottle: 2, algin solution (3.2 g algin in 100 ml water); 3, 200-μl pipetter tips; 4, bottom view; 5, compressed air; 6, air vent.

RESULTS

Uronate assay of algin

The percent recovery of uronic acid in the pure alginic acid was determined to be 31.87% in the colorimetric method [2.801 mg of hydrolyzed uronic acid (0.01444 mmol) was recovered from 10 mg of alginic acid (0.0453 mmol of uronic acid residues; 0.01444/0.0453 = 0.3187)]. Assuming that the percent recovery of uronate was also the same for algin, each gram of algin should contain 4.356 mmol (or 0.8624 g) of sodium uronate residues.

Batch absorption experiments

The results of all experimental runs are summarized in Table 1. Stable alginate beads were formed in all experiments. The total volume of liquid sample drawn (14 ml) was insignificant compared to the total initial liquid volume. More than 90% of the copper was absorbed by the 3–5 g of algin dispensed into the reactor (runs 12–15).

The mass of copper absorbed per unit dry mass of algin dispensed was about 0.1 Cu/g algin (Table 1). Comparing pairs of experimental runs under similar conditions but at different $NaNO_3$ concentrations, it was found that higher percentages of dissolved copper were absorbed at the lower $NaNO_3$ concentration of 0.01 M (Fig. 4). In runs 13 and 15 (the concentration of $NaNO_3$ was 0.01 M and the final copper concentrations were below 10 ppm), the spheres swelled significantly, likely due to the osmotic pressure between the beads and the solution. On the contrary, the beads shrank slightly in most of the experiments using 0.1 M $NaNO_3$ solutions.

About 20–30 min after the start of each experiment, the spheres gradually turned visibly blue indicating a strong absorption of hydrated Cu^{2+} by the alginate gel.

The time courses of the change in dissolved copper concentrations are presented in Fig. 5. It is shown that 90% absorption of the initial copper in each experiment can be achieved in 1 h and that the solution approached the final equilibrium concentration within the first 2 h of each experiment.

Absorption capacity and conditional stability constant

Results of calculation using the conventional Langmuir's model [equation (A3)] for experiments at two different $NaNO_3$ concentrations are presented in

Table 1. Summary of conditions and results of various runs

Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Initial $CuSO_4$ conc. (as ppm Cu)	204.4	200.5	162.8	150.1	100.4	104.0	55.0	189.1	202	203	196.9	201.3	233.4	187.9	216.3
Final Cu^{2+} conc. (ppm Cu) ($=C_{Cu^{2+}}$)	160.3	144.8	128.7	107.4	68.7	66.3	32.5	88.1	81.9	23.0	26.7	24.9	9.1	24.1	7.4
$NaNO_3$ added (mol/l)	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.01
% Cu absorbed	21.7	28.2	21.3	29.0	32.0	36.6	28.3	53.4	59.7	88.0	86.5	87.8	96.3	87.9	97.3
Dry wt algin* dispensed (g)	0.876	0.870	0.597	0.618	0.554	0.550	0.305	1.84	1.70	2.90	2.68	3.69	3.65	4.59	4.66
g Cu absorbed/g dry algin ($=Q$)	0.0941	0.1204	0.1076	0.1304	0.1074	0.1282	0.060	0.101	0.131	0.112	0.114	0.0862	0.110	0.063	0.078
Estimated No. beads	1445	1431	1047	1125	1243	716	687	3566	3851	4446	4829	6011	6728	8216	7616
Average final diameter of beads (cm)	0.295	0.310	0.275	0.308	0.280	0.347	0.293	0.280	0.321	0.336	0.367	0.395	0.412	0.358	0.452
Final pH of solution	4.63	4.76	4.70	4.65	4.89	4.40	4.98	4.57	4.13	4.88	4.66	5.00	5.01	5.05	5.33
Temperature (C)								21 ± 1 (all runs)							

*Weight of algin solution dispensed × 3.2 g algin/103.2 g algin solution.

