

## Biosorption Model for Binary Adsorption Sites

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**Abstract** The binding of heavy metals by a biosorbent with binary functional groups was mathematically modeled. An FT-IR spectrophotometer analysis was employed to determine the stoichiometry between the protons in the functional groups of alginic acid and lead ions as a model system. The results calculated using an equilibrium constant agreed well with the experimental results obtained under various operating conditions, such as pH and metal ion concentration. It was also shown that the overall adsorption phenomenon of alginic acid was mainly due to its carboxyl groups. The equilibrium constants for each functional group successfully predicted the lead adsorption of  $\alpha$ -cellulose. Furthermore, the biosorption model could predict the adsorption phenomena of two metal ions, lead ions and calcium ions, relatively.

**Key words:** Modeling, biosorption, ion exchange, heavy metals, functional groups

The metal-ion binding mechanism in biosorption involves different processes, such as complexation, coordination, electrostatic attraction, microprecipitation, and ion exchange. Most existing biosorption models use Langmuir or Freundlich sorption isotherms, where the binding of metal ions is determined as a function of the equilibrium metal ion concentration in the solution. The major advantage of these models is their simplicity, however, they fail to predict the effect of important factors, such as pH and ionic strength. Some alternative models have been developed recently to overcome these problems. Crist *et al.* [1] utilized a multicomponent Langmuir model that considered the effect of competing ions. The deficiency of this model is that it assumes a constant number of free sites, which is true in a constant pH system, yet does not hold for a system with a changing pH. Kim *et al.* [7] described the effects of pH, ionic strength, concentration of metal ion, and other factors on the lead adsorption capacity of *Undaria*

*pinnatifida* using a complexation model. Even though this model can easily be applied to a single heavy metal system, the predicted result of each adsorption capacity in a multi-metal system is not in good agreement with experimental data. Schiewer and Volesky [11] observed that ion exchange plays an important role in metal sorption by an algal biomass, and modeled the binding of heavy metal ions and protons as a function of metal concentration and equilibrium pH. Various researchers have introduced ion-exchange models to describe biosorption mechanisms that take into account the reversibility of the ion-exchange reactions with equilibrium constants. Ion exchange is a stoichiometric process, in which, if one ion enters the solid phase in a binary ion-exchange system, another ion must leave the solid. Also, an ion-exchange mechanism assumes that all sites to which the metal ions are sorbed are initially occupied, i.e., the number of free sites stays constant. Crist *et al.* [2] compared the fit of the Langmuir sorption isotherm model and one using ion-exchange constants, and found that the differences between the two models were especially pronounced at low metal ion concentrations, because of the effect of the reverse reaction involving the displaced ion. Similarly, it has been postulated that the Langmuir model applies only at higher metal ion concentrations where the binding of the displaced ion is low. Therefore, the approach of ion exchange is modeled perhaps somewhat closer to reality than the simple Langmuir model. Generally, most biosorbents have various functional groups, however, most ion-exchange models are limited to only a mono-functional group. There are few biosorption models that consider multifunctional groups of a biosorbent.

Accordingly, to develop a biosorption model with multifunctional groups, alginic acid which has two functional groups (carboxyl and hydroxyl groups) was selected as a model biosorbent in this work [15]. Until now, various mathematical models describing the mechanism of the heavy metal removal with alginic acid have been proposed. Yasuhiro *et al.* [16] determined the sorption capacity and distribution equilibrium constants by comparing experimental data with theoretical predictions which are based on the

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assumption that sorption takes place because of ion-exchange reaction between divalent and trivalent metal ions and alginic acid. Another model which produced the effective binding group density and binding stability constants for copper and hydrogen ions simultaneously was presented by Jang *et al.* [5]. However, this model is an extended Langmuir model based on an ion-exchange reaction considering stoichiometry. Otherwise, a general model for the complexation between divalent metal ions and acidic sites on alginic acid was applied to explain the adsorption mechanism of lead ion on the adsorbent by Hideshi *et al.* [4]. Even though alginic acid has two functional carboxyl and hydroxyl groups, most of the modeling studies with alginic acid have dealt only with carboxyl functional groups. However, Slabbert *et al.* [13] reported that hydroxyl compounds are responsible for the metal binding capacity of an algal biomass. They reported that the ortho-dihydroxyl group on the flavonoid  $\beta$ -ring of condensed tannins is the main group involved in metal complexation.

