

## Biosorption of heavy metals onto nonliving *Laminaria japonica*

Jun Xiao, Miyamoto Chikanori, Ke-Feng Yu, Seki Hideshi, Maruyama Hideo and Pei-Min He

### ABSTRACT

In this paper, study of the biosorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  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  $\text{L}^{-1}$ , 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  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  being  $5.72 \times 10^3$  and  $6.24 \times 10^4$   $\text{L mol}^{-1}$ , respectively. The adsorption process of *L. japonica* followed the pseudo-second-order kinetics.

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

Jun Xiao

Ke-Feng Yu

Pei-Min He (corresponding author)

College of Fisheries and Life Science,

Shanghai Ocean University,

Shanghai,

China

E-mail: pmhe@shou.edu.cn

Miyamoto Chikanori

Seki Hideshi

Maruyama Hideo

Graduate School of Fisheries Science,

Division of Marine Life Science,

Hokkaido University,

Japan

### 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 (Zübeyde *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 crassifolia*), which present high capacities for heavy metal removal, were investigated in several studies and showed varying removal efficiencies, biosorption characteristics and mechanisms (İlhami *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  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by

measuring the acid-dissociation characteristics of its acidic sites using potentiometric and conductometric titrations, discussed its biosorption mechanism for  $\text{Cd}^{2+}$  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  $\text{NaNO}_3$  at 16 °C under magnetic stirring. To eliminate  $\text{CO}_2$ ,  $\text{N}_2$  gas was continuously bubbled through the system. After reaching thermal equilibrium at 16 °C, the suspension was titrated with a volumetric standard  $\text{HNO}_3$  (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  $\text{HNO}_3$  (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  $\text{NaNO}_3$  (0.1 M) containing  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$  in the range of  $1 \times 10^{-4}$ – $4 \times 10^{-4}$  mol  $\text{L}^{-1}$  was mixed with algae fragments in the range of 0.25–0.75 g  $\text{L}^{-1}$  in a shaker at 16 °C. After adjusting pH to the target value by  $\text{HNO}_3$ , 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:

$$q_e = \frac{(C_i - C_e)V}{w} \quad (1)$$

where  $q_e$  (mol  $\text{g}^{-1}$  dry weight) is the amount of metal adsorbed at equilibrium,  $C_i$  (mol  $\text{L}^{-1}$ ) is the initial concentration of metal in solution,  $C_e$  (mol  $\text{L}^{-1}$ ) 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  $\text{NaNO}_3$  (0.1 M) and  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$  in the range of  $1 \times 10^{-4}$ – $3 \times 10^{-4}$  mol  $\text{L}^{-1}$  was adjusted to 6.0. After reaching thermal equilibrium at 16 °C, 0.20 g  $\text{L}^{-1}$  *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*

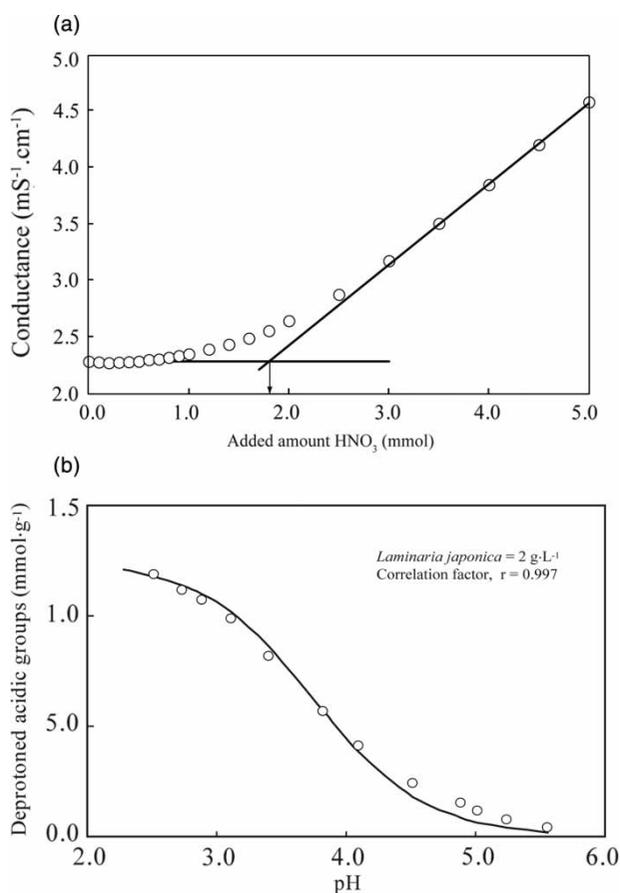
Assuming the major acidic sites on *L. japonica* are carboxylic groups of alginic acid (Liang et al. 1980), the acid dissociation reaction can be written as