Table 2. Summary of results of calculation

Run No.	1	3	5	7	8	10	12	14	2	4	6	9	11	13	15
$NaNO_3$ added (mol/l)				0.1								0.01			
$C_{Cu^{2+}} \times 10^3$ (mol/l)	2.523	2.026	1.080	0.511	1.387	0.362	0.392	0.378	2.279	1.690	1.043	1.289	0.420	0.143	0.116
$C_{Cu^{2+}}/Q \times 10^2$ (mol/l)/ (g Cu absorbed/g algin)	2.682	1.883	1.005	1.134	1.367	0.324	0.454	0.600	1.893	1.296	0.814	0.984	0.368	0.129	0.148
Conventional Langmuir's model	$k_1 = 0.1085$ g Cu absorbed/g algin; $k_c = 5.262 \times 10^3$ l/mol; correlation coefficient = 0.94 (excluding Run 14)								$k_1 = 0.1247$ g Cu absorbed/g algin; $k_c = ?$ (negative y-intercept)						
V_p (g water)	18.22	14.0	14.8	11.03	45.5	81.13	120.2	186.5	25.13	19.3	14.45	52.8	95.34	168.0	457.0
$(\overline{Na^+})/(Na^+)$	1.366	1.215	1.187	1.144	1.237	1.126	1.245	1.296	1.986	1.338	1.602	1.159	1.736	1.465	1.413
$(\overline{Cu^{2+}})/(Cu^{2+})$	1.867	1.476	1.409	1.309	1.531	1.269	1.549	1.680	3.943	1.789	2.565	1.344	3.014	2.147	1.996
$(\overline{Cu^{2+}}) \times 10^4$ (mol/l)	5.479	6.517	3.341	1.620	4.639	1.008	1.331	1.402	3.412	1.205	1.115	0.670	0.499	0.118	0.087
Q_p (g Cu bound/g algin)	0.087	0.103	0.105	0.099	0.098	0.111	0.085	0.061	0.097	0.124	0.123	0.127	0.111	0.110	0.077
$(\overline{Cu^{2+}})/Q_p \times 10^1$ (mol/l)/ (g Cu bound/g algin)	11.72	6.333	3.188	1.638	4.737	0.909	1.570	2.298	28.11	9.740	9.077	5.249	4.500	1.069	1.12
Modified Langmuir's model	$K_1 = 0.1226$ g Cu bound/g algin; $K_c = 1.556 \times 10^4$ l/mol (Runs 1–13); correlation coefficient = 0.992														

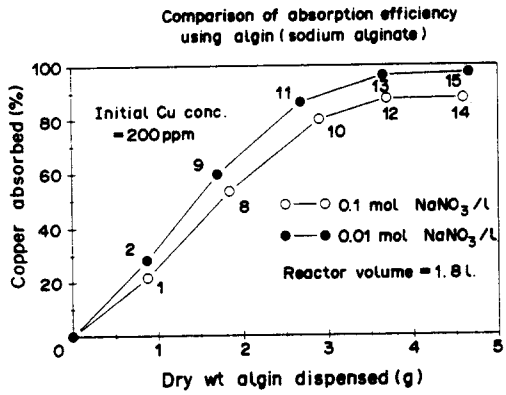

Fig. 4. Percent recovery of copper from solutions containing an initial concentration of dissolved copper at 200 ppm.

Table 2 (top half) and Fig. 6. For data points at 0.1 M $NaNO_3$, the *absorption* capacity k_1 (for covalently-bound Cu^{2+} plus electrostatically-held Cu^{2+}) was 0.1085 g Cu/g algin and the conditional stability constant k_c [for interactions between all Cu^{2+} *absorbed* and Cu^{2+} in the bulk solution, defined in equation (A2)] was 5.262×10^3 l/mol as determined from the slope and the intercept of the best-fit straight line passing through open symbols in Fig. 6.

For data points of experiments at a $NaNO_3$ concentration of 0.01 M, the slope of the best-fit straight line passing through closed symbols in Fig. 6 gives an *absorption* capacity $k_1 = 0.1247$ g Cu/g algin. Since the line passing through closed symbols (0.01 M $NaNO_3$) is below that through open symbols (0.1 M $NaNO_3$), one would expect to obtain a higher conditional stability constant k_c with the former case. A large k_c should result in a small positive intercept on the Langmuir's plot. However, any experimental error that caused a slight shift in the data points may lead to a small negative intercept, as observed in this case. Nevertheless, qualitatively speaking the k_c for experiments at 0.01 M $NaNO_3$ was a large number.

