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SORPTION EQUILIBRIUM OF COPPER BY PARTIALLY-COAGULATED CALCIUM ALGINATE GEL

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The sorption equilibrium of dissolved copper by spherical partially-coagulated gels of calcium alginate was investigated in this work. The gels were formed by dispensing a viscous algin (food grade sodium alginate from kelp) solution with a multi-tip dispenser into 0.05 M $CaCl_2$ solution in a loop fluidized bed reactor. The resultant semi-rigid spherical gels were then transferred to another reactor operated batchwise to absorb dissolved copper at low concentrations (10–40 ppm). When the concentration of the inert neutral salt $NaNO_3$ added to the reactor fluid was 0.01 M, the amount of copper absorbed was found to be substantially higher than that at 0.1 M $NaNO_3$. The conventional Langmuir's model based on the concentration of copper in solution yielded different values of conditional stability constant at different ionic strengths in the reactor fluid. However, by defining the copper-binding stability constant on the basis of copper activity in the gel phase with the competition from calcium for metal binding sites taken into account, a unique copper-binding stability constant and a unique calcium-binding stability constant were obtained. The numerical procedure for estimating the activity of copper in the gel fluid was modified from Jang *et al.* Water Research, 1990, in press).

KEYWORDS Alginic acid Sodium Alginate Calcium alginate Copper binding Fluidized bed reactor.

INTRODUCTION

In our recent work [1], we reported that stable spherical alginate gels were formed in the loop fluidized bed reactor when the viscous, water-soluble sodium alginate solution was directly dispensed into the reactor fluid containing 60–200 ppm dissolved copper. The newly formed gels then circulated in the reactor to absorb copper until final equilibrium was reached. The approach of directly dispensing the sodium alginate solution into the reactor fluid to form stable gels failed, however, at dissolved copper concentrations below 60 ppm.

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In this work, we prepared partially-coagulated calcium alginate gels to absorb copper from solution at low concentrations. To minimize the competition from calcium with copper for metal binding sites in the alginate gels, a special technique was used to prepare stable semi-rigid alginate gels that were only partially saturated with calcium.

In the process of Cu^{2+} binding to alginate gel, the gel may define a separate phase in the solution, with the outer surface serving as a semi-permeable membrane only allowing simple electrolytes to permeate through (Fig. 1). Since metal-binding reactions take place in the gel phase, it is more reasonable to define the mass-action equilibrium constant (the metal-binding stability constant) based on the conditions in the gel phase.

Although the alginate gel is electrostatically neutral as a whole, the ionic environment in the gel is different than that in the bulk solution due to the existence of the unoccupied charged ionized sites. Each Cu^{2+} or Ca^{2+} entering the gel phase is exchanged with two Na^+ originally associated with the uronate residues (repeating monomer units, each carrying a carboxyl group) 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 salt such as $NaNO_3$ added to the solution to adjust the ionic strength could also invade the gel phase (through the "membrane" on the surface of the gel). As a result, the gel phase contains a higher concentration of Na^+ than the bulk solution.

The Cu^{2+} and Ca^{2+} *absorbed* by the alginate gel exists in two states: *bound* (chemically to binding sites) and *free* (i.e., held electrostatically by charged

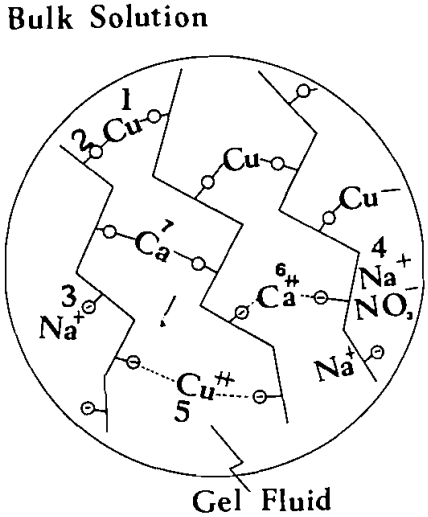

FIGURE 1 A conceptual picture showing the gelation of alginate in the presence of Cu^{2+} and Ca^{2+}. Each section on the polymer chain represents a uronate residue. Hydroxyl groups are not shown in the figure. 1: copper bound 2: occupied carboxyl groups 3: Na^+ that remain in the gel to balance the unoccupied carboxyl groups 4: $NaNO_3$ that invades the gel phase 5: free, unbound Cu^{2+} in the gel fluid (The dashed lines represent electrostatic interaction between Cu^{2+} or Ca^{2+} and unoccupied carboxyl groups). 6: free, unbound Ca^{2+} in the gel fluid 7: calcium bound.

functional groups while freely migrating in the gel fluid enclosed by the outer "membrane"). Figure 1 also illustrates the mechanism of gel formation, the "egg-box" model [2,3]. Each binding site consists of two hydrolyzed (ionized) carboxyl groups and two or more hydroxyl groups on participating uronate residues on the alginate molecules. According to Donnan equilibrium theory, the partition of free Cu^{2+} and Ca^{2+} between the gel fluid and the bulk solution is controlled by the partition of Na^+ between these two phases [4,5] and, therefore, the gel fluid should also contain a higher concentration of Cu^{2+} and Ca^{2+} than the bulk solution.

