



## ADDITION OF COPPER-SEQUESTERING AGENTS TO ALGINATE GEL TO ENHANCE COPPER RECOVERY FROM AQUEOUS MEDIA

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**Abstract**—A mixture of sodium alginate and sodium polystyrenesulfonate (NaPSS) was used as the absorbent for copper in this work. A viscous solution of the mixture was dispensed into a copper-containing solution circulating in a loop fluidized bed reactor to form alginate gel *in situ*. Batch absorption data was treated by Langmuir model to yield copper binding capacity and binding stability constant. Results were compared with those of our previous work in which no NaPSS was added to Na-alginate. Based on the Langmuir parameters, the critical copper concentration above which the addition of NaPSS can enhance the copper loading of the alginate gel was calculated. The ratio of copper loading of the alginate gel with the addition of NaPSS to that without the addition of NaPSS at any copper concentration was predicted as well. Similar calculations were made for the case of using the mixture of Na-alginate and *Microcystis* as the copper absorbent.

**Key words**—copper recovery, alginate, sodium polystyrenesulfonate, *Microcystis*

### INTRODUCTION

In an earlier report (Jang *et al.*, 1990a), the feasibility of using alginate gel to recover dissolved copper from synthetic aqueous media was demonstrated. Viscous Na-alginate solution (3.2% by weight) was dispensed by a multi-tip dispenser into a loop-fluidized bed reactor to form Cu-alginate gel *in situ* (Fig. 1). A simple Langmuir model was successfully used to obtain conditional copper binding stability constant and binding capacity of the alginate gel at different neutral salt concentrations. When Donnan potential term was considered, intrinsic binding stability constant was obtained.

The possibility of enhancing the copper binding efficiency of the alginate gel by adding copper-sequestering agents such as EDTA (Jang *et al.*, 1990b) and *Microcystis* (cyanobacterial biomass) (Jang *et al.*, 1991) to the Na-alginate preparations prior to copper absorption experiments was also explored. On the basis of the Na-alginate mass present in the gel, it was found that copper binding capacity was increased but the binding stability constant was decreased with the addition of *Microcystis*.

In this work, the effects of adding sodium polystyrenesulfonate (NaPSS) to the Na-alginate preparations on the copper absorption efficiency of

the gel formed were investigated. The reason for choosing NaPSS as a model additive was because its polyelectrolyte properties were fairly well characterized (Chu and Marinsky, 1967; Reddy and Marinsky, 1970a, b; Marinsky 1967; Marinsky, 1985; Marinsky and Reddy, 1991) and its molecule has a high charge density [chain length being 2.44–2.67 Å (Chu and Marinsky, 1967)]. The 8% divinylbenzene cross-linked polystyrene sulfonic acid (Dowex-50) has a favorable ion exchange distribution coefficients for divalent metal ions (Marinsky and Reddy, 1991). It was hoped in this work that the linear NaPSS added to Na-alginate would be “immobilized” in the matrix of Cu-alginate gel formed to help attract more copper into the gel phase.

Batch absorption experiments using the mixture of Na-alginate and NaPSS as the copper absorbent were performed in this work. Calculations based on Langmuir model will yield copper binding capacity and stability constant of the alginate gel. The results will be compared with those of our previous work (Jang *et al.*, 1990a). A mathematical model will be developed to predict the critical copper concentration above which the addition of NaPSS will enhance the copper loading of the gel, as well as the ratio of copper loading of the gel with the addition of NaPSS to that without the addition of NaPSS as a function of copper concentration. Interpretations of our findings based on the morphology of the alginate gel in the presence and absence of NaPSS will be made.

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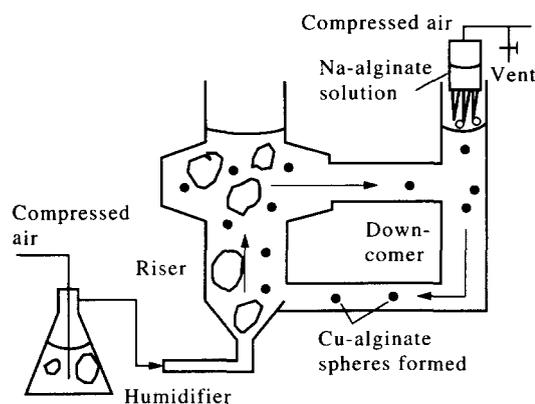


Fig. 1. The schematic diagram of the reactor used in the batch absorption experiments. The reactor contained 1.85 l synthetic solution of  $\text{CuSO}_4$  at an initial concentration of 200 ppm Cu. The concentration of the inert salt  $\text{NaNO}_3$  added was 0.1 M or 0.01 M. The additive NaPSS was blended with the Na-alginate solution prior to dispensing.

