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MODELING OF BIOSORPTION BY MARINE BROWN *Undaria pinnatifida* BASED ON SURFACE COMPLEXATION MECHANISM

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Abstract – Biosorption is one of the useful phenomena that can be used for removal of heavy metals in wastewater. To date, many researchers have used Langmuir or Freundlich isotherms to quantify sorption capacity; however, these isotherms lack physical meaning for the adsorption mechanism, and parameters in isotherm equations must be obtained by experiment whenever environmental conditions change. We used a surface complexation model that considered adsorption phenomena as chemical reactions in solution. Using titration, we determined a surface active site and equilibrium constants for binding parameters. This model can predict the pH effect on adsorption of Pb and could be applied to explain multi-ion and other competent chemicals such as EDTA.

Key words: Biosorption, Surface Complexation Mechanism, Heavy Metal Removal, Mathematical Modeling, Wastewater Treatment, Brown Algae

INTRODUCTION

Aqueous effluents from many industries such as mining and metal plating contain dissolved heavy metals, which, if discharged without adequate treatment, may have an adverse impact on the environment. As result, many processes have been studied for heavy metal removal from wastewater [Kim et al., 1996; Kim and Cho, 1997]. Recently, biosorption has been investigated to treat heavy metals in wastewater.

It is widely recognized that the surface of algae can bind various heavy metals from the surrounding environment [Volesky and Holan, 1995]. Several studies in which marine algae were used for removal of heavy metals from wastewater have been reported [Khummongkol et al., 1982; Greene et al., 1986; Kim et al., 1995]. The adsorption of heavy metals on aquatic organisms is frequently dependent on the species of the metallic ion, the pH and varieties of the complexation agents in natural water [Holan and Volesky, 1994; Chen et al., 1996]. Many researchers have used various types of isotherm adsorption equations, such as the Langmuir or Freundlich, for quantitative evaluation of metal uptake capacity [Babich and Stotzky, 1980; Sherbert, 1978]. However, these adsorption equations cannot explain the changes in uptake capacity when other metal ions exist or the pH changes. Furthermore, parameters used in these isotherm equations must be determined through experiments. Understanding an interaction mechanism of metal ions with the surface of algae is essential to build an intrinsic model capable of explaining the pH and multi-ion effects.

The major constituent of *Undaria pinnatifida* responsible for heavy metal removal is known to be alginic acid [Kim et al., 1995], which can be regarded as weak acid. Alginic acid, a polysaccharide, exists in the outer layer of marine algae. It seems to play a considerable role in ion fixation and particularly in facilitating the exchange of trace elements between solid organic particles and organisms [Buffle, 1988]. Alginic acid has carboxyl groups and hydroxyl groups. These acid/base groups which are present as side chains in polysaccharides are capable of contributing the metal binding capacity of algae.

We can suppose that the amphoteric property of alginic acid is a key to explaining metal uptake because alginic acid exists in the outer layer of the cell wall, which is known to actually be an impermeable barrier for heavy metals [Buffle, 1988]. Surface complexation models are capable of simulating the experimentally observed acid-base titration properties of metal-oxide minerals [Hohl and Stumm, 1976; Park and Huang, 1987]. In this study, we employed a surface complexation model, as well as acid-base titration properties of algal cells, to investigate the adsorption of lead on algal cell walls.

MATERIALS AND METHODS

Samples of brown alga *Undaria pinnatifida* were washed several times with deionized and distilled water and freeze-dried. Dried biomass was ground in a blender for 20 min, filtered through No. 35 sieve (500 μm) and stored in 4 °C refrigerator for further study.

1. Surface Area Measurement

The moisture-free marine algae prepared as above were placed in a surface area analyzer (Quantasorb Model QS-11, Quantachrone, USA) and the surface area was measured. Nitrogen gas was used as adsorbate molecules.

