Biosorption of heavy metals onto nonliving
*Laminaria japonica*

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**ABSTRACT**

In this paper, study of the biosorption of Cd$^{2+}$ and Pb$^{2+}$ by nonliving *Laminaria japonica* in a batch adsorption system is described. The content of acidic sites and the dissociation constant of carboxylic acid functional groups (metal-binding site) of *L. japonica* were experimentally determined by conductometric and potentiometric titrations and theoretically predicated by using monodentate and bidentate binding models. The models are based on the monodentate or bidentate binding reactions of bivalent metal ions to acidic sites. The acidic site content and carboxylic acid dissociation constants determined are 1.25 and 0.18 mmol L$^{-1}$, respectively. The results showed that the bidentate adsorption model fits well the biosorption of bivalent metal ions onto *L. japonica* with the bidentate binding constants for Cd$^{2+}$ and Pb$^{2+}$ being $5.72 \times 10^{3}$ and $6.24 \times 10^{4}$ L mol$^{-1}$, respectively. The adsorption process of *L. japonica* followed the pseudo-second-order kinetics.

**Key words** | biosorption, cadmium, *Laminaria japonica*, lead

**INTRODUCTION**

Toxic heavy metals have seriously polluted the water environment (Acharya et al. 2009; Saurav & Kannabiran 2010). Although they can be adsorbed and removed from aqueous solutions using various approaches such as chemical precipitation, chelating resins, membrane technology and ion exchange with extremely high efficiency (Aldrich & Feng 2000; Reddad et al. 2002; Kedar et al. 2006), these absorbents are often costly, and in many cases, not abundantly available in nature. Therefore, naturally available, nonhazardous biosorbents that are highly effective and generate low volumes of secondary nonhazardous waste have attracted greater attention (Bailey et al. 1999; Hashim & Chu 2004; Dhruv & Meenakshi 2005).

Biomaterials otherwise known as biomass have a high capacity and selectivity for assimilating specific heavy metals (Zübeidey et al. 2009; Fella et al. 2011) Biosorption, which uses the ability of biomass, is an emerging, effective and potential technology for the removal of heavy metals from wastewaters (Ozgür et al. 2008; Ali et al. 2009; Walter et al. 2011). The main advantages of this technique are the reusability of biomaterial, low material cost, easy handling, and no secondary hazards (Ahmet et al. 2008; Ozgür et al. 2008).

Among the various available biological materials, marine algae biomass has been reported to present high metal binding capacities. A number of algae species (*Posidonia oceanica*, *Chlamydomonas reinhardtii*, *Ulva* sp., *Hylocomium splendens*, *Gelidium*, and *Kjellmaniella crassiforia*), which present high capacities for heavy metal removal, were investigated in several studies and showed varying removal efficiencies, biosorption characteristics and mechanisms (Ilhami et al. 2005; Suzuki et al. 2005; Ahmet & Mustafa 2008; Ahmet et al. 2008; Mohammad et al. 2009). While algal materials have been widely studied for metal biosorption, the potential of brown seaweeds such as *Laminaria japonica* has been notably under-researched (Mohammad et al. 2009). Studies on metal adsorption by *L. japonica* have also been accomplished (Fan et al. 2008; Su et al. 2009; Qin et al. 2009); however, as far as the authors are aware, there is no further investigation reporting on the acid-base properties and biosorption mechanism of *L. japonica*. In addition, this biomaterial was chosen as the biosorbent in this study due to its abundant availability and thus low cost (Suzuki et al. 2005).

In this study, we investigated the use of nonliving *L. japonica* biomass for the removal of Cd$^{2+}$ and Pb$^{2+}$ by
measuring the acid-dissociation characteristics of its acidic sites using potentiometric and conductometric titrations, discussed its biosorption mechanism for Cd\(^{2+}\) binding using the metal-binding model proposed by Seki & Suzuki (1998), and explored the adsorption kinetics of metal ions to composite biosorbents.

**MATERIALS AND METHODS**

**Materials**

Cadmium nitrate, lead nitrate, sodium nitrate and sodium alginate were obtained from Wako Pure Chemical Industries (Japan). All chemicals used in this study were of analytical grade, and solutions were prepared using deionized and distilled water. To adjust pH, 0.1 or 1 M HCl and NaOH solutions were used. A sun-dried nontreated *L. japonica* sample was obtained from Hokkaido, Japan. The algae were washed with distilled water, and dried at 60 °C for 2 days. Then the algae were cut into practical sizes (ca. 2 × 2 cm to ca. 10 × 10 cm). The fragments were further stored in a desiccator.