### EXPERIMENTAL

A 2-l fluidized bed loop reactor (Fig. 1) was used to hold copper-containing solution in this work. Appropriate amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and inert neutral salt  $\text{NaNO}_3$  were weighed and added to the de-ionized water (volume: 1.85 l) circulating in the reactor (initial Cu concentration: 200 ppm,  $\text{NaNO}_3$  concentration: 0.01 or 0.1 M). The copper absorbent was prepared by blending Na-alginate (Algin, Keltone grade, Kelco Corp.), de-ionized water, and NaPSS (Flexan, National Starch Corp., 30% by weight in water, density 1.13 g/ml) in the ratio of 3.2 g:90 ml:10 ml. (In our previous work (Jang *et al.*, 1990a), the ratio of Na-alginate to water was 3.2 g:100 ml). Different amounts of the viscous absorbent were dispensed into the reactor in different exper-

imental runs in order to have a variation of final equilibrium copper concentration. The conditions are summarized in Table 1. Liquid samples were withdrawn at intervals and atomic absorption (AA) spectroscopy was used to determine copper concentration. Temperature of the solution in all runs was  $20 \pm 1^\circ\text{C}$ .

Langmuir model was used in this work to evaluate copper binding capacity and binding stability (equilibrium) constant of the alginate gel containing the additive NaPSS:

$$\frac{C_{\text{Cu}^{2+}}}{Q_{\text{Cu}}} = \frac{1}{k_1 K_{\text{Cu}}} + \frac{C_{\text{Cu}^{2+}}}{k_1} \quad (1)$$

where  $Q_{\text{Cu}}$  is the mass of copper absorbed into the gel divided by the mass of Na-alginate in the gel (g Cu/g Na-alginate),  $C_{\text{Cu}^{2+}}$  is the final equilibrium concentration of copper (mol/l),  $k_1$  is the binding capacity of the gel, i.e. maximum mass of copper that can be absorbed by the gel per unit Na-alginate mass contained in the gel (g Cu/g Na-alginate) and  $K_{\text{Cu}}$  is the binding stability constant (l/mol). The above equation treats the gel phase as having one type of binding sites; the existence of possible different types of binding sites was tentatively not considered. Rigorously speaking, the values of  $k_1$  and  $Q_{\text{Cu}}$  should be expressed as g Cu per unit gel volume or unit dry mass of the absorbent (Na-alginate plus NaPSS). However, it is evident from equation (1) that any mass basis or volume basis can be used to express  $k_1$  and  $Q_{\text{Cu}}$  because this mass or volume basis can be cancelled out from both sides of the equation without affecting the value of the stability constant  $K_{\text{Cu}}$ . Therefore, we choose unit Na-alginate mass basis for convenience. Choosing this mass basis has an added advantage: The binding stability constant (l/mol) and binding capacity of Na-alginate gel (g Cu/g Na-alginate) in the absence of any additive were determined in our previous work (Jang *et al.*, 1990a). Therefore, if we choose the same unit Na-alginate mass basis to express the binding capacity in this work, the effect of adding NaPSS on the binding capacity of the gel will be demonstrated more easily.

Table 1. Summary of conditions and results of absorption experiments by directly dispensing a mixture of algin/NaPSS into copper-containing aqueous media. Temperature =  $20 \pm 1^\circ\text{C}$