2. Titration of *Undaria pinnatifida*

A procedure suggested by Huang [Huang et al., 1978] was

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employed for the titration of the biomass. (1) Powdered biomass was transferred to a 2 L container filled with deionized and distilled water and purged with nitrogen gas for 10 minutes. (2) After purging, the biomass was allowed to settle down. (3) Supernatant was decanted and the container was refilled with deionized and distilled water. (4) Steps (1) through (3) were repeated until the conductivity of decanted supernatant approached that of deionized and distilled water. (5) The biomass contained in 2 L containers was divided into three 500 mL containers, and the ionic strengths of each container were adjusted to 10^{-4}, 10^{-2} and 10^{0} M of NaCl, respectively. (6) Samples in three 500 mL containers were distributed to a set of 15 bottles, each bottle containing 30 mL of the sample. (7) From No. 1 to No. 7 bottles, 0.05×No. mL aliquot of 0.1 M HCl was added, respectively. From No. 9 to No. 15 bottles, 0.05×(No. −8) ml of aliquot of 0.1 M NaOH was added, respectively. (8) Every bottle was incubated in a shaker for 24 hours at room temperature and the pH of every sample was recorded.

3. Measurement of Zeta-potential

Biomass was prepared as stated in 'titration of *Undaria pinnatifida*' through (1) and (3). Zeta-potential was measured with a Zeta potential analyzer (Zeta-meter, USA).

4. Adsorption in Single Metal System

Biomass was prepared as stated in 'titration of *Undaria pinnatifida*' through (1) and (3). Ionic strength was adjusted to 1×10^{-3} M. Biomass concentration was 2.0 g/L, and 30 mL suspended biomass was distributed to each plastic bottle. Various quantities of 0.1 M NaOH or 0.1 M HNO_3 were added for pH adjustment; 100 μL of lead nitrate (10^{-3} M) was added to each of the bottles. The bottles were placed in an incubation shaker for 24 hours at 20 °C. The concentration of metal in supernatant was analyzed by atomic absorption spectroscopy (Jarell-Ash, Japan) after centrifugation at 3,000 g.

RESULTS AND DISCUSSION

1. Acid-base Properties of the Algae

Surface acidity of the marine brown alga was measured by acid-base titration [Huang et al., 1978]. Algal cells contain various functional groups such as carboxyl, amine, hydroxyl and the functional side chain of amino acid residues, such as histidine, cysteine, aspartic acid and glutamic acid [Buffle, 1988]. The amphoteric properties of amino acid and other functional groups on the surface of algal cells can be simplified by the following equations:

$$RH_2^+ \leftrightarrow RH + H^+ \quad K_{a1} \tag{1}$$

$$RH \leftrightarrow R^- + H^+ \quad K_{a2} \tag{2}$$

K_{a1} and K_{a2} are equilibrium constants of Eqs. (1) and (2), RH_2^+, RH and R^- represent the positive sites, neutral and negative surface sites, respectively and RH_2^+ means a more acidic group than RH, but RH_2^+ and RH are not necessarily the same groups. The total number of surface active sites, X_T, is therefore the sum of these three groups.

$$X_T = \{RH_2^+\} + \{RH\} + \{R^-\} \tag{3}$$

Potentiometric titration provides a measure of the sequential binding of protons by various functional groups in the surface of the algae. The surface charge density can be calculated from the following charge balance equations.

$$(C_B - C_A + [H^+] - [OH^-])/S = \sigma/F \tag{4}$$

C_B and C_A are concentrations of strong base and strong acid consumed by the surface with reference to pH_{zpc}, respectively, and S is the total surface area of the algal cells, F is a Faraday constant (96,500 C/mole), and σ is surface charge.

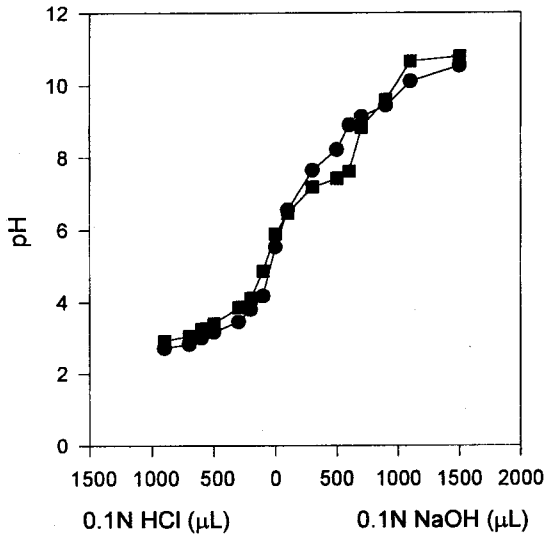

Fig. 1. Titration curve for natural *U. pinnatifida*.
●: in 0.001 M NaCl, ■: in 0.1 M NaCl

