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## AN EQUILIBRIUM MODEL FOR ABSORPTION OF MULTIPLE DIVALENT METALS BY ALGINATE GEL UNDER ACIDIC CONDITIONS

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**Abstract**—An extended Langmuir model was proposed in this work to describe the simultaneous absorption of multiple divalent metal ions and hydrogen ions from acidic metal-containing aqueous media by an absorbent having one kind of active functional group. A viscous Na–alginate solution was directly dispensed dropwise into the acidic aqueous media containing dissolved copper and zinc to form spherical Cu–Zn–H–alginate gels which subsequently absorb these ions until final equilibrium was reached in batch experiments. Initial pH of the aqueous media was in the range of 2.6–5.4. Binding group density and binding stability constants of alginic acid, cupric alginate and zinc alginate were obtained simultaneously by fitting data to the proposed model developed in this work. Application of the constants obtained to the prediction of the extent of absorption of copper and zinc from an aqueous medium having an initial pH in the range of 2.6–5.4 is illustrated and compared with experimental results. © 1999 Elsevier Science Ltd. All rights reserved

**Key words**—copper, zinc, alginate, selectivity, metal recovery, Langmuir model

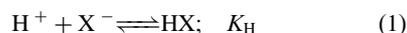
### INTRODUCTION

Many aqueous media such as mine drainage and metal ore leachates contain dissolved metal ions and have pH in the range 2–5. It is desired to recover or remove these metals from the aqueous media, so that water can be safely discharged or reused and valuable metals can be recovered for industrial use. One of the feasible approaches is the use of biopolymer (such as alginate from seaweed) which bear metal-binding functional groups to absorb metals.

In our previous work (Jang *et al.*, 1995a), a method of generating spherical gels of Cu–alginate in an acidic aqueous media containing dissolved copper was described. In this method, a viscous Na–alginate solution (3.2% by weight) was dispensed dropwise into the aqueous media to form Cu–alginate gels *in situ* which subsequently absorbed copper until final equilibrium was reached. The gelation phenomenon can be explained by the egg-box model (Rees and Welsh, 1977) in which each divalent metal ion binds to two carboxyl groups on adjacent alginate molecules.

In the first paper of this series (Jang *et al.*, 1999), a model developed earlier (Jang *et al.*, 1995b) was used to treat data of simultaneous absorption of multiple divalent metal species (copper and zinc) by alginate gel to yield conditional metal-binding capacity and stability constants under a given neutral or weakly acidic pH. Experimental data from Jang *et al.* (1999) were treated with an extended Langmuir model developed in this work to describe the simultaneous absorption of hydrogen ions and *n* divalent metal ions by carboxyl groups on the alginate molecules. The pH-independent binding stability constants of alginic acid, cupric alginate and zinc alginate and density of carboxyl groups in the alginate gel were calculated from batch absorption data.

Under the assumption that hydrogen ions and all divalent metal species compete for the same binding groups (i.e. carboxyl groups in the case of alginic acid), X<sup>-</sup>, and the major form of metal–alginate complex is bi-dentate, the binding equilibria can be defined as:



where M<sub>*i*</sub><sup>2+</sup> denotes the *i*th divalent metal species in the aqueous media and the equilibrium binding

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stability constants can be defined as follows:

$$K_H = \frac{Q_H}{(H^+)(\bar{X}^-)^2} \quad (3)$$

$$K_i = \frac{Q_i}{(M_i^{2+})(\bar{X}^-)^2} \quad (i = 1, 2, \dots, n) \quad (4)$$

where ( ) without an over bar denotes concentration in the aqueous phase (mol/(l solution)) and ( ) with an over bar denotes concentration in the gel phase (mol/(l gel)).  $Q_i$  denotes the concentration of metal species  $i$  bound to the gel phase (mol/(l gel)) and  $Q_H$  denotes the concentration of protonated carboxyl groups in the gel (mol/(l gel)). If the total concentration of carboxyl groups, bound and unbound, is  $k_X$  (mol/(l gel)), the concentration of free, unbound carboxyl groups is

$$(\bar{X}^-) = k_X - Q_H - 2 \sum_1^n Q_i \quad (5)$$

The coefficient 2 in equation (5) means each divalent metal ion bound will need 2 carboxyl groups.