Copper-binding capacity and intrinsic stability constant

The results of iterative calculation using the procedure outlined in the Appendix are listed in Table 2 (bottom half). When the modified Langmuir's model [equation (A15)] was used to treat experimental data, it is found that a single best-fit straight line with 99.2% coefficient of correlation is obtained for data points at different $NaNO_3$ concentrations (Fig. 7). From the slope and the intercept of Fig. 7, an intrinsic copper-binding stability constant K_c [for interactions between covalently-bound copper and electrostatically-held copper in the gel domain, defined in equation (A14)] independent of $NaNO_3$ concentration is calculated to be 1.556×10^4 l/mol and the *binding* capacity K_1 (for covalently-bound copper excluding electrostatically-held copper) is calculated to be 0.1226 g Cu/g algin.

DISCUSSION

The loop fluidized bed reactor offered several advantages: (1) the newly-formed soft spheres remained stable in the reactor likely due to the gentle circulating motion of the fluid. In a separate experiment, we found that newly-formed spheres were broken apart or torn into irregular shapes when the fluid was gently agitated with a magnetic stirrer; (2) the multi-tip dispenser allowed dispensing of the viscous algin solution within a short period of time (2–17 min), thus ensuring that the concentration of dissolved copper at the end of dispensing was sufficiently high to coagulate the algin upon contact with the fluid in the reactor; (3) in addition to copper

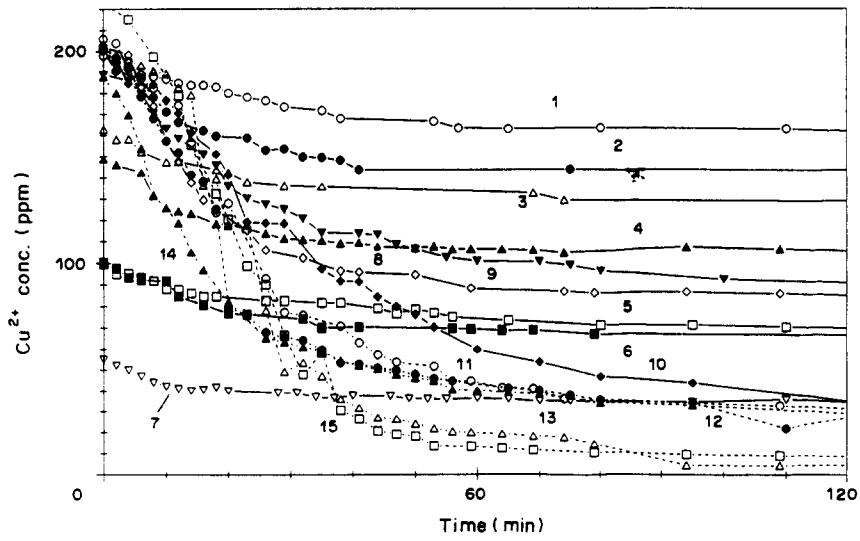

Fig. 5. Time courses of the change in dissolved copper concentration.

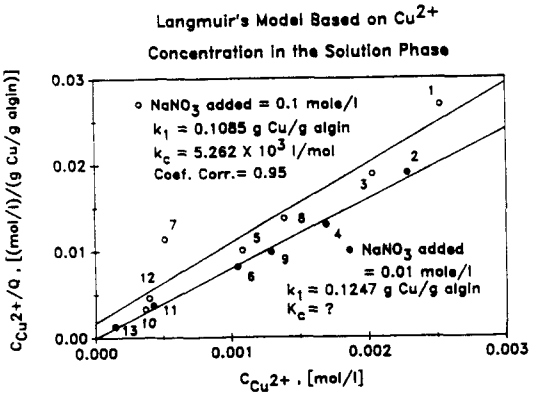

Fig. 6. Conventional Langmuir's plots of experimental data for runs 1–13 based on the concentration of dissolved copper in the bulk solution.

binding equilibrium, the kinetics of copper absorption can also be analyzed from the change in concentration of dissolved copper in the reactor fluid over time (Jang *et al.*, 1990b); and (4) spheres saturated with copper can be very easily removed from the reactor.

The reactor fluid had a final pH in the range of 4.6–5.0 because $CuSO_4$ is a weakly acidic salt. The formation of $Cu(OH)_2$ in the range of pH encountered in this work is known to be negligible. Since the pK_{HA} value of alginic acid [=2.96 (Jang *et al.*, 1989)] was almost two units below the pH of solution and copper has a strong affinity toward alginate, pH effect was not considered in this work. However, when using the present technology to absorb metals from mine drainages having a much lower pH, the binding capacity for metals is expected to be significantly lowered due to the competition from H^+ for metal binding sites.