Fig. 1 shows the titration curve of *Undaria pinnatifida* cells in NaCl with 0.1 N NaOH and 0.1 N HCl. The intersection point of titration curves with different ionic strength was pH 6.0. This point is pH_{zpc} at which summation of the surface charge of biomass equals zero. This value was somewhat higher than that measured with a Zeta-meter (pH_{zpc}=3.0). Other researchers also reported the same discrepancy between the two methods. Hiemenz [1977] noted that this difference resulted from the fact that electrophoresis measured the net charge inside the surface of the shear plane, while titration binds the H^+ or OH^- onto the surface of the molecule. One of the major cellular components of *Undaria pinnatifida* is alginic acid [30 (w/w) %]. This alginic acid is known to be cross-linked by Ca^{2+} which results in an egg-box shape in the cell wall structure [Kuyucak and Volesky, 1989]. The presence of trace metals such as Ca^{2+} on the surface of the cell may be partially responsible for the difference between pH_{zpc} determined by using titration and pH_{zpc} determined by using a Zeta-meter.

Fig. 2 shows the schematic cell surface structure. The outer layer of the cell is made up of polysaccharides with free carboxylic acid. The Transmission Electron Spectroscopy (TEM, Jeol, Japan) photograph of algal cells apparently shows the binding of lead ions occurring at the outer layer of the cell (Fig. 3). The electrodense part could be thought to be lead binding sites. This photograph indicates that no lead penetrated into the cell interior and a certain depth of lead-bound layer exists on the cell wall. It is similar to that of Al_2O_3 or silica surface bound with lead ions. Gouy-Chapman diffuse lay-

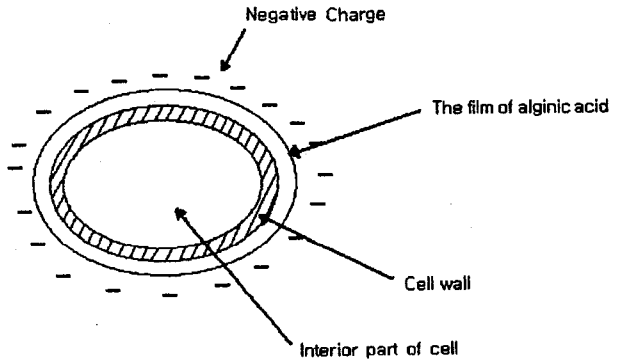

Fig. 2. Schematic diagram of the structure of *U. pinnatifida*.

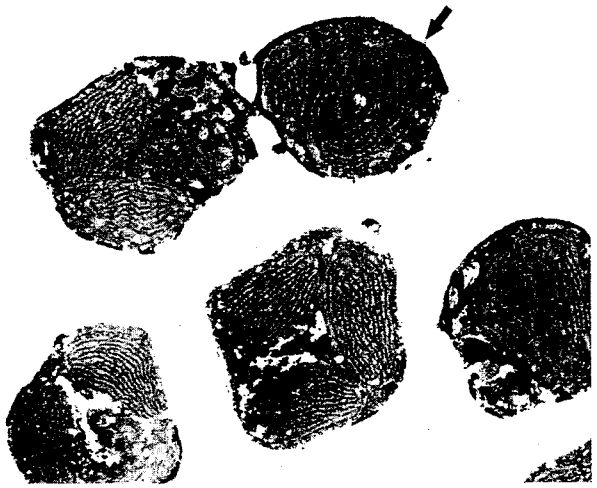

Fig. 3. TEM photograph of *U. pinnatifida* cell wall with Pb Arrow denotes lead-adsorption sites (magnification× 10,000).

er theory [Buffle, 1988] can thus be applied for calculating the surface potential, ϕ.