**Conductometric titration of algae**

The total number of acidic sites in a given amount of *L. japonica* was determined by conductometric titrations (Liang et al. 1980). For this purpose, algae fragments were suspended in 0.3 L of 0.1 M NaNO\(_3\) at 16 °C under magnetic stirring. To eliminate CO\(_2\), N\(_2\) gas was continuously bubbled through the system. After reaching thermal equilibrium at 16 °C, the suspension was titrated with a volumetric standard HNO\(_3\) (0.1 M) solution and its conductivity was measured with a conductometer (TOA Digital Conductometer CM-15A).

**Potentiometric titration of algae**

Potentiometric titration of algae was measured similarly to conductometric titration with the exception that 0.25 L of algae suspension was titrated in a standard HNO\(_3\) (0.1 M) solution, and then pH was measured by a pH meter (Orion Research 720A). The number of protonated acidic groups of algae was determined by the difference between the bulk proton concentrations in the presence and in the absence of algae.

**Biosorption equilibrium experiments**

A solution of NaNO\(_3\) (0.1 M) containing Cd(NO\(_3\))\(_2\) or Pb(NO\(_3\))\(_2\) in the range of \(1 \times 10^{-4} - 4 \times 10^{-4}\) mol L\(^{-1}\) was mixed with algae fragments in the range of 0.25–0.75 g L\(^{-1}\) in a shaker at 16 °C. After adjusting pH to the target value by HNO\(_3\), the solution was stirred till reaching adsorption equilibrium. Then the metal concentrations in the solution were measured using an atomic adsorption spectrophotometer (Hitachi A-1800). Aliquots (3 mL) of the solution were collected for the determination of residual cadmium or lead concentration. The amount of metal ion adsorbed by the algae was determined by the difference between the metal concentrations in the initial and the equilibrium states.

The amount of metal adsorbed at equilibrium by algae is calculated as:

\[
q_e \frac{(C_i - C_e)V}{w}
\]

where \(q_e\) (mol g\(^{-1}\) dry weight) is the amount of metal adsorbed at equilibrium, \(C_i\) (mol L\(^{-1}\)) is the initial concentration of metal in solution, \(C_e\) (mol L\(^{-1}\)) is the equilibrium concentration of metal in solution, \(V\) (L) is the volume of solution, and \(w\) is the dry weight of algae.

**Biosorption dynamical experiments**

The pH of the solution containing NaNO\(_3\) (0.1 M) and Cd(NO\(_3\))\(_2\) or Pb(NO\(_3\))\(_2\) in the range of \(1 \times 10^{-4} - 3 \times 10^{-4}\) mol L\(^{-1}\) was adjusted to 6.0. After reaching thermal equilibrium at 16 °C, 0.20 g L\(^{-1}\) *L. japonica* fragments were added into the solution under mechanical stirring. Aliquots (3 mL) of the solution were periodically collected to determine the concentrations of residual metal ions.

**RESULTS AND DISCUSSION**

**Acid-base properties of *L. japonica***

Assuming the major acidic sites on *L. japonica* are carboxylic groups of algicin acid (Liang et al. 1980), the acid dissociation reaction can be written as

\[
-COOH \leftrightarrow -COO^- + H^+
\]
The equilibrium number of protons bound to acidic sites, $q_H$ (mol g$^{-1}$), can be expressed as

$$q_H = N \frac{C_H}{K_H + C_H}$$

(3)

where $N$ (mol g$^{-1}$) is the number of carboxylic groups on *L. japonica*, $K_H$ (L mol$^{-1}$) is the acid dissociation constant, and $C_H$ (mol L$^{-1}$) is the equilibrium concentration of protons in solution. To determine the two constants, $N$ and $K_H$ in Equation (2), a nonlinear least-squares method was applied. The correlation coefficient ($r$) between the experimental and fitted values was 0.997. Figure 1(a) shows the total number of acidic sites in a given amount of *L. japonica* by the conductometric titration. The ordinate of the figure, $q_{HI}$, represents the equilibrium number of protons. The end point in the titration curves is the intersection of two straight lines. The content of the acidic sites on *L. japonica* determined from the titration curves is $1.25 \times 10^{-3}$ mol g$^{-1}$.