In order to apply efficiently the biosorption to an actual process, it is important to predict the adsorption capacity of heavy metals more accurately, and consider the investigation of the adsorption phenomena for each functional group. Therefore, the objective of the present study was to develop a biosorption model, which included both the hydroxyl and carboxyl groups of alginic acid, for an ion-exchange reaction. This model was applied to a two-metal system including calcium and lead ions, and then used to investigate the selectivity to metal ions for each functional group theoretically.

## MATERIALS AND METHODS

### Adsorption Experiments

Batch equilibrium experiments were conducted to obtain information on the metal uptake by alginic acid under varying pHs and initial concentrations of metal ions. The alginic acid used in this study was purchased from Sigma-Aldrich (U.S.A.). A total of 100 ml of a metal solution was added into 300-ml Erlenmeyer flasks. All metals were of nitrate form and purchased from Sigma-Aldrich (U.S.A.). Subsequently, appropriate amounts of alginic acid were added to the flasks, which were then placed in a shaking incubator at 30°C for 24 h. 1 N HNO<sub>3</sub> and 1 N NH<sub>4</sub>OH were used for pH adjustment. The solution was centrifugated at 10,000 rpm for 20 min, and the final metal concentration of the supernatant was then measured using AA (Atomic Absorption spectroscopy: Perkin-Elmer, U.S.A.) and ICP (Inductively Coupled Plasma Spectroscopy: Perkin-Elmer, U.K.) spectroscopies. The same procedure was followed for experiments where  $\alpha$ -cellulose (Sigma-Aldrich, U.S.A.) was used. It was selected to investigate the feasibility of the model equation used in this work.

### Number of Acidic Sites

The number of acidic sites for each functional group in the biomass was determined by the method of Schnitzer and Khan [12]. The calcium acetate method is widely used for determining the -COOH groups in the biomass. The biomass liberates acetic acid in a reaction with calcium acetate, and the acetic acid was then titrated with a standard sodium hydroxide solution. Acetylation with acetic anhydride in pyridine was used for estimating the total -OH groups in the biomass. The excess anhydride was hydrolyzed to acetic acid, which was then titrated with a standard base. To eliminate CO<sub>2</sub>, nitrogen gas was continuously bubbled through the system.

### Determination of Stoichiometric Number

To determine the stoichiometric number between the proton and lead ions in the functional groups of alginic acid, the following experiments were performed. Five lead ion solutions with an initial concentration of 100 ppm were prepared, and the initial pH of each solution was adjusted to 2.0, 3.0, 4.0, 5.0, and 6.0. Then, 0.02 g of alginic acid was added to each solution. The mixtures were shaken for 24 h. After an equilibrium was reached, the final pH of the solutions and the final metal ion concentrations were recorded. The stoichiometric number was obtained by comparing the released proton ions and adsorbed lead ion concentration. The proton ions released into the metal solutions were calculated from the difference between the initial and final pH value of the solutions.

### FT-IR Spectrum Analysis

The infrared spectra of the pure alginic acid and lead-loaded alginic acid were recorded using an FT-IR (Perkin Elmer 1725x, 400–2,000 cm<sup>-1</sup>, U.S.A.) spectrophotometer. One hundred mg KBr disks containing 2% finely ground powder of each sample were prepared less than 24 h before recording.

## RESULTS AND DISCUSSION

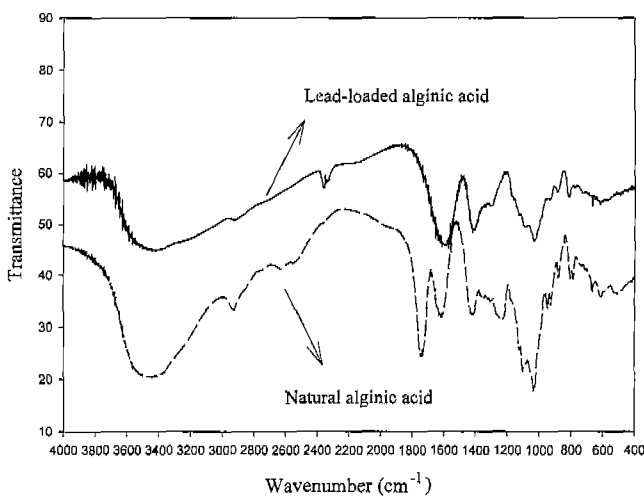
### Determination of Stoichiometric Number