In the Gouy-Chapman model, the surface potential can be calculated by the following Eq. (5).

$$\phi = \frac{2RT}{ZF}\,\mathrm{Sinh}^{-1}\sqrt{\frac{\pi\sigma}{2RT\varepsilon I}} \tag{5}$$

R, T, I, ε, and Z are the gas constant, the absolute temperature, the ionic strength, the dielectric constant, and the valence of inert electrolyte ions, respectively. According to the Boltzmann equation, the concentration of hydrogen ions in the immediate proximity of the charged surface, H^+, is related to that of the bulk solution $[H^+]$ by Eq. (6).

$$H^+ = [H^+]\exp\left(\frac{-F\phi}{RT}\right) \tag{6}$$

At pH < pH_{zpc}, the surface is positively charged, therefore

$$X_T=\{RH_2^+\}+\{RH\} \tag{7}$$

At pH > pH_{zpc}, the surface is negatively charged, therefore

$$X_T=\{RH\}+\{R^-\} \tag{8}$$

$\{RH^{2+}\}$ and $\{R^-\}$ can be determined from the potentiometric titration by calculating surface charge.

$$\{RH_2^+\}=\sigma^+/F \tag{9}$$

$$\{R^-\}=\sigma^-/F \tag{10}$$

By substituting the above Eqs. into equations. (1) and (2), the following equations can be derived for parameter estimation such as K_{a1}, K_{a2} and X_T.

$$\frac{1}{[H^+]\exp\left(\frac{-F\phi}{RT}\right)} = \frac{\{X_T\}}{\{\sigma^+\}K_{a1}} - \frac{1}{K_{a1}} \tag{11}$$

$$[H^+]\exp\left(\frac{-F\phi}{RT}\right) = \frac{\{X_T\}K_{a2}}{\{\sigma^-\}} - K_{a2} \tag{12}$$

A plot of $1/\{H^+\}$ versus $1/\sigma^+$ for the positive surface and of $\{H^+\}$ versus $1/\sigma^-$ for the negative surface will yield intercepts and slopes which allow the determination of the intrinsic acidity constants, K_{a1}, and K_{a2} and X_T. Fig. 4 (a, b) shows the plot for determining the intrinsic acidity constants. Fig. 5 shows the potentiometric and conductivity titration curve of protonated *Undaria pinnatifida* biomass. Free protons disso-

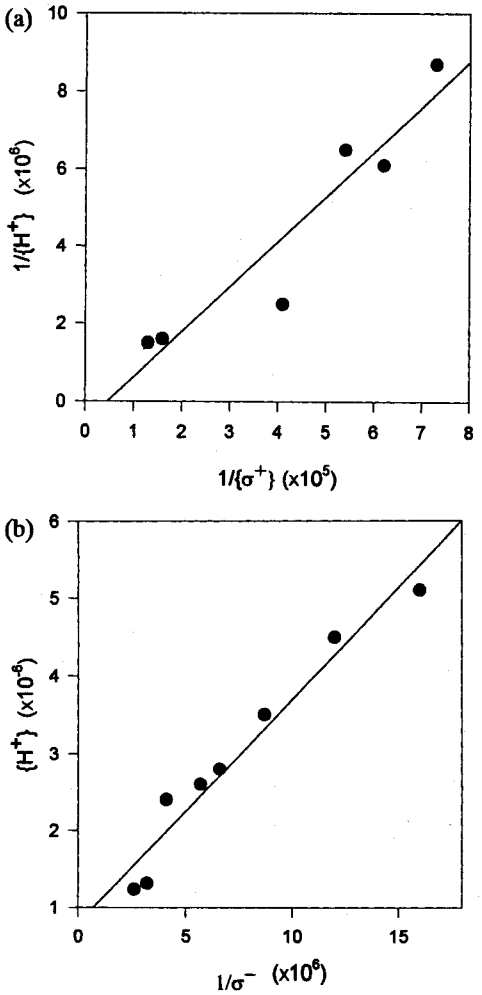

Fig. 4. Regression plot for determining binding parameters. (a) for binding parameter, K_{a1}, (b) for binding parameter, K_{a2}