If the activity of Cu^{2+} in the gel fluid and the amount of $NaNO_3$ invading the gel phase can be estimated, an improved value of copper-binding stability constant based on the conditions in the gel fluid may be obtained. However, these two quantities are not known *a priori*.

In this communication, we will outline the theory for predicting simultaneously the amount of $NaNO_3$ invading the gel fluid and the activity of copper in the alginate gel in the presence of competing calcium. Batch absorption data at different ionic strengths will be treated with the conventional Langmuir's model (based on the concentration of copper in solution) and the modified model (based on the activity of copper in the gel phase). The values of the copper-binding stability constant determined by both models will be compared and discussed.

THEORY

Alginic acid is known to bind both copper and calcium strongly, with the selectivity for copper being several times more favorable than for calcium [6–8]. When both metal ions compete for the same type of binding sites in the alginate gel, binding reactions can be expressed as

$$M^{2+} + BS = M^{2+} - BS \tag{1}$$

where M is Cu or Ca and BS is the free, unoccupied binding sites in the alginate gel. Traditionally, the metal-binding stability constant that describes the relationship between free metal in the solution and metal absorbed by the gel is given by

$$k_M = \frac{\overline{C_{M^{2+}-BS}}}{C_{M^{2+}}\overline{C_{BS}}} \quad (M = Cu \text{ or } Ca) \tag{2}$$

where the bar over a symbol denotes the gel phase, $C_{M^{2+}}$ is the concentration of the metal ion in the (external) solution, $\overline{C_{M^{2+}-BS}}$ and $\overline{C_{BS}}$ are moles of M^{2+} absorbed (including chemically-bound M^{2+} and M^{2+} attracted to and held in the gel phase electrostatically) and unoccupied sites (whose charges are balanced by Na^+ originally associated with uronate residues), respectively, per unit dry mass of alginate in the gel. Substituting $\overline{C_{BS}}$ by $[k_1 - \overline{C_{Cu^{2+}-BS}} - \overline{C_{Ca^{2+}-BS}}]$ into Eq. (2) (the classical Langmuir's treatment, where k_1 is the effective maximum absorption capacity in mole per unit dry mass of alginate) yields

$$\frac{C_{Cu^{2+}}}{Q_{Cu}} = \frac{1}{k_1 k_{Cu}} + \frac{C_{Cu^{2+}}}{k_1}\left[1 + \frac{Q_{Ca}}{Q_{Cu}}\right] \tag{3}$$

for copper (and calcium if the Cu is replaced by Ca and vice versa in Eq. (3)), where Q_M represents $\overline{C_{M^{2+}-BS}}$ (M = Cu or Ca). The values of k_1 and k_{Cu} can be obtained from the intercept and the slope of the plot of $C_{Cu^{2+}}/Q_{Cu}$ versus $[C_{Cu^{2+}}][1 + (Q_{Ca}/Q_{Cu})]$.

It has been verified in our recent work [1,9,10] that a rigorous definition of metal-binding stability constant should be based on the conditions in the gel phase where binding reactions actually occur. Furthermore, the non-ideality of the liquid contained within the gel phase needs to be taken into account by using the activities rather than the concentrations of the interacting species. Therefore, the definition in Eq. (2) can be modified to

$$K_M = \frac{\overline{(M^{2+} - BS)}}{\overline{(M^{2+})}\,\overline{(BS)}} \quad (M = Cu \text{ or } Ca) \tag{4}$$

In the equation above and hereafter, the parentheses ( ) denote the activity (activity coefficient multiplied by molal concentration). $\overline{(M^{2+})}$ is the activity of free cupric ion in the gel fluid in equilibrium with chemically-bound copper whose activity is denoted by $\overline{(M^{2+} - BS)}$. The activity of the unbound sites is denoted by $\overline{(BS)}$. The ratio of the activity coefficients of bound to unbound sites has been proven to be unity because their respective non-ideality cancels [11]. Therefore, the ratio $\overline{(M^{2+} - BS)}/\overline{(BS)}$ is equal to the ratio of mols of bound sites to mols of unbound sites.

Substituting $[K_1 - \overline{(Cu^{2+} - BS)} - \overline{(Ca^{2+} - B2)}]$ for $\overline{(BS)}$ into Eq. (4) yields the equation below for copper:

$$\frac{\overline{(Cu^{2+})}}{Q_{p,Cu}} = \frac{1}{K_1 K_{Cu}} + \frac{\overline{(Cu^{2+})}}{K_1}\left[1 + \frac{Q_{p,Ca}}{Q_{p,Cu}}\right] \tag{5}$$

and for calcium (if Cu is replaced by Ca and vice versa in Eq. (5)). In Eq. (5), $Q_{p,M}$ represents $\overline{(M^{2+} - BS)}$ (M = Cu or Ca). Therefore, K_1 is the maximum number of mols of sites available to bind metal ions chemically.