(a) Concentration of $\text{NaNO}_3 = 0.1 \text{ M}$						
Run No.	12	8	7	3	9	
Initial Cu concentration (ppm)	181.15	192.85	197.9	199.8	200.3	
Final Cu concentration (ppm)	129.2	127.05	115.9	89.25	53.3	
% Cu absorbed	28.7	34.1	41.4	55.3	73.4	
Dry weight algin dispensed (g)	0.6885	1.0489	1.4560	2.0833	2.8167	
g Cu absorbed	0.1424	0.1164	0.1060	0.0991	0.09718	
g dry algin						
Estimated No. of beads	1162	1342	2898	3212	5094	
Average final diameter (cm)	0.3084	0.3320	0.3030	0.3424	0.3398	
$C \times 10^3$ [mol/l]	2.033	2.000	1.824	1.405	0.839	
$C/Q \times 10^2$ [mol/l]	1.428	1.715	1.721	1.418	0.863	
[g Cu/g algin]						
Final pH	4.78	4.81	4.85	5.03	5.04	
(b) Concentration of $\text{NaNO}_3 = 0.01 \text{ M}$						
Run No.	11	6	5	1	4	2
Initial Cu concentration (ppm)	200.75	182.65	208.5	199.65	201.4	214.05
Final Cu concentration (ppm)	128.2	91.05	100.7	85.5	56.8	51.65
% Cu absorbed	36.1	50.2	51.7	57.2	71.2	75.6
Dry weight algin dispensed (g)	0.7324	1.0219	1.443	1.7813	2.5408	2.8453
g Cu absorbed	0.1912	0.1680	0.1406	0.1209	0.1074	0.1070
g dry algin						
Estimated No. of beads	1502	1706	2562	2766	6058	5574
Average final diameter (cm)	0.3594	0.3592	0.3622	0.3683	0.3637	0.3683
$C \times 10^3$ [mol/l]	2.018	1.433	1.585	1.346	0.894	0.813
$C/Q \times 10^2$ [mol/l]	1.055	0.853	1.127	1.113	0.832	0.759
[g Cu/g algin]						
Final pH	4.64	4.66	4.70	4.64	5.40	5.60

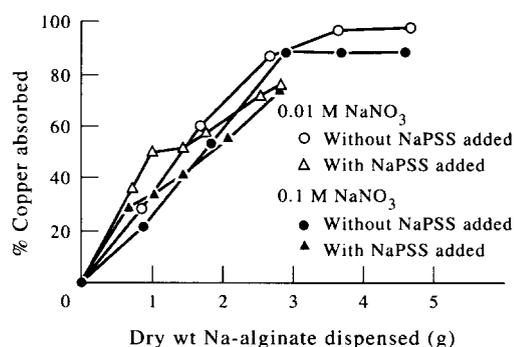


Fig. 2. Comparison of the percent copper recovery by Na-alginate with and without the addition of NaPSS in batch absorption experiments under the condition of limited liquid volume.

### RESULTS

When the Na-alginate/NaPSS mixture was dispensed dropwise into the copper-containing solution at an initial concentration of 200 ppm, stable rigid spheres with dia  $\sim 3$  mm were formed. The results of batch absorption experiments are summarized in Table 1. The values of  $C_{Cu^{2+}}/Q_{Cu}$  needed for the Langmuir model are also calculated and listed in Table 1. The percentage of copper recovery by the Na-alginate/NaPSS mixture was plotted in Fig. 2. In Fig. 2, results of our previous work (Jang *et al.*, 1990a) are also plotted for comparison. When  $C_{Cu^{2+}}/Q_{Cu}$  is plotted against  $C_{Cu^{2+}}$ , two parallel lines with satisfactory fits are obtained (Fig. 3). According to equation (1), the copper binding capacity and stability constant at different ionic strengths are calculated from the slopes and intercepts of the best-fit lines on Fig. 3:

0.01 M  $NaNO_3$ :

$$k_1 = 0.2817 \text{ g Cu/g Na-alginate}; K_{Cu} = 707 \text{ l/mol}$$

0.1 M  $NaNO_3$ :

$$k_1 = 0.2902 \text{ g Cu/g Na-alginate}; K_{Cu} = 367 \text{ l/mol}$$

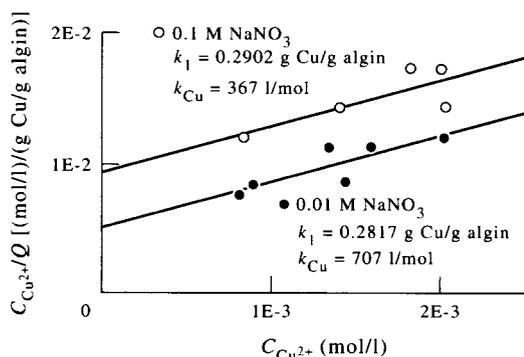


Fig. 3. The Langmuir plots for the absorption of  $Cu^{2+}$  by the gels formed by the mixture of Na-alginate and NaPSS. The parameters are calculated according to equation (1).

### DISCUSSION

According to our previous work (Jang *et al.*, 1990a, b), the values of copper binding capacity and stability constant of Na-alginate in the absence of NaPSS are

0.01 M  $NaNO_3$ :

$$k_1 = 0.1247 \text{ g Cu/g Na-alginate}; K_{Cu} \sim 8000 \text{ l/mol}$$

0.1 M  $NaNO_3$ :

$$k_1 = 0.1085 \text{ g Cu/g Na-alginate}; K_{Cu} = 5260 \text{ l/mol}$$

Compared with the results obtained in this work, it is evident that adding NaPSS to the Na-alginate preparations increased the binding capacity of the gel phase. However, the binding stability constant was decreased.