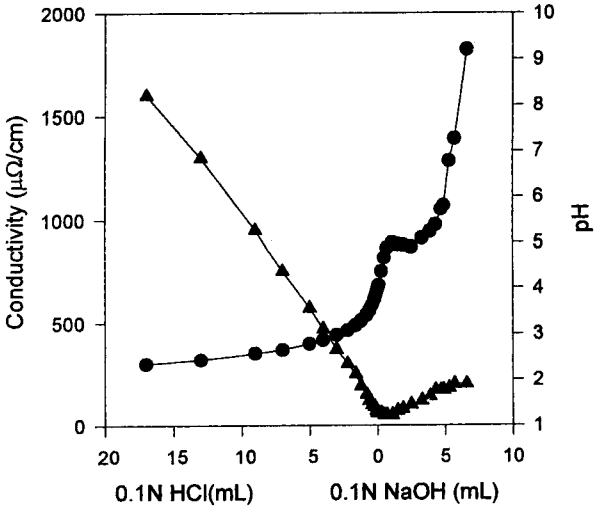

Fig. 5. Conductivity titration for evaluation of total ion exchange capacity.
strong acid groups=1 mmol/g, weak acid groups=2.5 mmol/g, ▲: conductivity, ●: pH

ciated from acidic groups bring the characteristic decrease in conductivity. A known amount of strong acid (HCl) was added to the suspension before titration to distinguish between the strong acids and weak ones, as suggested by Fourest and Volesky [Fourest and Volesky, 1996]. The intersection between the linearly decreasing portion and slowly increasing point yielded a quantitative number of strong acidic groups because this point means the titration point of a weak acidic group. As shown in Table 1, this value approached about 1.0 mmol/g dry wt. When excess sodium hydroxide was added to the suspension, the conductivity started to increase because all the weak acidic groups had been neutralized. This value approached about 2.5 mmol/g dry wt. So the total number of acid groups approached about 3.5 mmol/g dry wt. This number is very close to the number determined by using other methods (X_T=3.7 mmol/g dry wt). Fourest and Volesky [Fourest and Volesky, 1996] reported similar results and indicated that strong acidic groups and weak acidic groups were believed to be sulfate groups of fucoidan (a kind of polysaccharide found in marine algae) and carboxyl group of alginic acid, respectively.

Table 1 shows a comparison of surface acidity constants with other reports. Deprotonation can easily occur for a solid with low pKa value.

The proton carboxylic acid dissociates at pH 3.5 (pKa_1), which is similar to that of terminal carboxyl groups of ribonuclease [Buffle, 1988]. Primary amino groups of ribonuclease showed about pK_{a2} 7.0-7.8, and secondary amine groups of ribonuclease showed pKa_2 10.2 [Buffle, 1988]. Thus, the second acidity constant (pKa_2 8.8) obtained in this study represents the proton transfer of primary and secondary amino groups because it is between pKa_2 7.0 and pKa_2 10.2. The pH of zero, pH_{zpc}, can be analytically calculated from Eq. (13).

$$pH_{zpc} = \frac{(pKa_1 + pKa_2)}{2} \quad (13)$$

The value obtained in this way (pH_{zpc}=6.15) is very close to that obtained from the intersection point (pH_{zpc}=6.0) of the two titration curves. The maximum titratable proton exchange capacity of the algal surface groups was found to be 1.10 mol/kg-algal-dry-wt.