An iterative procedure was modified from our previous work [1,9,10] to estimate $\overline{(M^{2+})}$ from the measured equilibrium concentration $C_{M^{2+}}$. The steps of calculation are as follows.

Step 1: Calculate the total number of moles of uronate residues in the algin (that is composed mainly of sodium alginate) added to the reactor fluid by using the results of colorimetric analysis of the hydrolyzed polymer [1].

Step 2: Estimate $\langle\overline{Na^+}\rangle$ (the number of moles of sodium originally associated with algin that has to remain in the gel phase to balance the negative charges of unoccupied uronate residues) as equal to the number of mols of uronate residues minus twice the number of mols of Cu^{2+} and Ca^{2+} absorbed by the gel. Hereafter in this communication, the brackets $\langle\ \rangle$ denote the number of mols of a species and the square brackets [ ] denote a grouping of mathematical terms.

Step 3: The number of mols of sodium nitrate invading the gel phase, $\langle\overline{NaNO_3}\rangle$, and the moles of free, unbound M^{2+} in the gel fluid, $\langle\overline{M^{2+}}\rangle$ (M = Cu or Ca) are both stes at $\langle\overline{Na^+}\rangle$ initially.

Step 4: Calculate the ionic strengths of the bulk solution and the gel fluid at final equilibrium:

$$I = [C_{Na^+} + C_{NO_3^-} + 4C_{SO_4^{2-}} + 4C_{Cu^{2+}} + 4C_{Ca^{2+}}]_{solution}/2 \quad (6)$$

($CuSO_4$ was used in this work)

$$\bar{I} = [\langle\overline{Na^+}\rangle + \langle\overline{A^-}\rangle + 4\langle\overline{Cu^{2+}}\rangle + 2\langle\overline{NaNO_3}\rangle + 4\langle\overline{Ca^{2+}}\rangle]_{gel}/2V_p \quad (7)$$

In Eq. (7), $\langle\overline{A^-}\rangle$ 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+} and Ca^{2+} chemically bound to binding sites (excluding the free, unbound Cu^{2+} and Ca^{2+} in the gel fluid) and V_p is the water content (in g, total wet weight of the gel minus the dry mass of the polymer, to be discussed in detail) 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.

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 [12]. (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 $NaNO_3$ = 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 [13] or by the following equations [9,12]:

$$[\gamma_{Na^+}] = \frac{[\gamma_{\pm NaCl}]^2}{[\gamma_{\pm KCl}]} \quad \text{at } I \text{ and } \bar{I} \quad (8)$$

$$[\gamma_{M^{2+}}] = \frac{[\gamma_{\pm MCl_2}]^3}{[\gamma_{\pm KCl}]^2} \quad \text{at } I \text{ and } \bar{I} \text{ (M = Cu or Ca)} \quad (9)$$

Step 6: Apply Donnan equilibrium theory to correct the value of $\langle\overline{NaNO_3}\rangle$. Since the product of the activities of Na^+ and NO_3^- must be the same for the two phases in equilibrium, we have

$$[\gamma_{\pm NaNO_3}]_I^2 C_{Na^+} C_{NO_3^-} = [\gamma_{\pm NaNO_3}]_{\bar{I}}^2 \frac{\langle\overline{Na^+}\rangle + \langle\overline{NaNO_3}\rangle}{V_p} \frac{\langle\overline{NaNO_3}\rangle}{V_p} \quad (10)$$

By treating $\langle\overline{NaNO_3}\rangle$ as an unknown variable, Eq. (10) becomes a quadratic equation and the improved value of $\langle\overline{NaNO_3}\rangle$ can be calculated easily.

Step 7: Apply Donnan equilibrium theory to correct the values of $\langle\overline{M^{2+}}\rangle$. The activities of M^{2+} and Na^+ in the gel phase and the bulk solution can be related [4,5,9,10] by

$$\text{Partition coefficient for } M^{2+} = [(\overline{M^{2+}})/(M^{2+})] = [(\overline{Na^+})/(Na^+)]^2 \quad (11)$$

where

$$(\overline{M^{2+}}) = [\gamma_{M^{2+}}]_{\bar{I}} \langle\overline{M^{2+}}\rangle / V_p \quad (12)$$

$$(M^{2+}) = [\gamma_{M^{2+}}]_I C_{M^{2+}} \quad (13)$$

$$(\overline{Na^+}) = [\gamma_{Na^+}]_i \frac{\langle \overline{Na^+} \rangle + \langle \overline{NaNO_3} \rangle}{V_p} \tag{14}$$

$$(Na^+) = [\gamma_{Na^+}]_l C_{Na^+} \tag{15}$$

(M = Cu or Ca)

By substituting Eqs. (12–15) into Eq. (11) and rearranging, improved values of $\langle \overline{Cu^{2+}} \rangle$ and $\langle \overline{Ca^{2+}} \rangle$ can be obtained.