By following a procedure of linearization of equation similar to that outlined in our previous work (Jang *et al.*, 1995a, 1995b), the following equations are obtained

$$\frac{\sqrt{(M_i^{2+})}}{Q_i} = \frac{1}{k_X} \sqrt{\frac{1}{K_i}} + \frac{\sqrt{(M_i^{2+})}}{k_X \sqrt{Q_i}} \left( Q_H + 2 \sum_1^n Q_j \right) \quad (\text{for } i = 1, 2, \dots, n) \quad (6)$$

and

$$\frac{(H^+)}{Q_H} = \frac{1}{k_X K_H} + \frac{(H^+)}{k_X Q_H} \left( Q_H + 2 \sum_1^n Q_j \right) \quad (7)$$

Briefly, equation (6) is obtained by substituting equation (5) into equation (3) followed by inverting and taking the square root on the equation and finally rearranging the equation. Equation (7) is obtained by substituting equation (5) into equation (4) followed by inverting and rearranging the resultant equation.

In this work, batch experiments of simultaneous absorption of cupric ions and zinc ions ( $n=2$ ) from acidic aqueous media with limited volume were performed to test data against the proposed model. Values of  $k_X$ ,  $K_{Cu}$  and  $K_{Zn}$  were calculated from the intercepts and slopes of the best-fit lines according to equations (6) and (7). If the proposed model is correct, the values  $k_X$  obtained from equations (6) and (7) should be very close. In the above equations,  $Q_i$  and  $Q_H$  can be calculated from material balance for batch absorption processes:

$$Q_i = \frac{V_R[(M_i^{2+})_0 - (M_i^{2+})]}{V_g} \quad (i = 1, 2) \quad (8)$$

and

$$Q_H = \frac{V_R[(H^+)_0 - (H^+)]}{V_g} \quad (9)$$

where the subscript "0" denotes the initial condition,  $V_R$  is the volume of the reactor fluid (l),  $V_g$  is the volume of the gels at final equilibrium and  $(H^+)$  is the hydrogen ion concentration (mol/l):

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

#### PREDICTION OF EXTENT OF BATCH ABSORPTION

With the constants  $k_X$ ,  $K_H$ ,  $K_{Cu}$  and  $K_{Zn}$  (assuming  $n=2$  and subscript  $i=1$  denotes Cu and  $i=2$  denotes Zn) obtained from the procedure above, one may attempt to predict the extent of absorption of  $H^+$ ,  $Cu^{2+}$  and  $Zn^{2+}$  when a certain amount of alginate solution is dispensed into an aqueous media with a given volume and known initial concentrations of  $H^+$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . Substituting  $Q_H$  from equation (9) into equation (3) and rearranging yield:

$$(H^+) = \frac{V_R(H^+)_0}{K_H V_g (\bar{X}^-) + V_R} \quad (11)$$

From equation (3), we have

$$Q_H = K_H (H^+) (\bar{X}^-) \quad (12)$$

Likewise, substituting  $Q_i$ 's from equation (8) into equation (4) and rearranging yield  $n$  equations for the  $n$  metal species

$$(M_i^{2+}) = \frac{V_R (M_i^{2+})_0}{K_i (\bar{X}^-)^2 V_g + V_R} \quad (i = 1, 2, \dots, n) \quad (13)$$

From equation (4), we have

$$Q_i = K_i (M_i^{2+}) (\bar{X}^-)^2 \quad (i = 1, 2, \dots, n) \quad (14)$$

Finally, substituting equations (11)–(14) into equation (5) yields an objective function

$$(\bar{X}^-) - k_X + Q_H + 2 \sum_1^n Q_i = 0 \quad (15)$$

which is a non-linear function of  $(\bar{X}^-)$  and can be solved for by using any root-finding methods. Once  $(\bar{X}^-)$  at final equilibrium is solved, the equilibrium concentrations of  $H^+$  and  $(M_i^{2+})$  can be calculated from equations (11) and (13).