Figure 1(b) shows the dissociation characteristics of the acidic sites on *L. japonica* in acidic media measured by the potentiometric titration. The constants $N$ and $K_H$ for *L. japonica*, which best fit the experimental data (in Figure 1(b)), are $1.25 \times 10^{-3}$ mol g$^{-1}$ and $1.79 \times 10^{-4}$ (pK = 3.76), respectively. The solid line in Figure 1(b) represents the theoretical curve calculated from Equation (3) using the constants above. The total number of acidic sites calculated by Equation (3) is in good agreement with the number obtained from the conductometric titration, $1.25 \times 10^{-3}$ mol g$^{-1}$ *L. japonica*.

In comparison with the results described in other studies concerning the acid-base properties of brown seaweeds which were also measured by conductometric and potentiometric titrations, the content of acidic sites and the acid dissociation constant of *L. japonica* are almost the same as those of three other brown algae, $N = 0.87 \times 10^{-3}$ mol g$^{-1}$ (Macrocystis pyrifera), $N = 1.16 \times 10^{-3}$ mol g$^{-1}$ (Kjellmanniella crassifolia), and $N = 1.21 \times 10^{-3}$ mol g$^{-1}$ (Undaria pinnatifida) (Seki & Suzuki 1998), indicating that the acid dissociation constant determined by the potentiometric titration agrees well with the results reported and the seaweed *L. japonica* used in this study can be classified as a good adsorbent based on its $N$ and $K_H$.

**Biosorption of bivalent metal ions onto *L. japonica***

As previously detailed, the major acidic sites on brown algae are the carboxylic groups of alginic acid (Liang et al. 1980). There are two metal complexation models to describe the binding of carboxylic groups to bivalent metal ions; one is the monodentate binding model which can be written as

$$-S^- + M^{2+} \leftrightarrow SM^+; K_M$$

(4)

and the other is the bidentate binding model which can be written as

$$2(-S^-) + M^{2+} \leftrightarrow (-S)M^2; K_M$$

(5)

$M^{2+}$ in Equations (4) and (5) represents the bivalent metal ions, and $-S^-$ represents the metal binding site. The adsorption of bivalent metal ions to acidic sites fixed on a rigid plane, such as the sites on inorganic and microorganism adsorbents, usually fits the monodentate binding model (Suzuki et al. 1994; Seki et al. 1998). The equilibrium constant of the monodentate binding model, $K_M$ (L mol$^{-1}$) in Equation (4) is defined as:

$$K_M = \frac{\theta}{((1-\theta)\alpha)[C_M]}$$

(6)
or

\[
\theta = \frac{K_H K_M C_M}{K_H K_M C_M + K_H + C_H}
\]  

(7)

The bidentate binding model needs the acidic sites fixed on a flexible 3-D framework. Therefore, the binding of bivalent metal ions to biopolymers, such as alginic acid and humic acid, usually fits the bidentate binding model (Seki & Suzuki 1995; Seki et al. 2000; Seki et al. 2006). The equilibrium constant of the bidentate binding model, \(K_M\) (L mol\(^{-1}\)) in Equation (5) is defined as:

\[
K_M = \theta / [(1 - \theta) \alpha] C_M
\]  

(8)

or

\[
\theta = \left(P - \sqrt{P^2 - 4}\right) / 2
\]

\[
P = 2 + \frac{(K_H + C_H)^2}{K_M C_M R^2}
\]  

(9)

where \(\theta\) represents the fraction of carboxylic groups occupied by metal ions, \(\alpha\) is the degree of dissociation of carboxylic groups, and \(C_M\) (mmol L\(^{-1}\)) is the equilibrium concentration of metal in solution. The number of metal ions bound to 1 g of dry brown algae, \(X_e\) (mmol g\(^{-1}\)), can be expressed as

\[
X_e = N\theta / 2
\]  

(10)

Figure 2(a) shows the pH dependence of cadmium adsorption to \(L. japonica\) at 16 C. The ordinate, \(X_e\), is the equilibrium number of cadmium ions bound to \(L. japonica\). A nonlinear least-squares method was applied to find the cadmium-binding constants, \(K_M\), using Equations (9) and (10). In this calculation, the number of carboxylic groups, \(N\), and acid dissociation constant, \(K_H\), obtained from the conductometric titration and potentiometric titrations were used. The solid lines in Figure 2(a) represent the theoretical curves calculated from Equations (9) and (10) using the constants \(N\) and \(K_H\). The cadmium binding constant in the bidentate binding model was determined as 5.72 \(\times\) 10\(^5\) L mol\(^{-1}\). The correlation coefficient \((r)\) between the experimental and the fitted values was 0.987. For comparison, Equations (7) and (10) of the monodentate binding model were also applied to the experimental data in Figure 2(a).