Step 8: Substitute the improved values of $\langle \overline{NaNO_3} \rangle$ and $\langle \overline{M^{2+}} \rangle$ into Eqs. (6) and (7) and iterate between Step 4 and Step 7 until the values of $\langle \overline{NaNO_3} \rangle$ and $\langle \overline{M^{2+}} \rangle$ from successive trials converge. Then calculate the values of $(\overline{M^{2+}})$ using Eq. (12).

Step 9: Calculate Q_{Cu}, Q_{Ca}, $Q_{p,Cu}$, and $Q_{p,Ca}$ by performing mass balance on copper and calcium of the entire system. Then use Eq. (3) to determine k_1, k_{Cu}, and k_{Ca} (the conventional Langmuir's model based on the concentration of copper in solution) and Eq. (5) to determine K_1, K_{Cu}, and K_{Ca} (the modified Langmuir's model based on the activity of copper in the gel fluid).

EXPERIMENTAL

Reactor. The schematic diagram of the 2.0-liter glass reactor is shown in Figure 2. Air was sparged from the bottom of the left side of the reactor loop (the riser) causing the fluid to circulate in the direction shown. Air flow rate was maintained

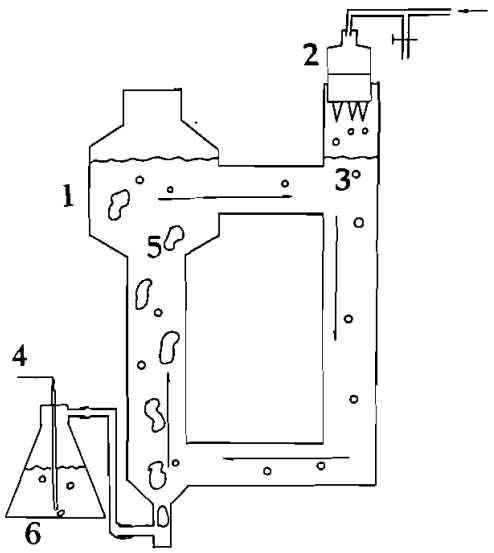

FIGURE 2 A schematic diagram of the loop fluidized bed reactor for producing Ca-alginate gel. 1: the glass reactor 2: dispenser 3: newly-formed Ca-alginate gels 4: compressed air 5: air bubbles 6: humidifier. A second identical reactor (without the dispenser) is used to investigate the copper absorption by the gels.

at 0.4–0.5 l/min. Two such reactors were used in this work, one for producing partially-coagulated calcium alginate gels and the other for investigating copper absorption by the gels.

Calcium alginate gel. The number of moles of uronate residues (the active component responsible for binding Cu and Ca) per unit weight of algin (Kelton grade sodium alginate for food additive, courtesy of Kelco) was determined in our recent work [1]. (Result: 4.356 mmol sodium uronate per gram dry algin). An algin solution was prepared by mixing 3.2 g algin with 100 ml deionized (DI) water (NANOpure System). The resultant viscous algin solution was subsequently dispensed into a 0.05 M $CaCl_2$ solution in a loop fluidized reactor by using a multi-tip dispenser designed in our laboratories (Figure 3). Upon contact with the $CaCl_2$ solution, the drops of algin solution gelled into 4 mm diameter spheres that were later used in copper absorption experiments. Only 10 minutes were required to completely dispense 100 ml of the viscous algin solution. (It would have taken at least one hour to dispense the same amount of algin solution if a single-tip dispenser had been used). Then a nylon net was immediately inserted through the downcomer (the right side of the reactor loop) to catch the spherical gels that were carried by the fluid flowing clockwise. The semi-rigid, partially-coagulated calcium alginate gels were then briefly rinsed with DI water and transferred to a DI water bath to "dialyze" excess calcium from the gels overnight.

Initial and final calcium concentrations in the reactor and also the concentration of calcium in the soaking water were determined by atomic absorption

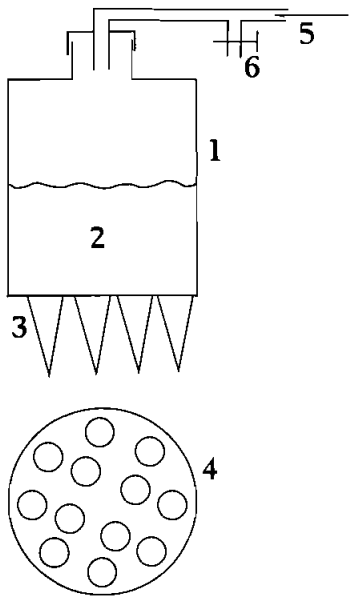

FIGURE 3 A schematic diagram of the dispernser. 1: side view of a 200-ml plastic bottle 2: algin solution 3: 200-μl pipetter tips 4: bottom view 5: compressed air 6: air vent.