#### EXPERIMENTAL

The experimental condition and procedure is described elsewhere (Jang *et al.*, 1999). It is noted that the pH of the solution was not controlled, which allows evaluation of the amount of the hydrogen ions absorbed in each experiment. Therefore, binding capacity and binding stability constants for Cu–alginate, Zn–alginate and alginate acid can be simultaneously obtained with the proposed model.

Table 1. Results of calculation for initial pH~2.6 (from experimental data in Jang *et al.* (1998))

	Run No.			
	71	72	73	74
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.1795	0.1542	0.1687	0.1122
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.02150	0.01446	0.01984	0.007879
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.6892	0.4393	0.4701	0.3611
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.08258	0.04118	0.05530	0.02532
$[(\text{H}^+)/Q_{\text{H}}] [(\text{mol/l soln.})/(\text{mol/l gel})]$	0.03575	0.02778	0.02247	0.01809
$[(\text{H}^+)/Q_{\text{H}}] [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] (\text{mol/l soln.})$	0.004284	0.002643	0.002605	0.001298

Table 2. Results of calculation for initial pH~3.4

	Run No.			
	79	80	81	82
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.1335	0.1073	0.08954	0.06820
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.01788	0.01432	0.009351	0.004844
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.4189	0.3568	0.3280	0.2823
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.05610	0.044762	0.03425	0.02005
$[(\text{H}^+)/Q_{\text{H}}] [(\text{mol/l soln.})/(\text{mol/l gel})]$	0.02259	0.01929	0.01334	0.009019
$[(\text{H}^+)/Q_{\text{H}}] [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] (\text{mol/l soln.})$	0.003025	0.002575	0.001393	0.000641

## RESULTS AND DISCUSSION

*Batch absorption experiments*

Results and terms in equations (6) and (7) necessary for fitting the equilibrium model are summarized in Tables 1–4. (Data from Jang *et al.* (1999), Table 5, were not used to fit the present model because at pH 5.4 the competition from hydrogen ions was very weak). Data of  $[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2}$  versus  $[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2Q_{\text{Cu}} + 2Q_{\text{Zn}}]$  are plotted in Fig. 1. Data of  $[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2}$  versus  $[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2Q_{\text{Cu}} + 2Q_{\text{Zn}}]$  are plotted in Fig. 2. Data of  $(\text{H}^+)/Q_{\text{H}}$  versus  $[(\text{H}^+)/Q_{\text{H}}] [Q_{\text{H}} + 2Q_{\text{Cu}} + 2Q_{\text{Zn}}]$  are plotted in Fig. 3. It is found that a satisfactory fit

was obtained in all three figures with a coefficient of correlation  $R$  of 0.91, 0.93 and 0.96, respectively. The values of  $k_{\text{X}}$ ,  $K_{\text{H}}$ ,  $K_{\text{Cu}}$  and  $K_{\text{Zn}}$  are calculated from the slopes and intercepts of the best-fit straight lines and the results with *all* data points included are summarized as follows:

$$k_{\text{X}} = 0.167 \text{ mol X/l gel (Fig. 1).}$$

$$k_{\text{X}} = 0.176 \text{ mol X/l gel (Fig. 2).}$$

$$k_{\text{X}} = 0.164 \text{ mol X/l gel (Fig. 3).}$$

$$K_{\text{Cu}} = 2.703 \times 10^4 (\text{l/mol})^2.$$

$$K_{\text{Zn}} = 1684 (\text{l/mol})^2.$$

$$K_{\text{H}} = 1196 (\text{l/mol}).$$

Table 3. Results of calculation for initial pH~4.0

	Run No.			
	52	53	54	55
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.1269	0.1160	0.09101	0.07426
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.01765	0.01449	0.01059	0.006233
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.5559	0.4534	0.3038	0.2716
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.07732	0.05663	0.03534	0.02280
$[(\text{H}^+)/Q_{\text{H}}] [(\text{mol/l soln.})/(\text{mol/l gel})]$	0.001440	0.001076	0.001432	0.000765
$[(\text{H}^+)/Q_{\text{H}}] [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] (\text{mol/l soln.})$	0.0002003	0.0001344	0.0001666	0.0000642

