

## Selective Biosorption of Mixed Heavy Metal Ions using Polysaccharides

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**Abstract**—Although much research has been conducted on the separation of single species of heavy metal, the selective adsorption of two or more heavy metals in mixture is relatively little known. In this study, polysaccharide beads were prepared to selectively remove the targeted heavy metal ion from mixture. Among the biomasses, polysaccharide was examined due to its low cost and easy accessibility. In a single metal ion system, chitosan,  $\lambda$ -carrageenan, and alginic acid showed high affinity to mercury, copper, and lead, respectively. In the ion mixture, the same trend shown in the single metal ion solution was observed. The optimum electrolyte concentration was investigated to adsorb the metal ion selectively, and it was possible to remove the targeted metal ion selectively with chitosan, alginic acid and  $\lambda$ -carrageenan at 1 mmol concentration of electrolyte. In order to demonstrate the feasibility of selective biosorption, two packed-bed reactors in series containing chitosan and alginic acid beads in each were studied and selective adsorption to  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ , respectively, was observed.

Key words: Selective Biosorption, Polysaccharides, Heavy Metal Ion, Bioseparation

### INTRODUCTION

In recent years, there has been increasing public awareness of the long-term effects of water containing dissolved heavy metal ions. Numerous industrial processes, such as metal plating facilities, mining operations, and tanneries, generate aqueous effluents containing heavy metal pollutants [Joseph, 1995; Lovely and Covas, 1997]. These heavy metal concentrations of the effluents must be reduced and recovered to meet the legislative standards that are constantly amended. The European Economic Community has issued a directive on pollution caused by certain dangerous substances, including heavy metals, discharged into the aquatic environment [Brierly, 1990]. And the World Health Organization has announced a list of most immediate concern involving heavy metals, aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead.

Carbon adsorbents have become a popular medium for the general physicochemical treatment of wastewater, and chemical precipitation and electrolytic methods have become the most common processes for heavy metal treatment. However, these conventional methods for treating a large volume of the waste with low pollutant concentration tend to be costly, entailing large capital and operating costs. And modern heavy metal removal technologies, such as ion exchange, reverse osmosis and membrane systems, are integrated into systems to recover and reuse heavy metals, which are more costly and often not feasible [Brierly, 1990]. To overcome these drawbacks, biosorption, which means the removal of heavy metals in water by microorganisms or their metabolic products, should be further exploited as a promising method in that it is comparatively efficient and cost-effective [Bedell and Darnall, 1990; Chen and Yiaccoumi, 1997].

The advantage of biosorption is that it uses biomass and industrial waste such as chitosan and carrageenan, which are cheap and abundant [Volesky, 1990]. Broad-range biosorbents can collect all the heavy metals from the solution, and a certain concentration of a specific heavy metal could be achieved either during the adsorption uptake by manipulating the properties of a biosorbent, or upon desorption during the regeneration cycle of these biosorbent [Bailey and Trudy, 1999; Jang et al., 1999; Oyrton et al., 1999]. There have been numerous studies on the adsorption of heavy metals from aqueous solutions by microbial biomass, demonstrating that various microorganisms including algae, bacteria, and fungi were capable of collecting toxic heavy metals ( $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ), precious metals ( $\text{Au}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ag}^{+}$ ), base heavy metals ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ), and radionuclides ( $\text{U}^{6+}$ ,  $\text{Th}^{4+}$ ) [Volesky, 1986; Asai et al., 1986; Ting, 1991; Peniche-Covas et al., 1992; Gimenez et al., 1995; Singh et al., 1998; Yoshinari et al., 1998; Terry and Stone, 2002; Jeon and Höll, 2004]. Furthermore, Udaybhasker and coworkers reported that the presence of electrolyte affected the removal of heavy metal ion, such as  $\text{Cr}^{3+}$ , claiming the electrostatic attraction as the main removal mechanism [Udaybhaskar et al., 1990].