As shown in Table 1, an average of about 2.1 moles of protons were displaced when 1.0 mole of lead ion was adsorbed. Rees *et al.* [10] explained the gelation phenomenon using the egg-box model, in which each divalent metal ion binds to two carboxyl groups on adjacent alginate molecules. Treen-Sears *et al.* [14] reported that 2 protons are released for each uranyl ion sorbed by *Rhizopus arrhizus* in a flow-through packed biosorption bed. Also, Crist *et al.* [1] showed that the total charge of the released ions (Ca, Mg, and H) equals to the charge of the metal ion taken up, demonstrating a perfect ion-exchange behavior.

**Table 1.** Determination of stoichiometric number for proton and lead ion exchange.

pH change	Stoichiometric number
2.0	1.88
2.5	1.92
3.0	2.09
3.5	2.12
4.0	2.06
4.5	2.02
5.0	2.05

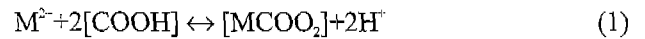
To confirm the validity of the egg-box model, an FT-IR spectrum analysis of the pure alginic acid and lead-adsorbed alginic acid was performed, respectively. This approach identified two absorbance peak shifts, characteristic of coordination compounds between carboxyl groups and heavy metals. “ $\Delta$ ” is defined as the distance between  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$ , and this distance between the two peaks reflects relative symmetry of the carboxyl group and as well as the nature of the coordination number [8]. As shown in Fig. 1, the spectra of the alginic acid typically displayed absorbance peaks at  $1,738\text{ cm}^{-1}$ , corresponding to the stretching band of a free carbonyl double bond from the carboxyl functional group. After contact with a highly concentrated lead solution, the alginic acid exhibited spectra with a clear shift in the carbonyl stretching band from  $1,740$  to  $1,600\text{ cm}^{-1}$ . This shift is typical of the complexation of the carbonyl group by dative coordination. Another shift from  $1,240$  to  $1,420\text{ cm}^{-1}$  was observed, corresponding to the complexation of the oxygen from the carboxyl C-O bond. From these results, the distance between the two peaks (C=O and C-O) of pure alginic acid and lead-loaded alginic acid was about 500 and 180, respectively. These values reflected an increase in the relative symmetry of the


**Fig. 1.** Comparison of IR-spectrum between lead-loaded alginic acid and natural alginic acid.

carboxyl functional groups, thereby physically demonstrating that the lead binding resulted from bridging or bidentate complex formation with the carboxyl groups of the alginic acid, which is consistent with the “egg-box” model as described by Rees and co-workers [10].

### Development of Biosorption Model Considering Binary Adsorption Sites

The functional groups considered with this model are carboxyl and hydroxyl groups. The ion-exchange reactions between the divalent metal ions and each functional group of alginic acid are given as follows, respectively.



where  $[\text{COOH}]$  and  $[\text{OH}]$  are the functional groups which bind heavy metal ions. These reactions are reversible, in that the metal and hydrogen ions exchange with each other. Therefore, a change of pH has an influence on the metal ion concentration. In this study,  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$  solutions were used to keep the pH constant. Equation (2) is referred from the equation presented by David *et al.* [3]. Let  $K_{e, \text{COOH}}$  and  $K_{e, \text{OH}}$  be the equilibrium constants for each functional group of alginic acid. Then, from equations (1) and (2), the equilibrium constants can be represented as follows:

$$K_{e, \text{COOH}} = \frac{q_{\text{MCOO}_2} C_{\text{H}}^2}{C_{\text{M}} [\text{COOH}]^2} \quad (3)$$

$$K_{e, \text{OH}} = \frac{q_{\text{MO}_2} C_{\text{H}}^2}{C_{\text{M}} [\text{OH}]^2} \quad (4)$$