To take into account the non-ideality of both the bulk solution and the gel fluid (due to interactions between cations and anions) in this work, the activity instead of the concentration of Cu^{2+} was used to define the intrinsic copper-binding stability constant. Equations (A6) and (A7) that were used to estimate the single-ion activity coefficients were derived

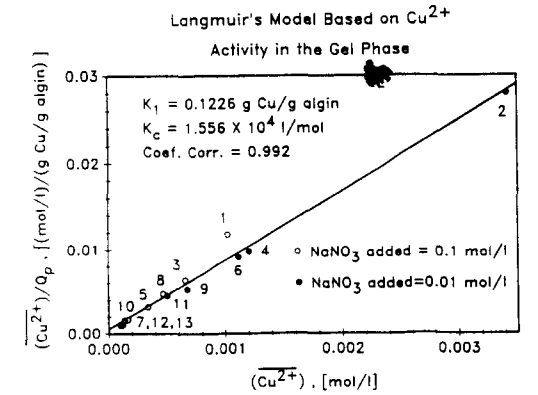

Fig. 7. Modified Langmuir's plot of experimental data based on the activity of electrostatically-held Cu^{2+} in the gel fluid.

considering the effect of the sizes of ionic species on their mutual interactions (Robinson and Stokes, 1959; Jang *et al.*, 1989). Other more sophisticated models that may explain specific ion effects better are available (Jang *et al.*, 1989). Since the computation involved in these models are more complicated, equations (A6) and (A7) were used throughout this work. Experiments using different cupric salts should be conducted in the future to reveal any effects the anions may have on copper binding to biopolymers.

The improvement in data fit from Figs 6 to 7 and the existence of a single intrinsic copper-binding constant independent of the ionic strength of the bulk solution justify our assumption that an appropriate description of copper-binding equilibrium should be based on the conditions in the gel domain. Our argument is further supported by the values of the partition coefficient [ratio of the Cu^{2+} activity in the gel domain to Cu^{2+} activity in the bulk solution, defined by equation (A9)] which ranged in 1.5–4 (Table 2); the lower the ionic strength in the bulk solution, the higher the value of the partition coefficient. Therefore, if the Cu^{2+} activity in the reaction zone (i.e. the gel domain) instead of the Cu^{2+} activity in the bulk solution is used to define binding equilibrium, an intrinsic stability constant can be obtained that truly reflects the intrinsic affinity of copper toward biopolymer.

Thus, there is no fundamental difference in the process of copper binding to biopolymers at different ionic strengths of the bulk solution. The difference in the apparent affinity factor (the conditional stability constant) simply reflects the difference in the change of free energy as a Cu^{2+} migrates from the bulk solution (across the "membrane" on the surface of the gel) to the gel domain. The lower the ionic strength of the bulk solution, the greater the difference in this free energy change. The free energy associated with the actual binding reaction itself in the gel domain depends mainly on the chemical nature of interacting species and the morphology of the biopolymer chains but is unaffected by environmental conditions.

The *binding* capacity K_1 (=0.1226 Cu bound/g algin) determined from the modified Langmuir's model was somewhat lower than the maximum possible binding density 0.1383 g Cu/g algin determined from uronate assay of algin (0.1383 = 0.862 Na-alginate/g algin ÷ 198 g Na-alginate/mol ÷ 2 mol Na-alginate/mol Cu × 63.54 g Cu/mol). According to the supplier, the ratio of mannuronate to guluronate residues was 61-to-39 in algin. It is likely that regions of the algin enriched in mannuronate did not bind (covalently) the copper entering the gel phase as effectively as regions of the algin enriched in guluronate. The former exhibit an unfavorable ribbon-like morphology (as opposed to the coil-like morphology of the guluronate blocks that provided more favorable cavities for copper). However, these unbound, negatively-charged mannuronate blocks

contributed to the ionic environment of the gel phase and thus indirectly enhanced the partition of both Na^+ and free, unbound Cu^{2+} between the gel fluid and the reactor fluid.