The equilibrium number of protons bound to acidic sites,  $q_H$  ( $\text{mol g}^{-1}$ ), can be expressed as

$$q_H = N \frac{C_H}{K_H + C_H} \quad (3)$$

where  $N$  ( $\text{mol g}^{-1}$ ) is the number of carboxylic groups on *L. japonica*,  $K_H$  ( $\text{L mol}^{-1}$ ) is the acid dissociation constant, and  $C_H$  ( $\text{mol L}^{-1}$ ) 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,  $q_H$ , 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  $1.25 \times 10^{-3} \text{ mol g}^{-1}$ .



**Figure 1** | (a) Conductometric titration curve of 0.3 L solution containing 1.44 g *Laminaria japonica* at 16 °C. (b) Acid dissociation of 2.0 g L<sup>-1</sup> *Laminaria japonica* in 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub> at 16 °C.

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  $1.25 \times 10^{-3} \text{ mol g}^{-1}$  and  $1.79 \times 10^{-4}$  ( $\text{pK} = 3.76$ ), 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,  $1.25 \times 10^{-3} \text{ mol g}^{-1}$  *L. japonica*.

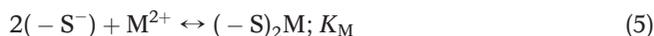
In comparison with the results described in other studies concerning the acid-base properties of brown seaweeds which were also measured by conductometric and potentiometric titrations the content of acidic sites and the acid dissociation constant of *L. japonica* are almost the same as those of three other brown algae,  $N = 0.87 \times 10^{-3} \text{ mol g}^{-1}$ ,  $\text{pK} = 3.14$  (*Macrocystis pyrifera*),  $N = 1.16 \times 10^{-3} \text{ mol g}^{-1}$ ,  $\text{pK} = 3.19$  (*Kjellmaniella crassifolia*), and  $N = 1.21 \times 10^{-3} \text{ mol g}^{-1}$ ,  $\text{pK} = 3.20$  (*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



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



$M^{2+}$  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,  $K_M$  ( $\text{L mol}^{-1}$ ) in Equation (4) is defined as:

$$K_M = \frac{\theta}{\{(1 - \theta)\alpha\}C_M} \quad (6)$$

or

$$\theta = \frac{K_H K_M C_M}{K_H K_M C_M + K_H + C_H} \quad (7)$$

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,  $K_M$  ( $L \cdot mol^{-1}$ ) in Equation (5) is defined as:

$$K_M = \frac{\theta}{\{(1 - \theta)\alpha\}^2 C_M} \quad (8)$$

or

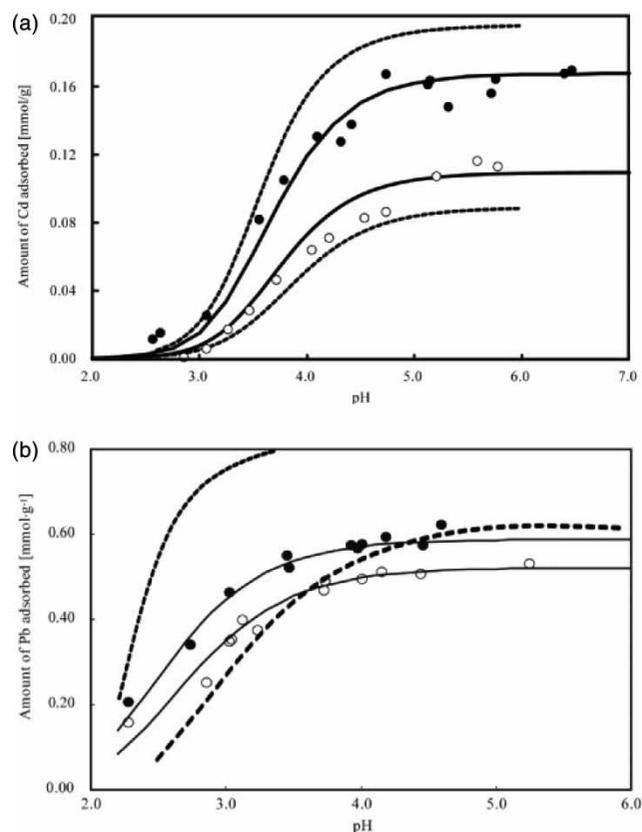
$$\theta = (P - \sqrt{P^2 - 4})/2$$

$$P = 2 + \frac{(K_H + C_H)^2}{K_M C_M K^2} \quad (9)$$

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

$$X_e = N\theta/2 \quad (10)$$

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  $5.72 \times 10^5 L \cdot mol^{-1}$ . 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).



**Figure 2** | pH dependence of metal adsorption onto *Laminaria japonica* in 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub> at 16 °C. Solid curves were calculated from Equations (9) and (10). The broken lines were calculated from Equations (7) and (10). (a) pH dependence of  $1 \times 10^{-4} mol L^{-1} Cd^{2+}$  adsorption onto  $0.50 g L^{-1} Laminaria japonica$  (open symbol) and  $2 \times 10^{-4} mol L^{-1} Cd^{2+}$  adsorption onto  $0.75 g L^{-1} Laminaria japonica$  (solid symbol). (b) pH dependence of  $2 \times 10^{-4} mol L^{-1} Pb^{2+}$  adsorption onto  $0.50 g L^{-1} Laminaria japonica$  (open symbol) and  $4 \times 10^{-4} mol L^{-1} Pb^{2+}$  adsorption onto  $0.25 g L^{-1} Laminaria japonica$  (solid symbol).

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 non-linear least-squares method. The cadmium binding constant in the monodentate binding model was determined as  $1.89 \times 10^{-2} L \cdot mol^{-1}$ . 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  $6.28 \times 10^4 L \cdot mol^{-1}$  and  $1.06 \times 10^{-1} L \cdot mol^{-1}$  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

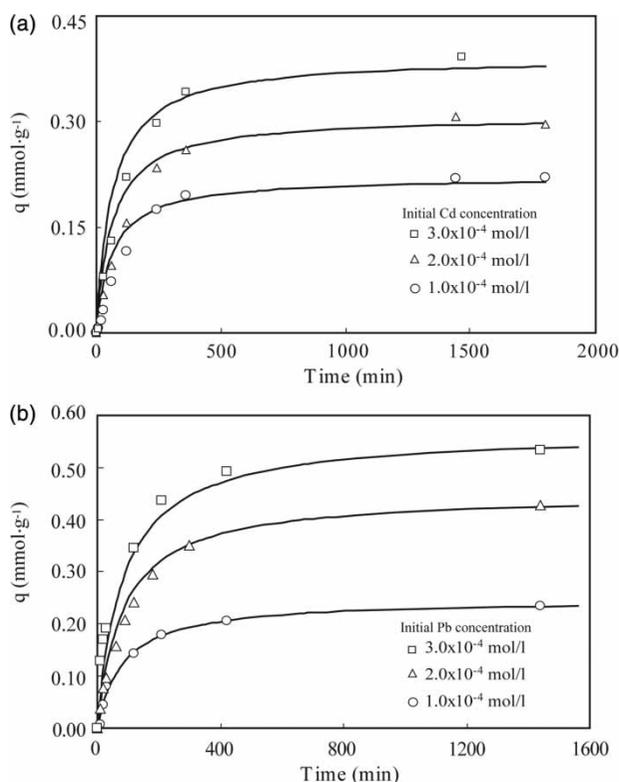
bidentate binding model. These results indicate that the biosorption mechanism of bivalent metal ions onto *L. japonica* is the bidentate binding model.