In the above equations,  $C_{\text{M}}$  and  $C_{\text{H}}$  indicate the metal and hydrogen ion concentrations (mmol/l) in the liquid phase, respectively. Also,  $q_{\text{MCOO}_2}$  and  $q_{\text{MO}_2}$  represent the adsorption capacities (mmol/g) for the carboxyl and hydroxyl groups. Here, let  $Q_{\text{COOH}}$  and  $Q_{\text{OH}}$  be the maximum carboxylic acid and hydroxyl group sites in the solid phase of alginic acid. Then,  $[\text{COOH}]$  and  $[\text{OH}]$ , which indicate the unoccupied binding sites with a metal ion, can be transformed into equation (5).

$$[\text{COOH}] = Q_{\text{COOH}} - 2q_{\text{MCOO}_2}, \quad [\text{OH}] = Q_{\text{OH}} - 2q_{\text{MO}_2} \quad (5)$$

The resulting equation for solving  $q_{\text{MCOO}_2}$  and  $q_{\text{MO}_2}$  can be obtained by substituting equation (5) into equations (3) and (4).

$$q_{\text{MCOO}_2} = \frac{(4Q_{\text{COOH}}K_{e, \text{COOH}}C_{\text{M}} + C_{\text{H}}^2)}{-C_{\text{H}}\sqrt{C_{\text{H}}^2 + 8Q_{\text{COOH}}K_{e, \text{COOH}}C_{\text{M}}}} \quad (6)$$

$$q_{\text{MO}_2} = \frac{(4Q_{\text{OH}}K_{e, \text{OH}}C_{\text{M}} + C_{\text{H}}^2)}{-C_{\text{H}}\sqrt{C_{\text{H}}^2 + 8Q_{\text{OH}}K_{e, \text{OH}}C_{\text{M}}}} \quad (7)$$

**Table 2.** Number of acidic sites for each functional group in the biomass.

Biomass	Carboxyl groups (mequiv/g)	Hydroxyl groups (mequiv/g)
Alginic acid	7.02	1.63
$\alpha$ -Cellulose	–	1.22

Therefore, the total adsorption capacity ( $q_T$ ) for the divalent metal ions of alginic acid can be expressed as in equation (8).

$$q_T = \frac{(4Q_{\text{COOH}}K_{e,\text{COOH}}C_M + C_H^2)}{8K_{e,\text{COOH}}C_M} - \frac{C_H \sqrt{C_H^2 + 8Q_{\text{COOH}}K_{e,\text{COOH}}C_M}}{8K_{e,\text{COOH}}C_M} + \frac{(4Q_{\text{OH}}K_{e,\text{OH}}C_M + C_H^2)}{8K_{e,\text{OH}}C_M} - \frac{C_H \sqrt{C_H^2 + 8Q_{\text{OH}}K_{e,\text{OH}}C_M}}{8K_{e,\text{OH}}C_M} \quad (8)$$

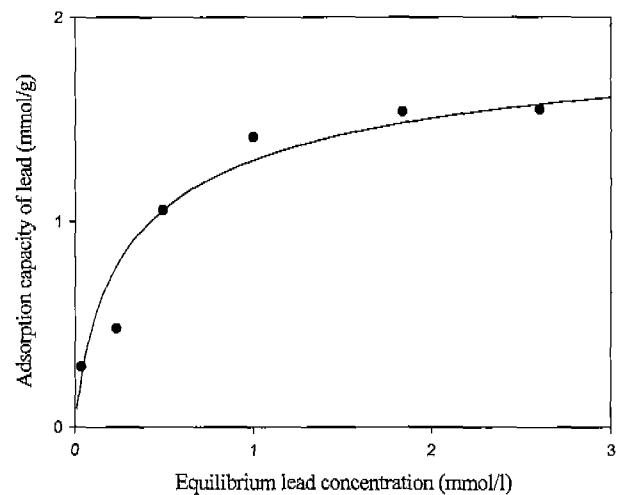
### Parameter Estimation and Application to a Single Metal Ion System

To estimate the parameters, the number of acidic sites for each functional group in the biomass were measured three times and the average values are presented in Table 2. Furthermore, to estimate the equilibrium constants between each functional group in the alginic acid and divalent metal ions simultaneously, an optimization program in Sigmaplot (Ver 5.0) was used.