Table 4. Results of calculation for initial pH~4.7

	Run No.			
	83	84	85	86
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.1245	0.1007	0.07901	0.06316
$[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.01630	0.01257	0.009000	0.004725
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [(\text{mol/l soln.})/(\text{mol/l gel})]^{1/2}$	0.4131	0.4393	0.4701	0.3611
$[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] [(\text{mol/l soln.})(\text{mol/l gel})]^{1/2}$	0.08258	0.04118	0.05530	0.02532
$[(\text{H}^+)/Q_{\text{H}}] [(\text{mol/l soln.})/(\text{mol/l gel})]$	0.03575	0.02778	0.02247	0.01809
$[(\text{H}^+)/Q_{\text{H}}] [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})] (\text{mol/l soln.})$	0.004284	0.002643	0.002605	0.001298

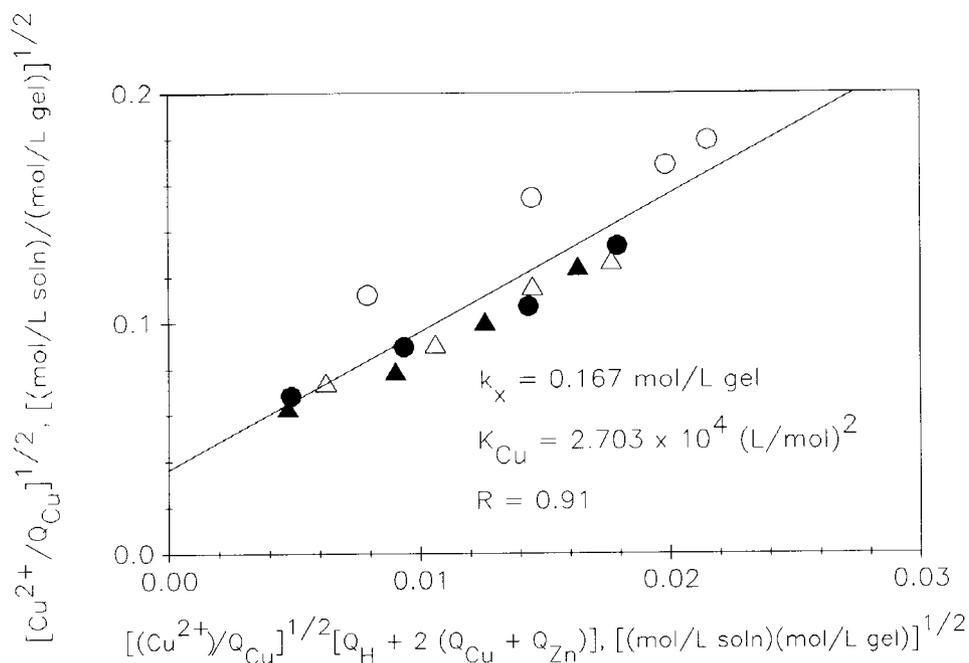


Fig. 1. Plot of  $[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2}$  versus  $[(\text{Cu}^{2+})/Q_{\text{Cu}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})]$  for all experimental data points of initial pH 2.6 (○), 3.4 (●), 4.0 (△) and 4.7 (▲).

It is found that the three  $k_x$  values agree fairly well, supporting one assumption made in the model: the three species  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{H}^+$  compete for the same binding group  $\text{X}^-$ . Note that the conditional binding capacity  $q$  (mol metal binding site/g Na-alginate) determined in Jang *et al.* (1999)

decreases with decreasing pH while the binding capacity  $k_x$  determined in this work is independent of pH.

Multiplying the mean  $k_x$  value (0.169 mol X/l gel) by the average unit gel volume (with run No. 74, 82 and 86 excluded due to significant gel swell-