The partition coefficients of Cu^{2+} obtained in this work were just a few folds of unity because a substantial fraction of the negative charges on uronate residues (due to hydrolyzed carboxyl groups) was neutralized (or "inactivated") by the bound copper. This in turn generated a mild electric field in the gel. Therefore, the activity of Na^+ in the gel fluid (Na^+ that remained to balance the charges of the unbound uronate residues plus the $Na^+NO_3^-$ invading the gel phase) was only a factor of 1.126–1.986 greater than that in the bulk solution (Table 2). A relatively small partition coefficient (1.5–4) for Cu^{2+} was obtained and, therefore, the observed binding affinity of alginate gel for copper was not dependent on the ionic strength of the bulk solution very strongly.

In our recent work (Jang *et al.*, 1990a), a special technique was used to produce partially-coagulated alginate gels to absorb copper from synthetic solutions containing copper at a low initial concentration (10 ppm) that did not allow formation of stable alginate gels by direct dispensing. A strong dependence of the apparent binding affinity on the ionic strength in the bulk solution was observed in this case. Our two-phase approach was again successful in explaining this phenomenon and obtaining an intrinsic copper-binding stability constant (Jang *et al.*, 1990a).

CONCLUSIONS

(1) A 3.2% by weight of algin solution is a favorable absorbent for dissolved copper. Alginate beads can be formed by directly dispensing the algin solution into the aqueous media containing dissolved copper at initial concentrations above 60 ppm in the loop fluidized bed reactor;

(2) The ionic strength of the copper-containing aqueous media affects the apparent copper-binding affinity of alginate to some extent. Conventional Langmuir's model based on the concentration of dissolved copper in the bulk solution cannot yield a unique copper-binding stability constant for aqueous media at different ionic strengths; and

(3) The two-phase model employed in this work allows estimation of the activity of free, unbound Cu^{2+} in the gel fluid. When the Langmuir's model is based on this quantity instead of the concentration of Cu^{2+} in the aqueous media surrounding the beads, a unique binding stability constant and a unique effective binding capacity are obtained with confidence. However, more work needs to be done in the range of low concentration of dissolved copper. A special technique is needed to prepare alginate beads under this condition.

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APPENDIX

The binding reaction between Cu^{2+} and free binding sites BS in the alginate gel can be expressed as

$$Cu^{2+} + BS \rightleftarrows Cu^{2+}\text{-}BS. \quad (A1)$$

The conditional stability constant k_c under a given set of environmental conditions (pH, ionic strength and temperature) is defined as

$$k_c = \frac{C_{Cu^{2+}\text{-}BS}}{C_{Cu^{2+}} C_{BS}}. \quad (A2)$$

In equation (A2), $C_{Cu^{2+}}$ is the concentration of free, unbound Cu^{2+} in the bulk solution. $C_{Cu^{2+}\text{-}BS}$ is the concentration, in the alginate gel, of copper bound covalently plus copper held electrostatically; no distinction is made between these two states of copper. C_{BS} is the concentration, also in the alginate gel, of unbound negatively-charged sites (each retaining two Na^+ to balance the negative charges on hydrolyzed carboxyl groups). Since $C_{Cu^{2+}\text{-}BS}$ and C_{BS} are based on the same volume of the gel phase, their concentrations can also be expressed on the basis of dry mass of the polymer contained in the gel. If the *absorption* capacity for copper bound covalently plus copper held electrostatically in the gel is k_1 g Cu absorbed/g polymer, substituting C_{BS} by (k_1-$C_{Cu^{2+}\text{-}BS}$) and rearranging equation (A2) yields the conventional Langmuir's model:

$$\frac{C_{Cu^{2+}}}{Q} = \frac{1}{k_1 k_c} + \frac{C_{Cu^{2+}}}{k_1} \quad (A3)$$

where Q stands for $C_{Cu^{2+}\text{-}BS}$. The values of k_1 and k_c can be determined from the slope and intercept of the plot of $C_{Cu^{2+}}/Q$ vs $C_{Cu^{2+}}$.

In the process of Cu^{2+} binding to alginate gel, the gel defines a separate phase in the system, with the outer surface serving as a semi-permeable membrane only allowing simple electrolytes to permeate through (Fig. 1). The ionic environment in the gel is different than that in the bulk solution due to the existence of the unbound ionized binding sites. Each Cu^{2+} entering the gel phase is exchanged with two Na^+ originally associated with the uronate residues on the alginate. The rest of the Na^+ has to remain in the gel fluid to balance the negative charges on the unoccupied binding sites. The inert neutral salts such as $Na^+NO_3^-$ added to the solution to adjust the ionic strength and $Cu^{2+}SO_4^{2-}$ could also invade the gel phase. As a result, the gel phase contains a higher concentration of Na^+ than the bulk solution.