TABLE 1

Conditions of Batch Absorption Experiments Using Partially-coagulated Calcium Alginate

Run No.	*21*	*22*	*23*	*24*	*27*	*28*	*29*	*30*	*31*	*32*	*33*	*34*	*35*	*36*	*37*
$NaNO_3$ added (M)	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.01	0.01	0.1	0.1	0.01	0.1	0.01	0.1
No. Spheres added	50	50	571	570	750	750	250	250	1050	1050	500	500	1000	1000	1500
Wt. algin(g)	0.0328	0.0328	0.375	0.374	0.492	0.492	0.164	0.164	0.689	0.689	0.328	0.3288	0.656	0.656	0.984
Max. Possible binding sites (mmol)	0.072	0.072	0.816	0.815	1.07	1.07	0.358	0.358	1.50	1.50	0.715	0.715	1.43	1.43	2.145
Initial Cu ppm	10.14	9.69	9.54	9.38	8.67	9.27	8.86	9.02	8.85	9.36	38.5	41.13	40.83	51.48	37.94
Total initial Cu (mmol)	0.303	0.290	0.285	0.280	0.259	0.277	0.265	0.270	0.265	0.280	1.15	1.235	1.221	1.539	1.134
Final Cu ppm	9.3	8.04	5.19	2.38	4.33	1.79	6.12	3.76	1.31	3.87	27.9	32.67	19.13	14.49	22.14
Initial Ca ppm	1.94	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Final Ca ppm	2.76	1.31	7.08	5.98	8.43	4.97	4.53	3.52	3.52	9.55	3.68	10.95	16.64	12.63	22.74
Final vol. (ml)	1784	1790	1797	1742	1837	1792	1840	1843	1838	1837	1877	1880	1878	1878	1878
Final dia. Spheres (cm)	0.435	0.366	0.387	0.415	0.439	0.418	0.405	0.406	0.400	0.370	0.380	0.376	0.368	0.330	0.419
Water Content of Final spheres (g) ($=V_p$)	2.0	2.0	12.2	15.0	22.0	19.0	6.21	7.0	25.5	29.0	9.69	6.97	17.9	20.0	28.1
$Q_{Cu} \times 10^3$ (mole/g algin)	0.741	1.46	0.333	0.529	0.260	0.441	0.490	0.940	0.322	0.234	0.766	0.990	0.984	2.66	0.477
$Q_{Ca} \times 10^3$ (mole/g algin)	0.238	0.306	0.494	0.651	0.571	0.904	0.081	0.390	1.00	0.724	0.306	0.846	0.473	1.07	0.183

spectroscopy (AA). The number of mols of calcium absorbed by each fresh spherical gel was calculated by mass balance.

Procedure. Prior to each batch absorption experiment, an appropriate amount of $CuSO_4 \cdot 5H_2O$ was added to the reactor (DI water holdup: 1900 ml) so that the initial concentration was 10–40 ppm of dissolved copper. Ionic strength was adjusted by adding 0.1 or 0.01 mole $NaNO_3$ to each liter of the reactor fluid.

The fresh calcium alginate gels were briefly dried on clean tissue papers, their diameters measured, weighed, and then poured into the reactor. At the time of initiation of each absorption experiment and at 2 minutes intervals thereafter for 30 minutes, 2 ml reactor fluid was withdrawn from the top of the riser. Afterwards the period of sampling was gradually increased. Each experiment lasted for 8–16 hours. The concentrations of copper and calcium in all samples were determined by AA. A material balance on Ca and Cu gives the amount of Ca and Cu absorbed by the gel at final equilibrium. (The amounts of Cu and Ca lost in sampling were taken into account). The conditions of experimental runs are summarized in Table I.

RESULTS

A total of 4878 spherical gels were prepared from 103.2 grams of the algin solution (containing 3.2 g dry algin). From the initial and final Ca concentrations in the first reactor and the Ca concentration in the soaking water, the average calcium load in the gels was calculated to be 9.00×10^{-4} mmol calcium per sphere or 1.37 mmols per g dry weight of algin. Since each gram of dry algin contains 4.356 mmols uronate residues (or 2.178 mmols of maximum possible binding sites), an average of 63% (=1.37/2.178) of charged binding sites were occupied by calcium in the fresh gels. Our technique produced translucent partially-

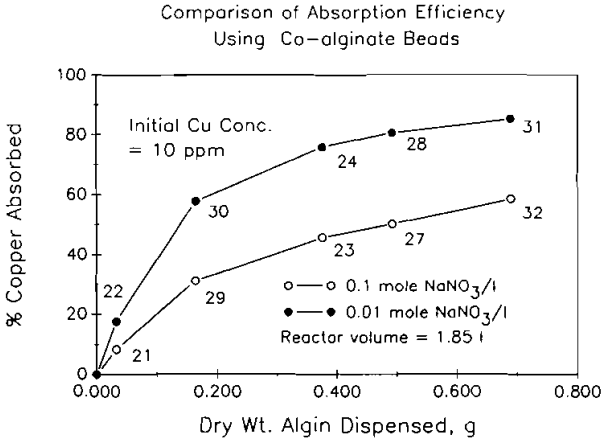

FIGURE 4 Percent copper absorbed from a solution containing 10 ppm initial concentration of copper by Ca-alginate gels at different ionic strengths.