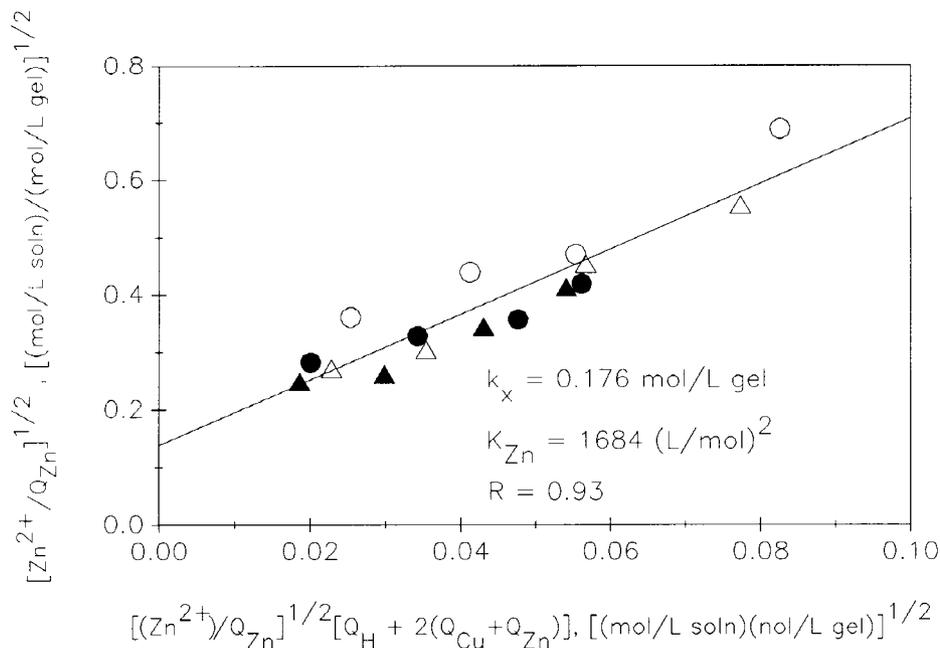


Fig. 2. Plot of  $[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2}$  versus  $[(\text{Zn}^{2+})/Q_{\text{Zn}}]^{1/2} [Q_{\text{H}} + 2(Q_{\text{Cu}} + Q_{\text{Zn}})]$ . The legends are the same as those in Fig. 1.

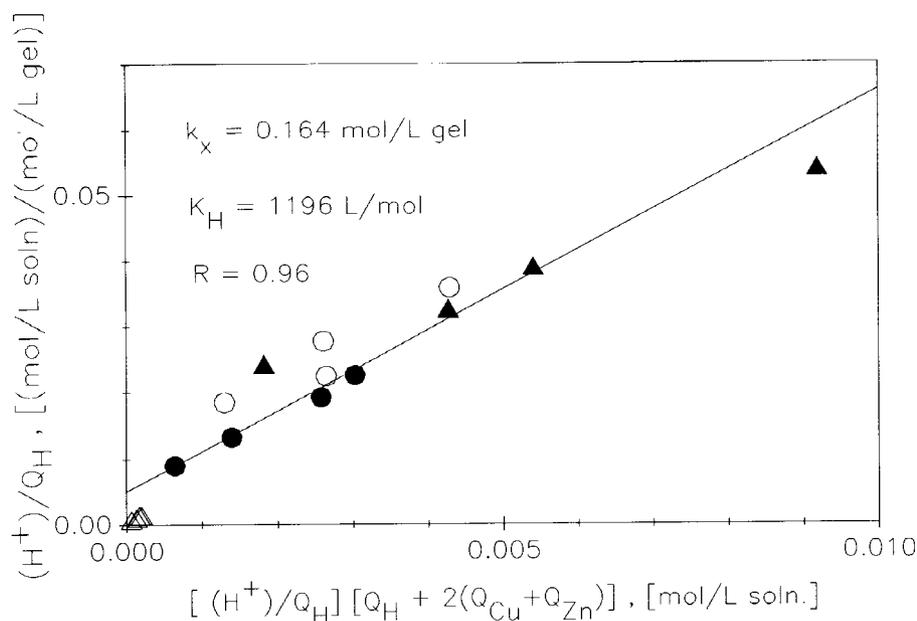


Fig. 3. Plot of  $[(H^+)/Q_H]$  versus  $[(H^+)/Q_H][Q_H + 2(Q_{Cu} + Q_{Zn})]$ . The legends are the same as those in Fig. 1.