According to Gibbs–Donnan theory, the ratio of Cu^{2+} activity in the gel fluid to Cu^{2+} activity in the bulk solution is controlled by the corresponding ratio for Na^+ [equation (A9) to be presented] (Marinsky *et al.*, 1982, 1985). Therefore, the gel fluid should also contain a higher concentration of Cu^{2+} than the bulk solution.

An iterative procedure was modified from our previous work (Jang *et al.*, 1989) to estimate the activity of Cu^{2+} held electrostatically in the gel fluid and the numbers of moles of $Na^+NO_3^-$ invading the gel phase. The steps of calculations are as follows.

Step 1

Calculate the total number of moles of uronate residues in the biopolymer (that is composed mainly of sodium alginate) added to the reactor fluid by using the results of colorimetric analysis of the hydrolyzed polymer.

Step 2

Estimate $\langle \overline{Na^+} \rangle$ (the number of moles of sodium originally associated with alginate that has to remain in the gel phase to balance the negative charges of unbound uronate residues) as equal to the number of moles of uronate residues minus twice the number of moles of Cu^{2+} absorbed by the gel. Hereafter in this Appendix, the brackets $\langle\ \rangle$ denote the number of moles of a species, the bar over a symbol denotes the gel domain, the parentheses ( ) denote the activity of an ionic species and the square brackets [ ] denote a grouping of mathematical terms.

Step 3

The number of moles of sodium nitrate invading the gel phase, $\langle \overline{Na^+NO_3^-} \rangle$, and the moles of Cu^{2+} held electrostatically in the gel fluid, $\langle \overline{Cu^{2+}} \rangle$, are both set at $\langle \overline{Na^+} \rangle$ initially.

Step 4

Calculate the ionic strengths of the bulk solution and the gel fluid at final equilibrium:

$$I = [C_{Na^+} + C_{NO_3^-} + 4\,C_{SO_4^{2-}} = +4\,C_{Cu^{2+}}]_{solution}/2 \quad (A4)$$

$$\bar{I} = [\langle \overline{Na^+} \rangle + \langle \overline{A^-} \rangle + 4\langle \overline{Cu^{2+}} \rangle + 2\langle \overline{Na^+NO_3^-} \rangle + 8\langle \overline{Cu^{2+}SO_4^{2-}} \rangle]_{gel}/2V_p. \quad (A5)$$

In equation (A5) $\langle \overline{A^-} \rangle$ is the number of moles of free, unbound uronate residues which equals the total uronate residues (in the sodium form initially) minus twice the number of moles of Cu^{2+} bound (excluding Cu^{2+} held electrostatically in the gel fluid) and V_p is the water content (in g, total wet weight of the gel minus the dry of the polymer) of the gel phase. The final concentration of Na^+ and NO_3^- in the solution can be easily calculated from the material balance and the initial and final volumes of the solution. Since the $CuSO_4$ concentrations were much lower than the $NaNO_3$ concentrations in the bulk solution in this work, the extent of neutral $Cu^{2+}SO_4^{2-}$ invading the gel phase should be negligible and will not affect the ionic strength in the gel fluid significantly. Therefore, the term $8\langle Cu^{2+}SO_4^{2-} \rangle$ was dropped from equation (A5) in the calculation.

Step 5

Calculate the mean activity coefficient $\gamma_{\pm NaNO_3}$ in the bulk solution and the gel phase at ionic strengths I and $\bar{I}$, respectively, using tabulated data of molal activity coefficients (Robinson and Stokes, 1959). [For dilute aqueous solutions, the molal concentration (m) is very close to the molar concentration (M). For example, 0.1 M $NaNO_3$ = 0.105 m and 0.01 M $NaNO_3 \approx$ 0.01 m]. Calculate the single-ion activity coefficients of Na^+ and Cu^{2+} in the bulk solution and the gel phase using the tabulated data (Kielland, 1937) or by the following equations

$$[\gamma_{Na^+}] = \frac{[\gamma_{\pm NaCl}]^2}{[\gamma_{\pm KCl}]} \quad \text{at } I \text{ and } \bar{I} \quad (A6)$$

$$[\gamma_{Cu^{2+}}] = \frac{[\gamma_{\pm CuCl_2}]^3}{[\gamma_{\pm KCl}]^2} \quad \text{at } I \text{ and } \bar{I} \quad (A7)$$

(Jang *et al.*, 1989).