### 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

$$\frac{d(q/q_e)}{dt} = k(1 - q/q_e)^2 \quad (11)$$



**Figure 3** | Time dependence of metal adsorption onto *Laminaria japonica* in 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub> at 16 °C. Solid curves were calculated from Equation (12). (a) Time dependence of  $1 \times 10^{-4}$ – $3 \times 10^{-4}$  mol L<sup>-1</sup> Cd<sup>2+</sup> adsorption onto 0.20 g L<sup>-1</sup> *Laminaria japonica*. (b) Time dependence of  $1 \times 10^{-4}$ – $3 \times 10^{-4}$  mol L<sup>-1</sup> Pb<sup>2+</sup> adsorption onto 0.20 g L<sup>-1</sup> *Laminaria japonica*.

or

$$q = q_e \frac{kt}{1 + kt} \quad (12)$$

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<sup>-1</sup>, 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<sup>2</sup> s<sup>-1</sup>, 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.

## ACKNOWLEDGEMENTS

Funds are provided by the Project for China National Science and Technology Supporting Plan (2012BAC07B00), and Pujiang Project (05PJ14086) of Shanghai Science Commission, in addition to Superiority Subject Sponsored Projects in Shanghai Municipal Education Commission (S30701), Shanghai, China.

## REFERENCES

- Acharya, J., Sahu, J. N. & Mohanty, C. R. 2009 Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. *Chemical Engineering Journal* **149**, 249–262.
- Ahmet, S. & Mustafa, T. 2008 Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass. *Journal of Hazard Materials* **152**, 302–308.
- Ahmet, S., Durali, M., Mustafa, T. & Mustafa, S. 2008 Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetics and thermodynamic studies. *Chemical Engineering Journal* **144**, 1–9.
- Aldrich, C. & Feng, D. 2000 Removal of heavy metals from wastewater effluents by biosorptive flotation. *Minerals Engineering* **13**, 1129–1138.
- Ali, G., Duygu, O., Celal, D., Volkan, N. B., Mustafa, S. & Hasan, B. S. 2009 Biosorption of Pb(II) Ions from aqueous solution by pine bark (*Pinus brutia* Ten). *Chemical Engineering Journal* **153**, 62–69.
- Antunes, W. M., Luna, S. A., Henriques, C. A. & da Costa, A. C. A. 2003 An evaluation of copper biosorption by a brown seaweed under optimized conditions. *Journal of Electronic Biotechnology* **6**, 174–184.
- Bailey, S. E., Olin, T. L., Bricka, R. M. & Adrian, D. D. 1999 A review of potentially low-cost sorbents for heavy metals. *Water Research* **11**, 2469–2479.
- Dhruv, K. S. & Meenakshi, S. 2005 Selective uptake and recovery of cadmium (II) by microcapsule containing chelating resin. *Separation and Purification Technology* **45**, 1–7.
- Fan, W. H., Xu, Z. Z. & Feng, L. J. 2008 Preparation of immobilized biosorbents and its sorption kinetics for Ni(II). *Environmental Protection of Chemical Industry* **28** (3), 196–200. (In Chinese).
- Fella, N. A., Nabil, M. & Eric, G. 2011 Pb(II) biosorption on *Posidonia oceanica* biomass. *Chemical Engineering Journal* **168**, 1174–1184.
- Gopala, R. M. & Gupta, A. K. 1982 Ion exchange process accompanied by ionic reactions. *Chemical Engineering Journal* **24**, 181–190.
- Hashim, M. A. & Chu, K. H. 2004 Biosorption of cadmium by brown, green, and red seaweeds. *Chemical Engineering Journal* **97**, 249–255.
- Ho, Y. S. & McKay, G. 2000 The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Resources Research* **34**, 735–742.
- İlhami, T., Gülay, B., Emine, Y., Gökben, B., Gökçe, Ç. & Arica, M. Y. 2005 Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto microalgae *Chlamydomonas reinhardtii*. *Journal of Environment Management* **77**, 85–92.