ling) of  $0.03321$  (g alginate) yields  $5.62 \times 10^{-3}$  mol X/g Na-alginate which can be converted to  $2.81 \times 10^{-3}$  (mol equivalent metal binding sites/g Na-alginate). It is noted that this value ( $2.81 \times 10^{-3}$  mol/g) is greater than all conditional capacities evaluated at acidic pH reported elsewhere (Jang *et al.*, 1999, Table 6). Also, the binding capacity  $5.62 \times 10^{-3}$  (mol X/g) is somewhat greater than that obtained in our previous work [ $4.353 \times 10^{-3}$  mol X/g alginate, based on biochemical assay of food-grade algin (Jang *et al.*, 1990b);  $4.360 \times 10^{-3}$  mol X/g alginate (Jang *et al.*, 1995b) and  $4.057 \times 10^{-3}$  mol X/g alginate (Jang *et al.*, 1995a) based on model fit]. This difference is to be expected because purified Na-alginate instead of food-grade algin was used in this work.

The three  $K$  values, also independent of pH, were calculated from the  $y$ -intercepts made by the best-fit lines and the  $k_X$  value obtained from respective plots. The Cu/Zn selectivity ratio was calculated as  $27030/1684 = 16.0$  for the whole pH range encountered in this work. The value of  $pK_{HA}$  ( $= -pK_H$ ) is calculated as  $\log(1196) = 3.078$ , which agrees very well with those reported in Lin (1981), Marinsky *et al.* (1985) and Jang *et al.* (1989).

#### Prediction of extent of batch absorption

For an aqueous medium of 0.5-l in volume under a given initial condition [copper concentration: 100.1 ppm, zinc concentration: 100.6 ppm, pH: 3.45,  $NaNO_3$  concentration: 0.01 M, and amount of Na-alginate solution dispensed: 15.5 ml (experimental final gel volume = 19.1 ml)], the final equilibrium concentrations of copper and zinc and pH were predicted by first finding the root of the non-linear

equation (15). Using Newton-Raphson algorithm, the root of equation (15) was calculated to be  $(\bar{X}^-) = 0.0676$  mol X/l gel. Using this  $(\bar{X}^-)$  value and equations (11) and (13), the final equilibrium condition was predicted and compared with experimental results shown in Table 5.

It is shown that a fair agreement exists between the predicted and the experimental results. Such predictions can be performed essentially for any pH in the range of 2.5–5.4 and metal ion concentrations sufficiently high to allow formation of stable gels. More work needs to be done to determine threshold ratio for concentration of divalent cation added to amount of Na-alginate added over which model is satisfactory (and no significant gel swelling occurs). The procedure illustrated here demonstrates that  $k_X$ ,  $K_H$ ,  $K_{Cu}$  and  $K_{Zn}$  can be obtained *simultaneously* (with all parameters being independent of pH) and these parameters can be used to predict the extent of metal absorption by the alginate at any pH. In the conventional approach, pH is maintained at a specific value and the results obtained are pH-specific that can only be applied to a solution with the identical pH. The procedure developed in this work allows pH to vary. Therefore, the current approach suits varying environmental conditions better than the conventional approach.

Table 5

	pH	Cu (ppm)	Zn (ppm)
Predicted	4.02	19.3	80.5
Experimental	4.00	19.1	77.2

*Effect of Donnan potential*

The result of calculation in the previous section shows that the concentration of free, unbound carboxyl groups ( $\bar{X}^-$ ) is 0.06757 mol/l gel. These negatively-charged carboxyl groups which are not neutralized by  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{H}^+$  have to be neutralized by those sodium ions that originally exist in the sodium alginate but are not displaced by hydrogen ions, cupric ions, or zinc ions. Therefore, the concentration of sodium ions in the liquid in the gel domain ( $\bar{\text{Na}}^+$ ) should be 0.06757 mol/l gel. A simple material balance yields the concentration of sodium ions in the aqueous medium at final equilibrium:

$$\begin{aligned} (\text{Na}^+) &= 0.01 \text{ M (orig. prep.)} + \frac{(k_X - \bar{X}^-)V_g}{V_R} \\ &= 0.0134 \text{ M} \end{aligned} \quad (16)$$