As shown in Table 3, the equilibrium constants for the carboxyl and hydroxyl groups of the lead ions were estimated as 5.95 and 1.59, respectively. These values were estimated from experimental data at pH 4. To investigate the validity of these parameters, the estimated values were applied to the calculation of the adsorption capacities at pH 2. As shown in Fig. 2, these parameters fit well with the experimental results at pH 2. To calculate the lead adsorption for each functional group in alginic acid, each equilibrium constant estimated from the total adsorption experimental results of alginic acid was used. The calculated lead ion adsorption capacities of the carboxyl and hydroxyl groups at pHs 2 and 4 are shown in Fig. 3(a) and 3(b). Because adsorption experimental data for each functional group in alginic acid have not yet been reported, a direct comparison with the adsorption capacities calculated from the model equation is impossible. However, the fact that most of the biosorption was performed by the carboxyl groups is the

**Table 3.** Equilibrium constant for each functional group in alginic acid.

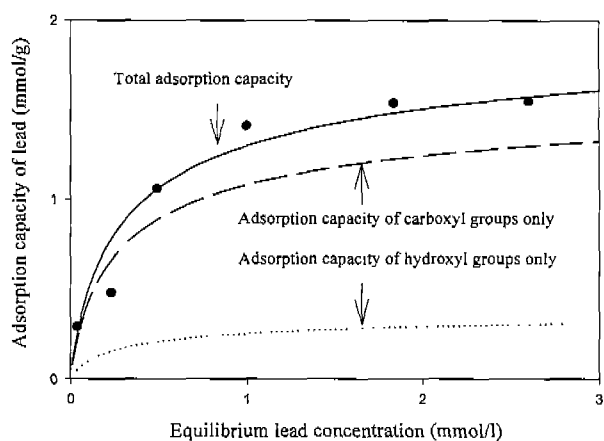
Metal ions	$K_{e,\text{COOH}}$	$K_{e,\text{OH}}$
Lead ion	5.95	1.59
Calcium ion	1.87	0.49

**Fig. 2.** Comparison of adsorption curves of total lead ion from experimental data and calculated values.

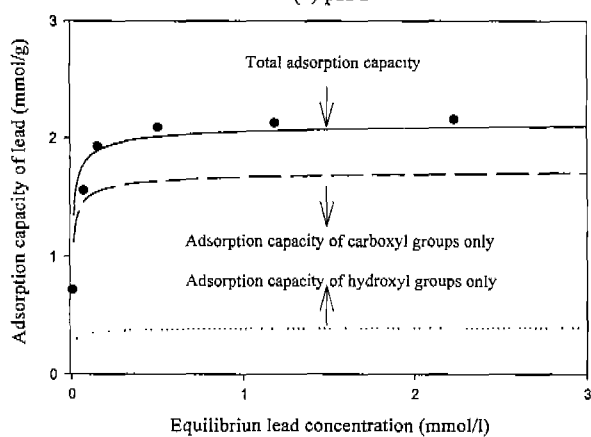
When estimated values obtained from experimental data at pH 4 are applied to predict adsorption capacity of lead ion at pH 2. ● Experimental data at pH 2. — Calculated values at pH 2.

same as the result reported by Kim *et al.* [6]. The equilibrium constant is defined as the ratio of the forward and backward reaction rate constants. In general, as the equilibrium constant increases, the overall reaction rate proceeds to the forward reaction. The fact that the equilibrium constant for the lead ion in the carboxyl groups ( $K_{e,\text{COOH}}$ ) was much higher than that in the hydroxyl groups ( $K_{e,\text{OH}}$ ) implies that the overall adsorption of alginic acid was mainly due to the carboxyl groups. It is also known that as the equilibrium constant increases, the change in Gibbs free energy,  $\Delta G$ , which is defined as  $-RT \ln K$ , decreases. The decrease in  $\Delta G$  means that the structure of the product is more stable than that of the reactant. Therefore, the estimated values obtained by nonlinear regression in this study showed that the structure of the lead ion bound by the carboxyl groups was more stable than that of the lead ion bound by the hydroxyl groups. Another important thing was that the heavy-metal adsorption mechanism by the hydroxyl groups was not ignored. A prediction of the lead adsorption capacity relative to the hydrogen ion concentration was also performed. In general, the adsorption capacity of metal ions increases as the pH increases. As shown in Fig. 4, the values calculated from the model equation predicted experimental result relatively well. The adsorption capacity of the lead ion beyond pH 5.0 was not pursued, because an insoluble lead-hydroxide-precipitate was observed in the solution [9].