Table 1. The comparison of acidity and surface active site between *Undaria pinnatifida* biomass and inorganic material, ✳-Al_2O_3 [Hohl and Stumm, 1976; Park and Huang, 1987]

	Protonated *Undaria pinnatifida*	γ-Al_2O_3
pK_1	3.5	7.7
pK_2	8.8	9.3
X_T	3.7 mmol/g-dry-wt	1.24 mmol/g-dry-wt
pH_{zpc}	6.0	9.3

2. Displacement of Titration Curves

The interaction of Pb^{2+} with algal cell surface is reflected in the shift in the titration curve as shown in Fig. 6. This shift at a given pH is related to the extent of association of Pb^{2+} to the binding groups of the cell surface [Kim et al., 1995]. As shown in Fig. 7, an average of 1.7 moles of protons were displaced when 1.0 mole of Pb^{2+} adsorbed. Park and Huang

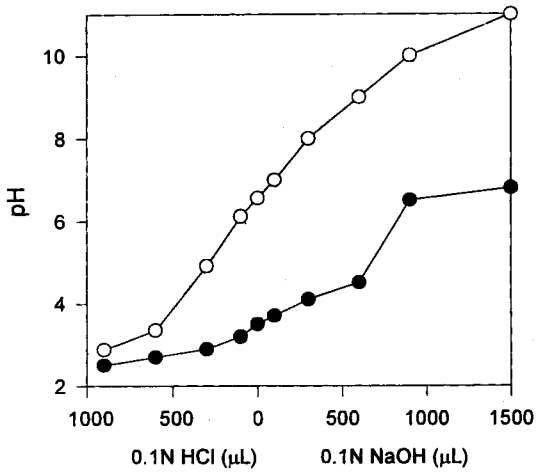

Fig. 6. The change of titration curve when Pb ions were sorbed.
○: without Pb, ●: with Pb

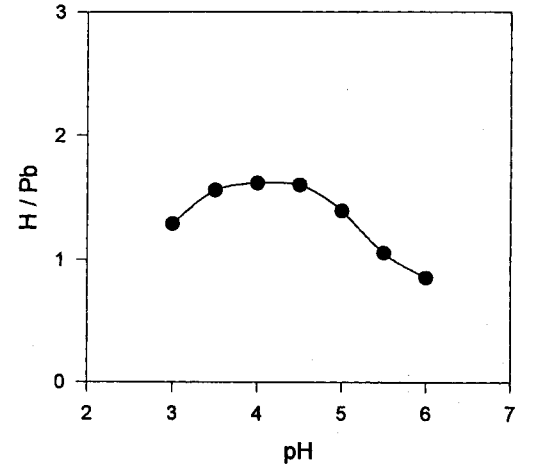

Fig. 7. Stoichiometric number determination for proton and Pb ions exchange.

[1987] determined a 1 : 1 ratio for the adsorption of heavy metals onto the hydrous CdS(s) surface. At a low pH region (pH <4.0), most binding groups are RH_2^+ or RH. When these binding groups form 1.0 mole of complex with lead ions, 2.0 moles of protons will be released. If other kinds of metals, such as Ca^{2+}, occupy the surface binding sites, protons will not be released even when lead ions are adsorbed on those sites. Thus a lower ratio of hydrogen to lead may be calculated than the theoretical ratio (2 : 1). Above pH 4.5, the ratio gradually decreased. In this model, we consider only one species of metal ions (Pb^{2+}), but other types of metals such $PbOH^+$, $Pb(OH)_2$ can be formed at high pH regions. If these types of metal are adsorbed on the cell surface, fewer protons will be released.

3. Metal Complexation Model

$$RH_2^+ + M^{2+} \leftrightarrow RM^+ + 2H^+ \qquad K_1 \tag{14}$$

$$2RH + M^{2+} \leftrightarrow R_2M + 2H^+ \qquad K_2 \tag{15}$$

$$2R^- + M^{2+} \leftrightarrow R_2M \qquad K_3 \tag{16}$$

If the pH is low enough not to form metal hydroxide precipitate (pH<6.0), the major metal species will be bare metal. Therefore, the total adsorption capacity was set to be equal to the sum of RM^+ and R_2M.

$$Q_T = \{RM^+\} + \{R_2M\} \tag{17}$$

If the stoichiometry between hydrogen and metal ion is 1: 2, the concentration of the surface functional groups RH_2^+, RH and R^- can be determined from the following formula.