The second term on the right-hand side of equation (16) is the increase of the sodium ion concentration in the aqueous medium due to the sodium ions on the sodium alginate molecules that are replaced by hydrogen, cupric, and zinc ions. Imagine that the surface of the gel serves as a semi-permeable membrane allowing only water and small ionic species to permeate. There exists a Donnan potential across the "membrane". Assuming ideal-solution behavior, the ratios of concentrations of cupric ions, zinc ions and hydrogen ions in the liquid enclosed in the gel domain to those in the external aqueous medium can be calculated as

$$\frac{(\bar{\text{H}}^+)}{(\text{H}^+)} = \frac{(\bar{\text{Na}}^+)}{(\text{Na}^+)} = \frac{0.0676 \text{ M}}{0.0134 \text{ M}} = 5.04 \quad (17)$$

$$\begin{aligned} \frac{(\bar{M}_i^{2+})}{(M_i^{2+})} &= \left[ \frac{(\bar{\text{Na}}^+)}{(\text{Na}^+)} \right]^2 = 25.4 \\ (i = 1 = \text{Cu}, i = 2 = \text{Zn}) \end{aligned} \quad (18)$$

according to Marinsky *et al.* (1985). The value 25.4 calculated above shows the existence of a significant Donnan potential across the surface of the gel. The Donnan potential term and the gel-domain concentrations of the cationic species under any other conditions can be calculated following the above procedure (Equations (11)–(18)). Rigorously speaking, the intrinsic binding constants  $K_{\text{H}}$ ,  $K_{\text{Cu}}$  and  $K_{\text{Zn}}$  should be based on the *activities* of ionic species in the *gel domain* instead of the concentrations of ionic species in the bulk solution (Jang *et al.*, 1990a, 1990b). The fact that the values of  $K_{\text{H}}$ ,  $K_{\text{Cu}}$  and  $K_{\text{Zn}}$  are uniquely resolvable with the approach presented in this work can be explained by a Donnan potential term which remains essentially constant over the acid dissociation range as pH (degree of dissociation) is varied. Since the ionic strength is somewhat constant (with 0.01 M  $\text{NaNO}_3$  added) among all experiments, it is expected that

the Donnan potential term was insensitive to the variation of degree of dissociation of the alginic acid. A similar observation was made by Lin (1981). In Lin's study, the  $\text{p}K_{\text{HA}}$  ( $= -\text{p}K_{\text{H}}$ ) values of alginic acid and sodium polystyrene sulfonate are insensitive to pH (degree of dissociation) under constant ionic strength. However, as the ionic strength increases, the Donnan potential decreases. Therefore, the projection of the alginic acid polymer as a phase separate from the solution is justified.

A procedure of refining the calculation illustrated in this work is proposed as follows. Since the maximum binding density  $k_X$  and the concentration of free, unbound carboxyl groups ( $\bar{X}^-$ ) are not known *a priori*, the first round of calculations should follow the procedure illustrated in this work. Once the model parameters (based on the concentrations of cationic species in the aqueous media) are obtained, numerical solution for ( $\bar{X}^-$ ) should be performed using equation (15). Then the Donnan potential term can be evaluated and the gel-domain concentrations of cationic species can be estimated. Further by applying physicochemical theories, activities of cationic species can be obtained. Finally, the concentrations of cationic species in equations (3) and (4) are replaced by their respective activities and data fitting with equations (6) and (7) will be performed using gel-domain concentrations. It is noted that in this procedure the ionic strength can be varied and, therefore, it can better simulate the actual environmental condition. As a result, improved *intrinsic* values of  $K_{\text{H}}$ ,  $K_{\text{Cu}}$  and  $K_{\text{Zn}}$ , independent of pH and ionic strength, can be obtained. This procedure is expected to be repeated a few times and will be our work in the near future.

In the current paper, we demonstrate how the model parameters can be applied to a prediction of the extent of batch absorption when the ionic strength of the aqueous media tested remain the same as those used in modeling.

*Factors affecting the accuracy of prediction*

There are some other factors that might affect accuracy of data obtained from such analyses. As mentioned earlier, the gels formed *in situ* displayed gel volumes that varied somewhat with experimental condition. In the model developed in this work a constant binding group density was assumed. In future work, an effort should be made to form gels, either *in situ* or *ex situ*, so that volume does not change with experimental condition to resolve the uncertainties related to the validity of the data points.