To investigate the feasibility of the model equation used in this work,  $\alpha$ -cellulose having hydroxyl groups without carboxyl groups was used as a control, and isothermal adsorption experiments on the lead ions were performed in the presence of both alginic acid and  $\alpha$ -cellulose or cellulose alone at pH 4. In the case of the former, half



(a) pH 2



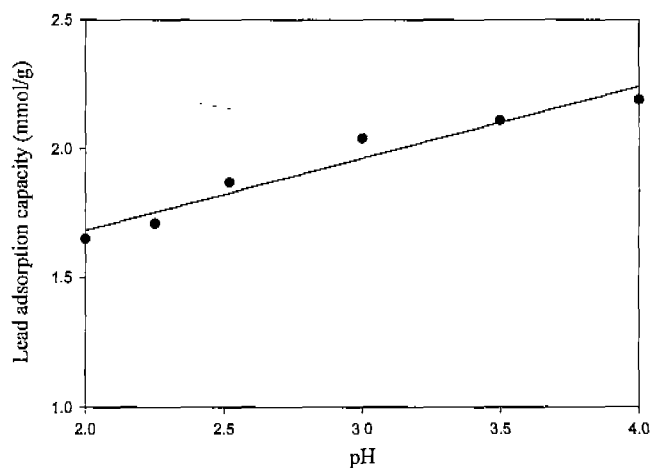
(b) pH 4

**Fig. 3.** (a) Lead-ion adsorption curve using the equilibrium constant calculated for each functional group in alginic acid at pH 2 ( $K_{s,COOH}=5.95$ ,  $K_{s,OH}=1.59$ ). (b) Lead-ion adsorption curve using the equilibrium constant calculated for each functional group in alginic acid at pH 4 ( $K_{s,COOH}=5.95$ ,  $K_{s,OH}=1.59$ ).

of the total amount added was loaded. The equilibrium constants obtained from each functional group of the alginic acid were applied to predicting the lead adsorption capacity of  $\alpha$ -cellulose. The total acid group number of  $\alpha$ -cellulose was determined using Schnitzer and Khan's method and calculated to be 1.22 meq/g. When the experimental data were compared with the calculated equilibrium isotherms using the equilibrium constant estimated from each functional group of the alginic acid (Fig. 5), the calculated results were in good agreement with the experimental results. Accordingly, it would appear that this model equation, considering each functional group, can be effectively applied to predicting the adsorption capacity of many polysaccharides, provided that the acid number of each functional group is known.

**Application to a Two-Metal System**

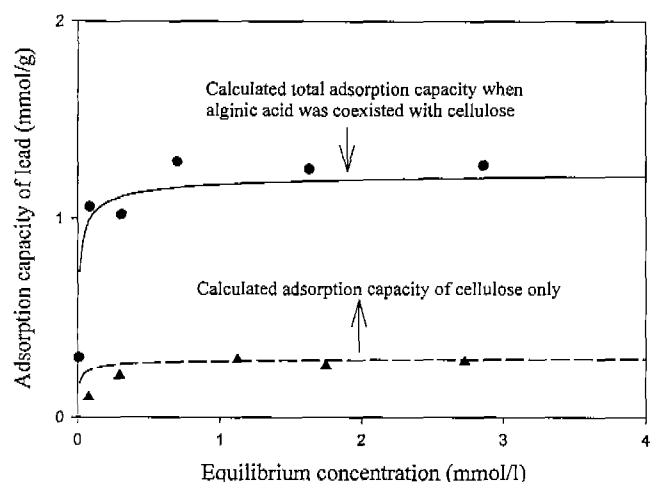
The proposed model equation was also applied to a system considering two binding sites and two metals, simultaneously.