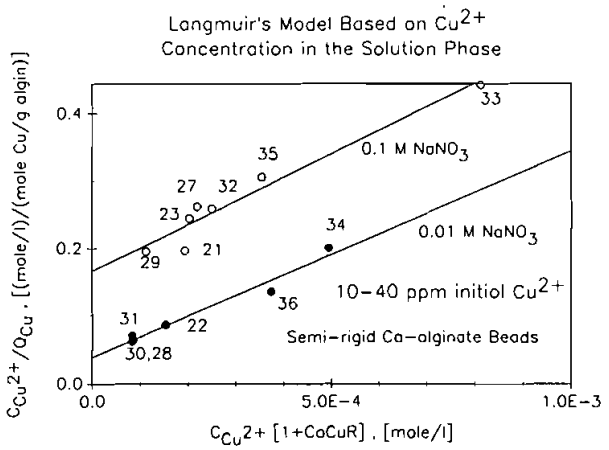

FIGURE 5 Langmuir's plot of copper absorption data based on the concentration of dissolved copper in the solution (reactor fluid). CaCuR = Q_{Ca}/Q_{Cu}.

coagulated spherical gels which were surrounded by semi-rigid shells and remained soft in the interior.

The values of Q_{Cu} and Q_{Ca} calculated from absorption data are also given in Table I. If the percent copper absorbed is plotted against the mass of algin contained in the gels used in the runs of initial copper concentration at 10 ppm ($=1.574 \times 10^{-4}$ M) (Figure 4), it is shown that ionic strength has a significant effect on the apparent affinity of copper toward calcium alginate gels; when the reactor fluid contained 0.01 M $NaNO_3$, the amount of copper absorbed by calcium alginate was almost twice that at 0.1 M $NaNO_3$. It was also observed that the final gels in the 0.01 M $NaNO_3$ solutions were significantly bluer than those in the 0.1 M $NaNO_3$ solutions.

When batch absorption data were treated with the conventional Langmuir's

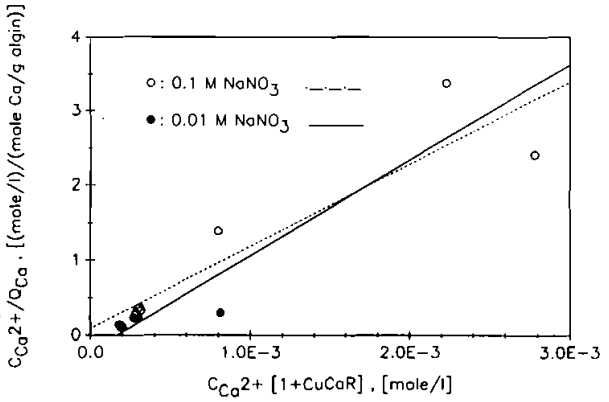

FIGURE 6 Langmuir's plot of calcium binding data based on the concentration of calcium in the solution. CuCaR = Q_{Cu}/Q_{Ca}.

TABLE II

Summary of results of calculation by iterative procedure

Run No.	*21*	*22*	*23*	*24*	*27*	*28*	*29*	*30*	*31*	*32*	*33*	*34*	*35*	*36*	*37*
$NaNO_3$ added, mol/l solution	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.1	0.01	0.1	0.1	0.01	0.1	0.01	0.1
$\langle\overline{Cu^{2+}}\rangle \times 10^3$, mmol	0.438	0.978	3.107	18.79	2.865	15.86	1.434	9.358	15.93	3.246	5.423	969.4	11.80	21.57	29.64
$\langle\overline{Ca^{2+}}\rangle \times 10^3$, mmol	0.204	0.253	6.642	74.97	8.691	69.80	1.639	13.89	104.7	12.48	1.129	398.9	15.91	29.81	50.50
$\langle\overline{NaNO_3}\rangle \times 10$, mmol	1.917	0.123	23.37	0.415	19.58	0.433	4.867	0.215	0.704	24.67	9.305	0.119	14.09	7.465	19.83
% uronate unoccupied	55.0	18.9	62.0	45.8	61.9	38.3	73.8	38.7	39.1	56.0	15.7	63.4	46.9	38.3	69.0
I, mol/l	0.112	0.0113	0.111	0.0114	0.108	0.113	0.109	0.011	0.011	0.108	0.108	0.0131	0.109	0.0138	0.109
$\bar{I}$, mol/l	0.136	0.0209	0.135	0.0650	0.144	0.064	0.164	0.0492	0.058	0.144	0.120	0.524	0.157	0.140	0.183
$(\overline{Na^+})/(Na^+)$	1.197	1.786	1.207	4.375	1.311	4.480	1.471	3.734	4.207	1.312	1.117	10.12	1.416	10.00	1.622
$(\overline{M^{2+}})/(M^{2+})$	1.433	3.190	1.456	19.14	1.718	20.07	2.165	13.95	17.70	1.722	12.48	102.5	2.005	100.0	2.632
$(\overline{Cu^{2+}}) \times 10^4$, mol/l	0.459	1.886	0.261	3.339	0.258	2.639	0.459	3.889	1.717	0.231	1.207	233.6	0.258	64.71	2.021
$(\overline{Ca^{2+}}) \times 10^4$, mol/l	0.228	0.591	0.595	0.174	0.838	0.131	0.212	0.279	11.28	0.134	0.967	124.1	0.838	0.990	0.768
$Q_{p,Cu}$, mole Cu/g algin	0.728	1.431	0.325	0.478	0.254	0.409	0.482	0.886	0.220	0.229	0.671	0.973	0.254	2.406	0.448
$Q_{p,Cu}$, mole Cu/g algin	0.232	0.228	0.476	0.450	0.552	0.761	0.071	0.306	0.851	0.705	0.290	0.800	0.552	0.881	0.132