$$\{RH_2^+\} = \{X_T - Q_T\}S_+ \tag{18}$$

$$\{RH\} = \{X_T - 2Q_T\}S_0 \tag{19}$$

$$\{RH^-\} = \{X_T - 2Q_T\}S_- \tag{20}$$

$$Q_T = [M^{2+}]\left(\frac{K_1\{RH_2^+\}}{[H^+]^2} + \frac{K_2\{RH\}^2}{[H^+]^2} + K_3\{R^-\}^2\right) \tag{21}$$

S_+, S_0 and S_- are the fractions of the positive, neutral and negative groups, respectively. The terms can be determined by using the following formula.

$$S_- = [H^+]^2/D \tag{22}$$

$$S_0 = K_{a1}/D \tag{23}$$

$$S_- = K_{a1}K_{a2}/D \tag{24}$$

$$D = [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}$$

Since the metal removal by basic groups can be eliminated in the region where pH is less than pH_{zpc}, Q_T can be rewritten as Eq. (25).

$$Q_T = [M^{2+}]\left(\frac{K_1\{RH_2^+\}}{[H^+]^2} + \frac{K_2\{RH\}^2}{[H^+]^2}\right) \tag{25}$$

K_1 and K_2 were determined by a nonlinear least-square method using MINEQL+[15]. As shown in Fig. 8, parameter values K_1 and K_2 were estimated by linear regression. Estimated

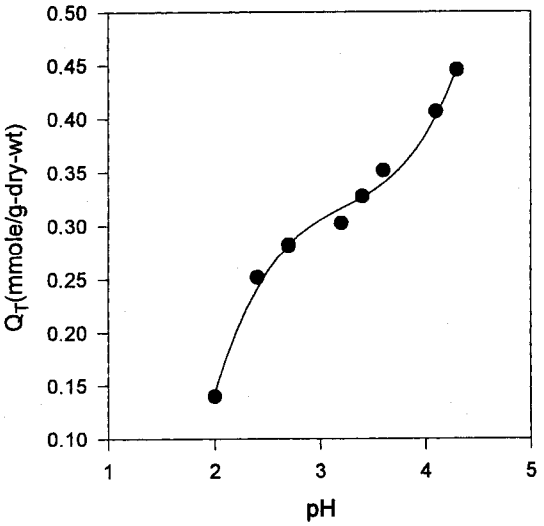

Fig. 8. Binding parameter determination between Pb ions and cell wall binding groups using MINEQL+.

values of K_1 and K_2 were 4.17×10^{-3} and 6.30×10^{-7}, respectively.

The following equation for Q_T can be derived by inserting Eqs. (18), (19) and (20) into Eq. (25).

$$4HK_2S_0^2Q_T^2 - (1 + 4HK_2S_0^2X_T + HK_1S_+)Q_T + HK_2S_0^2X_T^2 + HK_1X_TS_+ = 0 \tag{26}$$
$$H = [M^{2+}]/[H^+]^2$$

By solving Eq. (26), Eq. (27) for Q_T can be obtained.

$$Q_T = \frac{A - \sqrt{A^2 - 16K_2S_0^2X_T(K_1S_+ + K_2S_0^2X_T)}}{8K_2S_0^2} \tag{27}$$
$$A = 4K_2S_0^2X_T + K_1S_+ + [H^+]^2/[M^{2+}]$$

The surface complex model used here differs from the ion-exchange model because it considers the pH dependence of the surface concentration of the functional groups. Experimental results were compared with the adsorption equilibria cal-

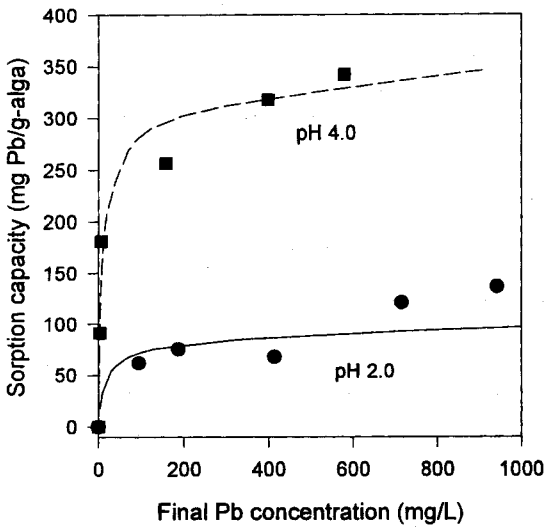

Fig. 9. Comparison of sorption curve between experimental data and calculated values for different pH conditions.