- Kedar, N. G., Katsutoshi, I., Keisuke, O. & Takehiro, H. 2006 adsorption study of metal ions onto crosslinked seaweed *Laminaria japonica*. *Bioresource Technology* **99**, 32–37.
- Liang, J. N., Stevens, E. S., Frangous, S. A., Morris, E. R. & Rees, D. A. 1980 Cation-specific vacuum ultraviolet circular dichroism behavior of alginate solutions, gels and solid films. *International Journal of Biological Macromolecules* **2**, 204–208.
- Mohammad, F., Ali, D. & Habibollah, Y. 2009 Biosorption equilibria of binary Cd(II) and Ni(II) systems onto *Saccharomyces cerevisiae* and *Ralstonia eutropha* cells: application of response surface methodology. *Journal of Hazardous Materials* **168**, 1437–1448.
- Ozgül, D. U., Ahmet, S., Mustafa, T. & Mustafa, S. 2008 Biosorption of Pb(II) and Cr(II) from aqueous solution by Lichen (*Parmelina tiliaceae*) Biomass. *Bioresource Technology* **99**, 2972–2980.
- Qin, Y. M., Chen, J., Song, J., Li, C. C., Ma, L. W., Ma, W. J., Zhou, Y. & Zhu, W. W. 2009 Adsorption of copper ions by chemically modified seaweeds. *Environmental Science and Technology* **32** (5), 147–153. (In Chinese).
- Reddad, Z., Gerente, C., Andres, Y. & Le Cloirec, P. 2002 Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental Science and Technology* **36**, 2067–2075.
- Saurav, K. & Kannabiran, K. 2010 Biosorption of Cd (II) and Pb (II) ions by aqueous solutions of novel alkalophilic *Streptomyces* VITSVK5 spp. Biomass. *Journal of Ocean University of China* **10** (1), 61–66.
- Seki, H. & Suzuki, A. 1995 Adsorption of heavy metal ions onto insolubilized humic acid. *Journal of Colloid and Interface Science* **171**, 490–494.
- Seki, H. & Suzuki, A. 1998 Biosorption of heavy metal ions to brown algae, *Macrocystis pyrifera*, *Kjellmaniella crassifolia* and *Undaria pinnatifida*. *Journal of Colloid and Interface Science* **206**, 297–301.
- Seki, H., Suzuki, A. & Mitsueda, S. 1998 Biosorption of heavy metal ions on *Rhodobacter sphaeroides* and *Alcaligenes eutrophus* H16. *Journal of Colloid and Interface Science* **197**, 185–190.
- Seki, H., Suzuki, A. & Iburi, Y. 2000 Biosorption of heavy metal ions to a marine microalga, *Heterosigma akashiwo* (Hada) Hada. *Journal of Colloid and Interface Science* **229**, 196–198.
- Seki, H., Yu, K. F., Maruyama, H. & Suzuki, A. 2006 Biosorption of heavy metals onto sphagnum peat moss. *Kagaku Kogaku Ronbunshu*, **32** (5), pp. 409–413.
- Su, F., Luo, S. L., Zeng, G. M., Xiao, X. & Cao, Z. 2009 Kinetics and thermodynamics of Cd(II) biosorption onto *Laminaria japonica*. *Chinese Journal of Environmental Engineering* **3** (5), 857–860. (In Chinese).
- Suzuki, A., Seki, H. & Maruyama, H. 1994 An equilibrium study of adsorption of divalent metal ions onto metal oxide adsorbent. *Journal of Chemical Engineering of Japan* **127**, 505–511.
- Suzuki, Y., Kametani, T. & Maruyama, T. 2005 Removal of heavy metals from aqueous solution by nonliving *Ulva* seaweed as biosorbent. *Water Research* **30**, 1803–1808.

Walter, N. L. dos S., Dannuza, D. C., Erik, G. P. da S., Cesário, F. das V. & Fabio, de. S. D. 2011 [Biosorption of Pb\(II\) and Cd \(II\) ions by \*Agave sisalana\* \(Sisal Fiber\)](#). *Microchemical Journal* **97**, 269–273.

Zübeyde, B., Ercan, Ç., Yasemin, B., Hüseyin, A. & Mehmet, D. 2009 [Equilibrium and thermodynamic studies on biosorption of Pb\(II\) onto \*Candida albicans\* biomass](#). *Journal of Hazard Materials* **161**, 62–67.

First received 27 July 2011; accepted in revised form 12 December 2011