model (Eq. (3)), two separate best-fit straight lines were obtained for copper (Figure 5), giving different values of conditional copper-binding stability constants ($k_{Cu} = 2.1 \times 10^3$ and 7.96×10^3 l/mole at $NaNO_3$ concentrations of 0.1 M and 0.01 M, respectively). The slopes of the two lines are about the same and the maximum effective absorption capacity k_1 was determined to be 2.86×10^{-3} and 3.26×10^{-3} mole/g algin at $NaNO_3$ concentrations of 0.1 M and 0.01 M, respectively. The data points for calcium (Figure 6) are somewhat scattered; no unique stability constant can be obtained.

The results of calculation by the iterative procedure are summarized in Table II. It is found that the partition coefficient for copper, i.e., the ratio of Cu^{2+} activity in the gel fluid to that in the reactor fluid, was substantially greater than unity. Furthermore, the partition coefficient at the lower ionic strength (0.01 M $NaNO_3$) was also substantially greater than that at the higher ionic strength (0.1 M $NaNO_3$). The fraction of unbound sites in the alginate gel used in each run (Table II) was higher than that observed in our recent work [1] in which the copper concentration used was 60–200 ppm. The results of iterative calculation also showed that the majority of copper and calcium in the gel phase was bound chemically to binding sites; copper and calcium held electrostatically in the gel fluid (not listed) accounted for about 5% of total copper and calcium in the gel phase.

When the activities of copper and calcium were substituted into Eq. (5), a unique best-fit straight line was obtained for copper (Figure 7) giving the maximum effective binding capacity of $K_1 = 1.13 \times 10^{-3}$ mols metal binding sites/g algin and the binding stability constant of $K_{Cu} = 4.08 \times 10^4$ l/mole. The corresponding results for calcium (Figure 8) are $K_1 = 1.20 \times 10^{-3}$ mols metal binding sites/g algin (very close to the value 1.13×10^{-3} calculated from Figure 7) and $K_{Ca} = 1.32 \times 10^4$. Therefore, the Cu/Ca selectivity, defined as K_{Cu}/K_{Ca}, for the alginate gel used in this work is roughly 3 ($=4.08 \times 10^4/1.32 \times 10^4$).

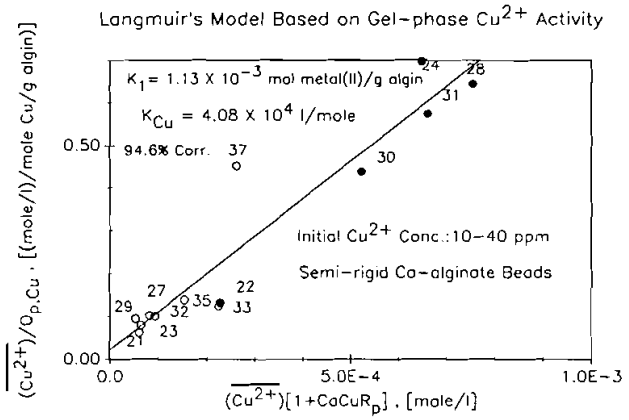

FIGURE 7 Treatment of copper binding data by using the modified Langmuir's model based on the activities of copper and calcium in the gel fluid. $CaCuR_p = Q_{p,Ca}/Q_{p,Cu}$.

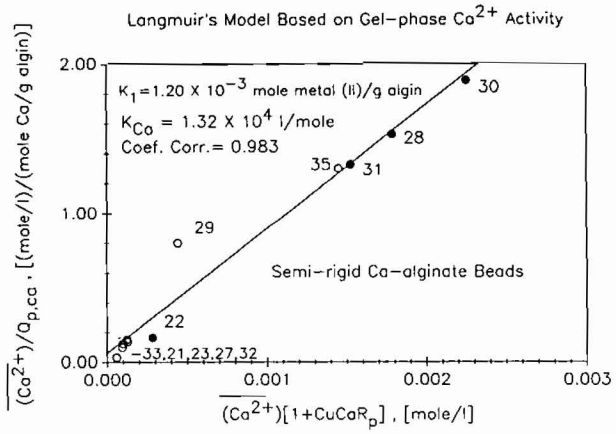

FIGURE 8 Treatment of calcium binding data by using the modified Langmuir' model based on the activities of calcium and copper in the gel fluid. $CuCaR_p = Q_{p,Cu}/Q_{p,Ca}$.