The broken lines in Figure 2(a) represent the theoretical curves calculated from Equations (7) and (10) using the metal binding constant separately determined by a nonlinear least-squares method. The cadmium binding constant in the monodentate binding model was determined as 1.89 \(\times\) 10\(^{-2}\) L mol\(^{-1}\). The correlation coefficient \((r)\) between the experimental and the fitted values was 0.837. Figure 2(a) demonstrates a fair agreement of the experimental data with the bidentate binding model.

Figure 2(b) shows the pH dependence of lead adsorption to \(L. japonica\) at 16 C. The lead binding constant, \(K_M\), was determined in the same manner as that for cadmium adsorption, and the values are 6.28 \(\times\) 10\(^4\) L mol\(^{-1}\) and 1.06 \(\times\) 10\(^{-1}\) L mol\(^{-1}\) for bidentate and monodentate binding models respectively. The correlation coefficient in the bidentate binding model between the experimental and the fitted values was 0.972. Figure 2(b) also demonstrates a good agreement of the experimental data with the
bidentate binding model. These results indicate that the biosorption mechanism of bivalent metal ions onto *L. japonica* is the bidentate binding model.

**Kinetics of biosorption of metal ions onto *L. japonica***

Figures 3(a) and (b) show the time dependence of cadmium and lead adsorption onto *L. japonica* under the same experimental conditions. The ordinate, \( q (\text{mmol g}^{-1}) \), denotes the amount of cadmium and lead ions onto *L. japonica* at time \( t \) (min). The initial concentration of metal ions is indicated in the figures. The pseudo-second-order rate model, which had been applied to predict the rate constant of biosorption of metal ions to biosorbents (Ho & McKay 2000; Antunes et al. 2003), was applied to the rate process of cadmium and lead adsorption to *L. japonica* fragments.

The pseudo-second-order rate equation is described as

\[
d\left(\frac{q}{q_e}\right) = k(1 - \frac{q}{q_e})^2
\]  

or

\[
q = q_e \frac{kt}{1 + kt}
\]  

where \( k (\text{s}^{-1}) \) is the pseudo-second-order rate constant, and \( q_e (\text{mol g}^{-1}) \) is the equilibrium concentration of metal ions in solution.

A nonlinear least-squares method was applied to find the rate constant, \( k \), using Equation (12). The rate constants of lead and cadmium were determined as 0.014 and 0.010 min\(^{-1}\), respectively, at the ratio of 1.4. The solid lines in Figures 3(a) and (b) represent the theoretical curves calculated from Equation (12). Figures 3(a) and (b) demonstrate a good agreement of the experimental data with the theoretical curves. Therefore, the pseudo-second-order rate model was adapted for description of the rate process of cadmium and lead adsorption onto *L. japonica*.

The ionic diffusivities of lead and cadmium in aqueous medium at infinite dilution are \( 9.3 \times 10^{-6} \) and \( 7.2 \times 10^{-6} \) cm\(^2\) s\(^{-1}\), respectively, at the ratio of 1.3 (Gopala & Gupta 1982). In comparison with the ratio of adsorption rate constants, it suggests that ion diffusion plays a key role in the whole rate process of cadmium and lead adsorption.

**CONCLUSIONS**

The use of *L. japonica* seaweed biomass as a biosorbent for the uptake of heavy metals was investigated. Conductometric and potentiometric titrations were performed to determine the properties of carboxylic acid groups on *L. japonica*. The bidentate binding model was applicable to the biosorption of bivalent metal ions and suitable to describe metal binding data. The adsorption process of *L. japonica* followed the pseudo-second-order kinetics. The results of this study indicate that the biomass of *L. japonica* is suitable for the development of an efficient metal removal material for recovery of cadmium and lead from aqueous media.

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