Step 6

Apply Donnan equilibrium theory to correct the value of $\langle \overline{Na^+NO_3^-} \rangle$. Since the product of the activities of Na^+ and NO_3^- must be the same for the two phases in equilibrium, we have

$$[\gamma_{\pm NaNO_3}]_I^2 C_{Na^+} C_{NO_3^-} = [\gamma_{\pm NaNO_3}]_{\bar{I}}^2 \times \frac{\langle \overline{Na^+} \rangle + \langle \overline{Na^+NO_3^-} \rangle}{V_p} \frac{\langle \overline{Na^+NO_3^-} \rangle}{V_p}. \quad (A8)$$

By treating $\langle \overline{Na^+NO_3^-} \rangle$ as an unknown variable, equation (A8) becomes a quadratic equation and the improved value of $\langle \overline{Na^+NO_3^-} \rangle$ can be calculated easily.

Step 7

Apply Donnan equilibrium theory to correct the value of $\langle \overline{Cu^{2+}} \rangle$. The activities of Cu^{2+} and Na^+ in the gel phase and the bulk solution can be related by

partition coefficient for Cu^{2+}

$$= [(\overline{Cu^{2+}})/(Cu^{2+})]$$

$$= [(\overline{Na^+})/(Na^+)]^2 \quad \text{(A9)}$$

where

$$(\overline{Cu^{2+}}) = [\gamma_{Cu^{2+}}]_f \langle \overline{Cu^{2+}} \rangle / V_p \quad \text{(A10)}$$

$$(Cu^{2+}) = [\gamma_{Cu^{2+}}]_f C_{Cu^{2+}} \quad \text{(A11)}$$

$$(\overline{Na^+}) = [\gamma_{Na^+}]_f \frac{\langle \overline{Na^+} \rangle + \langle \overline{Na^+NO_3^-} \rangle}{V_p} \quad \text{(A12)}$$

$$(Na^+) = [\gamma_{Na^+}]_f C_{Na^+}. \quad \text{(A13)}$$

By substituting equations (A10–13) into equation (A9) and rearranging, an improved value of $\langle \overline{Cu^{2+}} \rangle$ can be obtained.

Step 8

Substitute improved values of $\langle \overline{Na^+NO_3^-} \rangle$ and $\langle \overline{Cu^{2+}} \rangle$ into equations (A4) and (A5) and iterate between Step 4 and Step 7 until the values of $\langle \overline{Na^+NO_3^-} \rangle$ and $\langle \overline{Cu^{2+}} \rangle$ from successive trials converge. Then calculate the value of $(\overline{Cu^{2+}})$ using equation (A10). A Fortran 77 program based on the above algorithm was developed in this work.

Step 9

Define the intrinsic copper-binding stability constant K_c as

$$K_c = \frac{(\overline{Cu^{2+}\text{-}BS})}{(\overline{Cu^{2+}})(\overline{BS})} \quad \text{(A14)}$$

where $(\overline{Cu^{2+}\text{-}BS})$ is the activity of copper bound covalently in the gel domain, $(\overline{Cu^{2+}})$ is the activity of copper held electrostatically, and $(\overline{BS})$ is the activity of unbound charged sites. Let K_1 be the *binding* capacity of the alginate gel for covalently bound copper. By replacing $(\overline{BS})$ by $[K_1\text{-}(\overline{Cu^{2+}\text{-}BS})]$ and rearranging equation (A14), the following modified Langmuir's model based on the conditions in the gel domain is obtained:

$$\frac{(\overline{Cu^{2+}})}{Q_p} = \frac{1}{K_1 K_c} + \frac{(\overline{Cu^{2+}})}{K_1} \quad \text{(A15)}$$

where Q_p stands for $(\overline{Cu^{2+}\text{-}BS})$. The ratio of the activity coefficients of bound and unbound sites has been proven to be unity because their respective nonideality cancels (Marinsky *et al.*, 1990). Therefore, the ratio of the activities of bound to unbound sites in the gel phase is equal to the ratio of the concentrations of unbound to bound sites, either on the basis of the gel volume or the weight of polymer.