Inspection of Fig. 2 shows that at lower amounts of the absorbent dispensed, the copper recover efficiency was greater for the gel with the addition of NaPSS; while at the higher amounts of the absorbent dispensed, the copper recovery efficiency was greater for the gel without the addition of NaPSS. Since batch absorption experiments were performed, the greater the amount of the absorbent dispensed the lower the final equilibrium copper concentration. This comparison implies that the absorbent containing NaPSS enhanced copper absorption at higher copper concentrations.

This observation prompts the following question: In what range of copper concentration will the addition of NaPSS enhance the copper recovery efficiency of the alginate gel? We may make this prediction using the Langmuir parameters obtained from batch experiments using limited reactor volume in this work and our previous work as follows: Let  $k_w$  and  $k_{w0}$  be the binding capacity of the alginate gel with and without the addition of NaPSS, respectively;  $K_w$  and  $K_{w0}$  be the corresponding binding stability constants (l/mol); and  $Q_w$  and  $Q_{w0}$  be the corresponding copper loading. Assume that the liquid volume is *infinite* so that absorption does not affect the copper concentration. Upon substituting these parameters into equation (1) it is very easy to prove that the condition for  $Q_w > Q_{w0}$  is

$$C_{Cu^{2+}} > \frac{k_{w0} - k_w}{\frac{K_w}{K_{w0}} - K_w} \quad (2)$$

and the ratio of actual copper loading at any copper concentration can be expressed by

$$\frac{Q_w}{Q_{w0}} = \frac{(1 + K_{w0} C_{Cu^{2+}}) k_w K_w}{(1 + K_w C_{Cu^{2+}}) k_{w0} K_{w0}} \quad (3)$$

Therefore, for 0.01 M  $NaNO_3$

$$k_w = 0.2817 \text{ g Cu/g Na-alginate};$$

$$K = 707 \text{ l/mol}$$

$$k_{w0} = 0.1247 \text{ g Cu/g Na-alginate};$$

$$K_{w0} \sim 8000 \text{ l/mol}$$

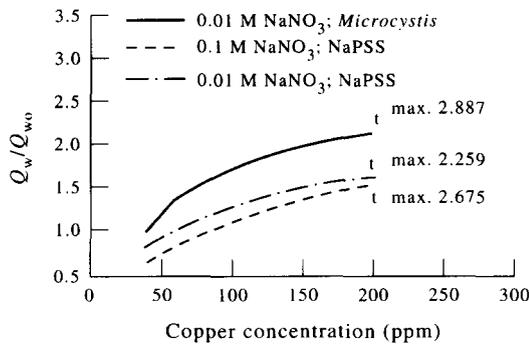


Fig. 4. Theoretical ratio of copper loading of the alginate gel with additives (NaPSS or *Microcystis*) to that without additives under the condition of infinite liquid volume.

and the critical copper concentration was calculated to be 57 ppm according to equation (2). Similarly, for 0.1 M NaNO<sub>3</sub>

$$k_w = 0.2902 \text{ g Cu/g Na-alginate;}$$

$$K_w = 367 \text{ l/mol}$$

$$k_{w0} = 0.1085 \text{ g Cu/g Na-alginate;}$$

$$K_{w0} = 5260 \text{ l/mol}$$

and the critical copper concentration was calculated to be 84 ppm. The ratio of copper loading of the alginate gel with the addition of NaPSS to that without the addition of NaPSS was calculated up to 200 ppm Cu (in an infinite liquid) according to equation (3) for both ionic strengths (Fig. 4). It is clear from equations (2)–(3) that such comparisons and calculations are possible only when  $k$ s and  $Q$ s are expressed on the same unit Na-alginate mass basis.

The approach of directly dispensing the Na-alginate (with or without the addition of copper sequestering agents) absorbent to form rigid gels worked at an initial copper concentration > 60 ppm (Jang *et al.*, 1990a, b, 1991). We may say that the purpose of

0.01 M NaNO<sub>3</sub>,

$$k_w = 0.3600 \text{ g Cu/g Na-alginate;}$$

$$K_w = 770 \text{ l/mol (Jang et al., 1991)}$$

$$k_{w0} = 0.1247 \text{ g Cu/g Na-alginate;}$$

$$K_{w0} \sim 8000 \text{ l/mol (Jang et al., 1990a)}$$

the critical copper concentration is calculated to be 39 ppm according to equation (3). The ratio of copper loading of the alginate gel with the addition of *Microcystis* to that without the addition of *Microcystis* is also plotted against copper concentration in Fig. 4.