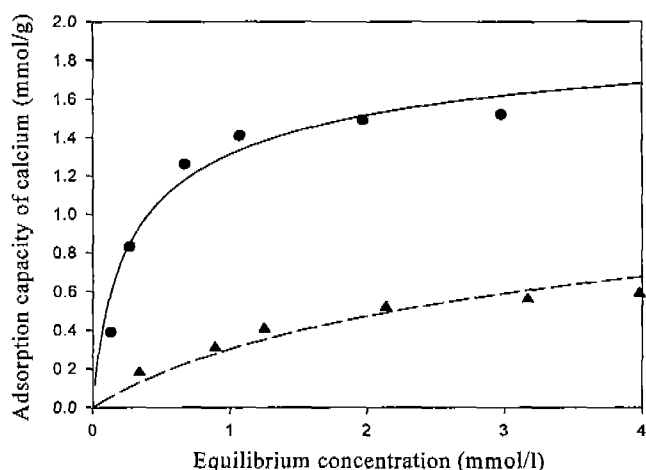
**Fig. 4.** Comparison of the adsorption capacity of lead ions between experimental data and calculated result relative to pH change.

● Experimental data. — Calculated result.

In order to investigate the effect of an alkaline metal ion on the adsorption of heavy metal ions, lead and calcium ions were selected as the model metals. The calcium ion is well known as a representative alkaline metal ion. The equilibrium constant between each functional group in the alginic acid and the calcium ion was also obtained by applying the nonlinear regression method to the isothermal adsorption experimental results for the calcium ion only. As shown in Fig. 6, the calculated results for the calcium ions were in good agreement with the experimental results. Table 3. shows the equilibrium constants for the lead and calcium ions. These equilibrium constants were used to predict the isothermal adsorption capacities for each metal ion in



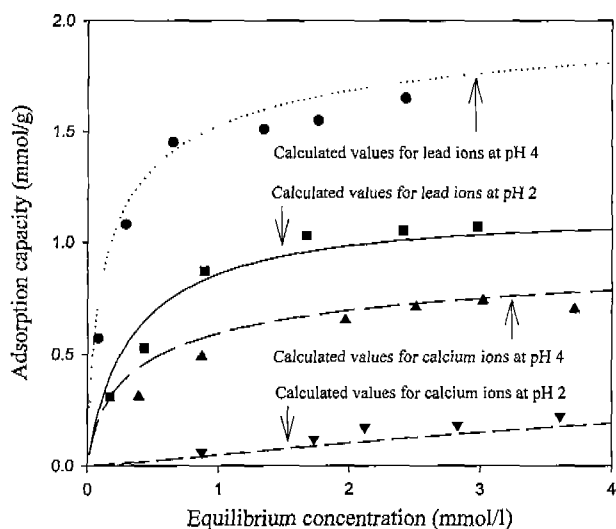
**Fig. 5.** Comparison of experimental data with the adsorption curve obtained using the equilibrium constant estimated from each functional group in alginic acid, when alginic acid coexists with  $\alpha$ -cellulose and when  $\alpha$ -cellulose exists alone.



**Fig. 6.** Comparison of adsorption curves of calcium ions between experimental data and calculated values relative to pH conditions ( $K_{a,COOH}=1.87$ ,  $K_{a,OH}=0.49$ ).

● Experimental data at pH 4. ▲ Experimental data at pH 2. --- Calculated adsorption capacity at pH 2. — Calculated adsorption capacity at pH 4.

a mixed system. Figure 7 shows a comparison of the adsorption curves for each metal ion between the experimental data and the calculated values relative to the pH conditions when lead ions were mixed with calcium ions. From the results, the adsorption model considering two metal ions predicted the adsorption phenomena of the lead and calcium ions relatively well. The difference in the adsorption capacities between the lead and calcium ions was due to selectivity, which then affected the equilibrium constants. Therefore, it would appear that the selectivity for the lead ions was stronger than that for the calcium ions, because the value of  $K_{a,COOH}$  for the lead ion was much higher than



**Fig. 7.** Comparison of adsorption curves for each metal ion from experimental data and calculated values relative to pH conditions, when lead ions coexist with calcium ions.

that for the calcium ion. From these results, it was concluded that the prediction of multi-metal adsorption phenomena using metal equilibrium constants, which were obtained from the presently used model equation, was effective.