DISCUSSION

The sensitivity of apparent metal binding affinity of calcium alginate gel observed in this work (Figures 4–9) is similar to the conclusions made by Marinsky *et al.* [4,5,11]. Since the conditional stability constants are affected by the environmental conditions, they should not be regarded as true thermodynamic equilibrium constants.

When the modified Langmuir's model based on the conditions in the gel phase was used, unique stability constants for copper and calcium independent of the ionic strength in the solution were obtained. In other words, there is no fundamental difference in the metal-binding phenomena at different ionic strengths of the solution. The difference in the apparent binding affinity reflects the difference in free energy associated with the migration of a cation from the (external) solution at different ionic strengths to the gel fluid.

The term V_p used in this work refers to the *total* water content of the alginate gel. In other words, an imaginary semi-permeable "membrane" on the surface of the gel separates the gel fluid completely from the (external) solution. This picture needs to be extensively modified, however, in the case of highly flexible ion-exchange gels such as Sephadex CM-50 [11]. Because the structure of highly flexible polymers is too open, a sizable fraction of the gel fluid is merely an extension of the external solution; only the fraction of the liquid surrounding the polymer chain, which is under the influence of the electric field due to the charged groups, can be considered as the true gel fluid. A similar observation was reported in the case of the polyelectrolyte coatings on graphite electrodes [14,15].

Had the water content V_p in the gel been exaggerated in this work, the two sets of data at different ionic strengths would not have merged to a single line using the modified Langmuir's model; instead, only a marginal improvement over the results using the conventional model would have been achieved and no unique

"intrinsic" stability constant could have been obtained. The fact that the two groups of data merged to a single line in Figures 7 and 8 justified our use of the total water content in the gel as V_p in this work.

The true gel fluid content V_p of a highly flexible ion-exchange resin can be estimated by modifying the iterative procedure outlined in this work: (1) An initial value of V_p is assumed in the first iteration; (2) The ratio $(\overline{Na^+})/(Na^+)$ can be estimated by

$$(\overline{Na^+})/(Na^+) = (\overline{H^+})/(H^+) \tag{16}$$

according to Donnan equilibrium theory, where (H^+) can be measured electrochemically and $(\overline{H^+})$ can be calculated from the intrinsic dissociation constant according to $p\bar{H} = pK_{HA}^{int} - \log[\langle HA\rangle/\langle A^-\rangle]$ where $\langle HA\rangle$ and $\langle A^-\rangle$ can be easily calculated from the stoichiometry of the metal-binding and acid-dissociation reactions of the polymer [9,10]; (3) An improved value of V_p can be generated by combining Eqs. (14–16) and rearranging:

$$V_p = \frac{[\gamma_{Na^+}]_i[\langle\overline{Na^+}\rangle + \langle\overline{NaNO_3}\rangle]}{[\gamma_{Na^+}]_f C_{Na^+}[(\overline{H^+})/(H^+)]} \tag{17}$$

Then the whole procedure is iterated using this improved V_p until values of V_p from successive trials converge. This approach is similar to the iterative procedure developed for predicting V_p for colloidal biopolymers [9].

The values of the Donnan potential term, i.e., the ratio of the Na^+ activity in the gel fluid to the Na^+ activity in the solution, ranged from 1.2 to 10.0, which were somewhat lower than those observed in our previous work on copper binding to colloidal alginic acid [9,10]. In the case of colloidal alginic acid, both copper and alginic acid were at concentrations well below levels needed to form gels and the mols of copper added was less than 5% of the mols of total binding ligands. Therefore, the majority of binding ligands remained unbound which results in a strong electric field around the polymer chain. (Thus, a large Donnan potential term was observed). In the present work, however, a substantial fraction of uronate groups in the alginate was bound because the concentration of dissolved copper used was much higher than that in our previous work. This in turn resulted in a relatively weak electric field in the gel phase and a weaker Donnan potential term was obtained.

CONCLUSIONS

(1) When the concentration of dissolved copper is below the threshold value that allows algin to be directly dispensed, partially-coagulated calcium alginate gels produced by our technique can be used to absorb copper with satisfactory capacity and affinity.

(2) Our two-phase approach is again successful in predicting the extent of neutral salt invasion and the activities of Cu^{2+} and Ca^{2+} in the gel fluid by using the iterative procedure developed in our laboratories. At low ionic strengths, the ratio of Cu^{2+} between the two phases (the gel fluid and the external solution) in

equilibrium is substantially greater than unity. Since more Cu^{2+} is attracted toward the gel fluid at lower ionic strengths of the solution, a greater conditional stability constant was observed than at higher ionic strengths.

(3) The modified Langmuir's model, based on the conditions in the gel fluid (instead of the solution) with the competition from calcium taken into account, yielded a unique value of copper-binding stability constant.

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