The difference in the absorption efficiency at different ionic strengths has been proven to be due to the Donnan potential effect (Jang *et al.*, 1990a). More work needs to be done to obtain intrinsic binding stability constant for the Na-alginate gel containing NaPSS. An iterative procedure outlined by Jang *et al.* (1990a) should be followed.

While the increase in the apparent binding capacity as the result of adding NaPSS or *Microcystis* was obvious, the decrease in the apparent binding stability constant was unexpected initially. Although NaPSS and *Microcystis* are good copper sequestering agents, they alone do not form gels in the copper-containing solution. It was possible that addition of them (“foreign” polymers) to Na-alginate may weakened the “egg-box” structure (Rees and Welsh, 1977) of the alginate gel leading to a decrease in the overall binding stability constant. However, the increase in binding capacity more than compensated the decrease in the binding stability when the absorption was operating at sufficiently high copper concentration, as suggested by Fig. 4.

The increase in the binding capacity due to the addition of NaPSS can be interpreted as follows: The biochemical analysis in our previous work (Jang *et al.*, 1990a) yielded  $4.356 \times 10^{-3}$  mol uronate residues per gram algin sample. Therefore, in a typical preparation using 3.2 g of algin and 10 ml Flexan,

$$\text{mols of uronate groups} = (3.2 \text{ g algin})(4.356 \times 10^{-3} \text{ mol uronate/g algin})$$

$$= 1.394 \times 10^{-2}$$

$$\text{mols of styrene sulfonate} = \frac{(10 \text{ ml})(1.13 \text{ g Flexan/ml})(0.3 \text{ g NaPSS/g Flexan})}{207 \text{ g/mol sodium styrene sulfonate}}$$

$$= 1.638 \times 10^{-2} \text{ mol.}$$

enhancing copper absorption efficiency in a reactor with limited volume was achieved, unless too much absorbent was dispensed causing the final copper concentration to drop below these two critical values.

Similar calculation can also be performed for the case of addition of *Microcystis* to Na-alginate. At

Thus the ratio of total functional groups with the addition of NaPSS to that without the addition of NaPSS is  $(1.394 + 1.638)/1.394 = 2.18$ , which is very close to the ratio of  $k_w$  to  $k_{w0}$  obtained in this work.

One important assumption made in the data treatment was that the polyelectrolyte NaPSS added to the Na-alginate preparations were totally “immobilized”

by the matrix of alginate upon gelation in the Cu-containing solution. If NaPSS had "leaked" out of the alginate matrix, it would have bound part of the copper in the solution. In this case, the total copper concentration as determined by AA would not have equated the concentration of "free" copper to be absorbed by the gel. To justify this assumption, a separate experiment was performed: to 1.85 l of solution containing ~180 ppm Cu and 0.01 M NaNO<sub>3</sub>, 117.2 ml of the NaPSS-containing Na-alginate absorbent was dispensed. The copper concentration was monitored with AA and cupric ion selective electrode (which determined the concentration of "free" copper in the solution). The initial and final copper concentrations are

	By AA	By Cu-electrode
Initial conc. (ppm)	177	173
Final conc. (ppm)	55	49

The Cu-electrode readings differ slightly from the AA readings. The result suggested that the copper in the solution essentially existed in the "free" state, i.e. no noticeable amount of NaPSS "leaked" into the solution. However, in another trial run when twice the amount of NaPSS were added to the Na-alginate preparations, the gel formed became very unstable and loose flocs were formed. In this case, we believe that significant fraction of NaPSS must have gone into the aqueous phase.

#### CONCLUSIONS

(1) The addition of NaPSS to Na-alginate according to the formula reported in this work increased the apparent binding capacity of the Cu-alginate gel formed. However, apparent binding stability constant was decreased as compared to the case without the addition of NaPSS.

(2) Based on the Langmuir model and the parameters obtained in this work and our previous work, we predicted the range of copper concentration in which the addition of NaPSS or the *Microcystis* to

the Na-alginate preparations can enhance copper absorption efficiency.

(3) A model was developed to predict the extent of enhancement of copper loading as a result of adding copper sequestering agents NaPSS and *Microcystis* to Na-alginate preparations.

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