## CONCLUSIONS

The biosorption phenomenon using alginic acid was mathematically modeled using an ion-exchange mechanism involving binary adsorption sites. By matching the isothermal experimental data and the nonlinear regression method, each equilibrium constant between the functional groups in the alginic acid and the metal ions was estimated. It was found that the equilibrium constant for the lead ion of the carboxyl groups ( $K_{a,COOH}$ ) was much higher than that of the hydroxyl groups ( $K_{a,OH}$ ), suggesting that the overall adsorption phenomenon of alginic acid was mainly due to the carboxyl groups; however, the heavy-metal adsorption mechanism by the hydroxyl groups should not be ignored. The equilibrium constants for each functional group in the alginic acid were successfully applied to predicting the lead adsorption capacity of  $\alpha$ -cellulose, thus demonstrating a potential application of adsorption capacity prediction to many polysaccharides. Furthermore, an extended ion-exchange model involving two metal ions predicted the adsorption phenomena of lead and calcium ions relatively well.

The modeling method proposed in this study predicts metal removal relative to changing operating conditions, such as the pH and metal ion concentration. It can also be useful in simulating the performance of various adsorbents and multi-metal systems.

## Acknowledgments

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## Appendix

The biosorption model considering two adsorption sites of alginic acid can be extended to a multi-metal ions system. Assuming there exist  $n$  metal species, the total adsorption capacity ( $Q$ ) given as a summation of each  $n$ -single metal species, which do not coexist with other metal ions, can be expressed as in equation (9).

$$Q = \frac{\left[ 4Q_{\text{COOH}} \sum_{k=1}^n (K_{e,k\text{COOH}} C_{M,k}) + C_{\text{H}}^2 \right] - C_{\text{H}} \sqrt{C_{\text{H}}^2 + 8Q_{\text{COOH}} \sum_{k=1}^n (K_{e,k\text{COOH}} C_{M,k})}}{8 \sum_{k=1}^n (K_{e,k\text{COOH}} C_{M,k})} + \frac{\left[ 4Q_{\text{OH}} \sum_{k=1}^n (K_{e,k\text{OH}} C_{M,k}) + C_{\text{H}}^2 \right] - C_{\text{H}} \sqrt{C_{\text{H}}^2 + 8Q_{\text{OH}} \sum_{k=1}^n (K_{e,k\text{OH}} C_{M,k})}}{8 \sum_{k=1}^n (K_{e,k\text{OH}} C_{M,k})} \quad (9)$$

where  $f_{M,k}$  is the mole fraction, which is defined as the ratio of the adsorption capacity of the  $k$ -th metal species only

( $q_{M,k}$ ) over the total adsorption capacity ( $Q$ ), and the value can be given as in equation (10).

$$f_{M,k} = \frac{q_{M,k}}{Q} = \frac{1}{1 + \frac{\sum_{j=1, j \neq k}^n K_{e,j\text{COOH}} K_{e,j\text{OH}} C_{M,j}^2}{K_{e,k\text{COOH}} K_{e,k\text{OH}} C_{M,k}^2}} \quad (10)$$

In the above equation (10), the equilibrium constant between each functional group and each  $n$ -single metal species can be estimated from equation (8). Therefore, the adsorption capacity of the  $k$ -th metal ion, denoted as  $Mq_{M,k}$  when  $n$ -metal ions are mixed, can be calculated as in equation (11).

$$Mq_{M,k} = q_{M,k} f_{M,k} = q_{M,k} = \frac{1}{1 + \frac{\sum_{j=1, j \neq k}^n K_{e,j\text{COOH}} K_{e,j\text{OH}} C_{M,j}^2}{K_{e,k\text{COOH}} K_{e,k\text{OH}} C_{M,k}^2}} \quad (11)$$

If two metal ions are considered, the adsorption capacity for the metal-1 ion in a mixed metal system ( $Mq_{M1}$ ) can be calculated as in equation (12).

$$Mq_{M1} = q_{M1} f_{M1} = \frac{1}{1 + \frac{K_{e,2\text{COOH}} K_{e,2\text{OH}} C_{M2}^2}{K_{e,1\text{COOH}} K_{e,1\text{OH}} C_{M1}^2}} \quad (12)$$