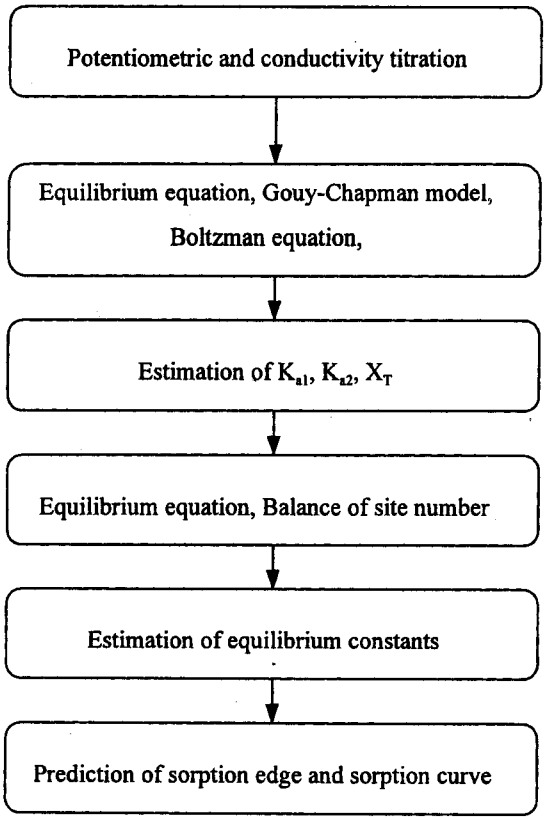

Fig. 10. Schematic diagram for prediction of sorption characteristics.

culated with the constants given above, and they agree well as shown in Fig. 9. The overall procedure is shown in Fig. 10.

This equation includes the pH effect on sorption of metal ions as well as the metal ion concentration effect. Since most sorption equations such as the Langmuir isothermal equation or Freundlich equation include terms representing only metal ion concentration, these equations are not able to predict the pH effect on sorption metal ions. Furthermore, since the equation developed in the present study includes a term representing the complexation strength between a specific binding site and metal ions, it may be possible to predict the sorption capacity even after the characteristics of the sorbent are changed. For example, when other chemical chelating groups are introduced to the sorbent, this equation can easily include the term corresponding to this additional binding group in predicting sorption capacity. Also, when multi ions are present in wastewater, as is usually the case, this model can include terms predicting adsorption capacity of each ion and the sorption edge curve. This prediction can help us to determine the optimal operating conditions, including pH, for selective adsorption of heavy metals. But this model does not consider the effect of precipitation in alkaline conditions. The expansion and applications of the model developed herein are left for further study.

NOMENCLATURE

C_A : strong acid concentration consumed by the surface with reference to pH_{zpc} [mole]
C_B : strong base concentration consumed by the surface with reference to pH_{zpc} [mole]
F : faraday constant [96,500 C/mole]
K_{a1} : equilibrium constant for the first ionization reaction
K_{a2} : equilibrium constant for the second ionization reaction
K_1 : equilibrium constant for metal adsorption reaction (14)
K_2 : equilibrium constant for metal adsorption reaction (15)
K_3 : equilibrium constant for metal adsorption reaction (16)
I : ionic strength [M]
M : metal concentration
pH_{zpc} : pH at zero potential charge
Q_T : total adsorption capacity
R : gas constant [J K^{-1} mol^{-1}]
R^- : functional group with negative charge
RH : functional group with zero charge
RH_2^+ : function group with positive charge
S : total surface area of the algal cells [m^2]
S_+ : fraction of the positive groups
S_0 : fraction of the neutral groups
S_- : fraction of the negative groups
T : absolute temperature [K]
X_T : total adsorption site number

Greek Letters

ε : dielectric constant
σ : surface charge [C/m^2]
ϕ : surface potential [V]

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