In this study, the biosorption process to selectively adsorb heavy metals from wastewater was exploited for polysaccharides immobilized in polyvinyl alcohol (PVA) bead. To demonstrate the feasibility of selective biosorption, packed-bed column reactors in series containing different polysaccharide were studied.

### EXPERIMENTAL

#### 1. Selection of Polysaccharides

Among various polysaccharides, alginic acid (Aldrich), chitosan (Showa) and carrageenan (Wako) were selected because of their unique functional group, as shown in Table 1. In addition to hydroxyl groups, alginic acid, chitosan, and carrageenan have carboxyl groups, amine groups, and sulphate groups, respectively. Furthermore,  $\lambda$ -

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**Table 1. Functional groups of polysaccharides**

Polysaccharides	Number of functional groups per monomer			
	Hydroxyl group	Carboxyl group	Sulfate group	Amine group
Alginate acid	2	1	-	-
$\lambda$ -Carrageenan	2-4	-	1-3	-
Cellulose	6	-	-	-
Chitosan	4	-	-	2

carrageenan was selected out of  $\kappa$ -,  $\iota$ -,  $\lambda$ -carrageenans having one, two, and three charge units per subgroup, respectively [Aspinall, 1985]. The results of the experiments conducted on the adsorption capacity of each adsorbent were compared with the results of cellulose having only hydroxyl groups.

## 2. Heavy Metal Adsorption Properties

The adsorption tests in a batch reactor were performed by suspending 0.1 g powdered biomass in heavy metal solution 100 ml at the designated pH set by adding 0.1 N HNO<sub>3</sub> and 0.1 N NH<sub>4</sub>OH. The solution was mechanically agitated at 250 rpm for 24 hrs, and then the suspending biomass was removed by centrifugation at 10,000 rpm for 20 min. The 10 ml supernatant was collected to measure the final concentration of heavy metal in supernatant by inductively coupled plasma spectroscopy (ICP, Perkin-Elmer). For the effect of electrolyte concentration on heavy metal uptake capacity, KNO<sub>3</sub> was applied as a control electrolyte.

The heavy metal adsorption capacity is given by:

$$Q = \frac{C_i \times V_i - C_f \times V_f}{m} \quad (1)$$

where Q is the heavy metal adsorption capacity (mmol/g), C<sub>i</sub> the initial heavy metal concentration (mmol/L), V<sub>i</sub> the initial volume (L), C<sub>f</sub> the final heavy metal concentration (mmol/L), V<sub>f</sub> the final volume (L), and m the initial biosorbent loading (g).

An up-flow double packed-bed column, a borosilicate glass column (i.d. 31×210 mm, 158 ml bed volume) was constructed to separate heavy metal ion from the mixture. The flow rate was varied by using a peristaltic pump, and the concentrations of heavy metal ions in influent and effluent were measured by ICP. Nitrate concentration of influent was controlled to be 1 mmol by using KNO<sub>3</sub>.

## 3. Immobilization of Polysaccharides

The immobilization of polysaccharides with PVA was performed through the modified method by Jeon et al. [2001]. 4.4 g of PVA (Sigma-Aldrich, MW 1500) was added to 50 ml of distilled water and mixed for 12 hrs at 60 °C, and then 7 g polysaccharide was mixed thoroughly with PVA solution at 60 °C. The mixture was then pumped by peristaltic pump at 15 ml/min to drop into a gently stirred bead forming solution (36 g of boric acid and 60 ml of 25% glutaraldehyde solution). To complete gelation inside beads, the beads were kept in a saturated boric acid and glutaraldehyde solution for 24 hrs with gentle stirring. Next, the beads were taken out, washed with distilled water and dried at room temperature. The chitosan bead diameter was 3 mm, and the other two polysaccharides bead diameters were 2 mm. These microporous beads having lower mass transfer resistance showed excellent mechanical strength, not cracking under 24 hrs batch operation at 800 rpm, and were stable under acidic condition (below pH 2.0). Furthermore, in the packed-bed column reactor, channeling and pressure drop were not observed through the operation.