Another major assumption made in this work was that the only form of metal–alginate complex was bi-dentate equation (2). We made this assumption based on our observation that metal alginate gels were formed as soon as drops of sodium alginate solution hit the aqueous media containing sufficiently high concentrations of dissolved metals.

Had it not been due to the formation of bi-dentate metal alginate complexes, stable alginate gels would not have been formed, an assumption also made in our previous publications (Jang *et al.*, 1995a, 1995b). However, it must be noted that satisfactory fit of experimental data with the proposed model is not a proof of the mechanism. We can not rule out the possibility of the existence of uni-dentate complex ( $M_2X^+$ ). In our previous work determining the binding constants of both uni-dentate and bi-dentate complexes between cupric ions in a *dilute* solution and *colloidal* alginate molecules, a small fraction of uni-dentate complex does exist (Jang *et al.*, 1990a). In this work, however, no further examination is to be made for possible existence of uni-dentate complexes. The long-chain alginic acid molecule contains two kinds of monomeric isomers: guluronic acid (G) and mannuronic acid (M). In the model developed in this work, no distinction is made between the binding group  $X^-$  on  $-GGG-$ ,  $-MMM-$  and  $-GMGM-$  segments of the alginic acid molecule.

The real-world aqueous media contain not only multiple metal species but also complexing agents such as humates and fulvates. The model requires extension to suit more complex situations. In our recent work, the competition of ferrous ions, an abundant metallic species in acid mine drainage liquors, for metal binding sites on alginate was evaluated and results will be submitted for publication very soon.

#### CONCLUSION

The results of simultaneous absorption of cupric ions and zinc ions from acidic aqueous solutions (pH 2.6–5.4) show that the extended Langmuir model proposed here fit data satisfactorily. The model parameters (binding group density and stability constants for alginic acid, cupric alginate and zinc alginate, all being pH-independent) obtained in

this work were used to predict the extent of batch absorption of copper and zinc from an acidic solution (pH 3.4) with satisfactory agreement with experimental results.

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#### REFERENCES

- Jang L. K., Harpt N., Uyen T., Grasmick D. and Geesey G. G. (1989) An iterative procedure based on Donnan equilibrium for calculating the polymer-subphase volume of alginic acid. *J. Polymer Sci. Part B: 27*, 1301–1315.
- Jang L. K., Harpt N., Grasmick D., Vuong L. N. and Geesey G. (1990a) A two-phase model for determining the stability constants for interactions between copper and alginic acid. *J. Phys. Chem.* **94**, 482–488.
- Jang L. K., Geesey G. G., Lopez S. L., Eastman S. L. and Wichlacz P. L. (1990b) Use of gel-forming biopolymer directly dispensed into a loop fluidized bed reactor to recover dissolved copper. *Water Res.* **24**, 889–897.
- Jang L. K., Nguyen D. and Geesey G. G. (1995a) Effect of pH on the absorption of Cu(II) by alginate gel. *Water Res.* **29**, 315–321.
- Jang L. K., Nguyen D. and Geesey G. G. (1995b) Selectivity of alginate gel for Cu versus Co. *Water Res.* **29**, 307–313.
- Jang L. K., Nguyen D. and Geesey G. G. (1999) Selectivity of alginate gel for Cu over Zn when acidic conditions prevail. *Water Res.* **33**, 2817–2825.
- Lin F.-G. (1981) Studies of hydrogen and metal ion equilibria in polysaccharides systems- alginic acid and chondroitin sulfate. Doctoral Dissertation, Chemistry Department, State University of New York at Buffalo.
- Marinsky J. A., Baldwin R. and Reddy M. (1985) Interpretation with a Donnan-based concept of the influence of simple salt concentration on the apparent binding of divalent ions to the polyelectrolytes polystyrene and dextran sulfate. *J. Phys. Chem.* **89**, 5303–5307.
- Rees D. A. and Welsh E. J. (1977) Secondary and tertiary structure of polysaccharides in solutions and gels. *Angew. Chem. Int. Ed. Engl.* **16**, 214–224.