## RESULTS AND DISCUSSION

### 1. Effects of Functional Groups of Polysaccharides

The effects of functional groups of polysaccharides, alginate acid, chitosan,  $\lambda$ -carrageenan, and cellulose, were studied on their adsorption capacity, as shown in Table 2. These observations were taken at pH 4.0 and 1,000 ppm initial metal concentration. Alginate acid with carboxyl groups showed about 6-15 times higher adsorption capacity to Pb<sup>2+</sup> than the other two metal ions, Hg<sup>2+</sup> and Cu<sup>2+</sup>, indicating selective adsorption to Pb<sup>2+</sup>. Chitosan with amine groups also showed its selective competency to adsorb Hg<sup>2+</sup>, having adsorption capacity 9.45 mmol/g. Similar to the other two polysaccharides, selective adsorption for Cu<sup>2+</sup> was observed with  $\lambda$ -carrageenan with sulfate groups, having adsorption capacity of 3.35 mmol/g. As expected, the adsorption capacities of cellulose only with hydroxyl groups were just 1-10% of adsorption capacities for alginate acid, chitosan, and  $\lambda$ -carrageenan, showing that cellulose is less capable of adsorbing any heavy metal ion. These results suggest that the functional group of polysaccharide is a key factor to determine its adsorption capacity to specific metal ion.

The metal ion specificity and the adsorption capacity of functional groups of polysaccharide were also examined in a mixed heavy metal system of Pb<sup>2+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup>. The selectivity of polysaccha-

**Table 2. The adsorption capacity in single heavy metal system and in heavy metal mixture system (pH=4; initial concentration, 1,000 ppm (single); each 1,000 ppm (mixed))**

Polysaccharide		Alginate acid	Chitosan	$\lambda$ -Carrageenan	Cellulose	
Functional groups		-COOH -OH	-NH <sub>2</sub> -OH	-SO <sub>4</sub> -OH	-OH	
Heavy metal	Single	Pb <sup>2+</sup>	4.04	0.22	2.07	0.076
		Hg <sup>2+</sup>	0.26	9.45	1.18	0.098
		Cu <sup>2+</sup>	0.64	4.57	3.35	0.342
	Mixed	Pb <sup>2+</sup>	3.35	0.12	0.45	0.050
		Hg <sup>2+</sup>	0.15	3.15	0.30	0.068
		Cu <sup>2+</sup>	1.47	1.00	1.12	0.529

\*Unit: mmol/g

ride to heavy metal ion was not changed even in a mixed system; however, the adsorption capacities of chitosan and  $\lambda$ -carrageenan to  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ , in a mixed system were about 1/3 of a single heavy metal system. Alginate acid was able to maintain its  $\text{Pb}^{2+}$  adsorption capacity at 83% of that for the single metal system. Bræk and co-workers reported that, in a two-metal system,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  uptake using algae may be synergistic or antagonistic and claimed that its antagonistic uptake was due to the competition for adsorption and/or transport sites on the cell membrane [Bræk et al., 1980]. Based on the results shown in Table 2, the adsorption capacities of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  to alginate acid, chitosan and  $\lambda$ -carrageenan were lower in a mixed system than in a single system. The adsorption of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  in a mixed system to the polysaccharide showing the selectivity to specific ion in a single system is antagonistic owing to the presence of other metal ions. Therefore, it is possible to deduce that all polysaccharides follow antagonistic behavior resulting from the competition of heavy metal ions to the adsorption sites, namely functional groups of polysaccharide.

## 2. Effects of Electrolyte Concentration in a Mixed Heavy Metal System

The effects of electrolyte concentration on ion selectivity and adsorption capacity in a mixed heavy metal system were examined with alginate acid to determine the optimum electrolyte concentration for ion selectivity. As shown in Table 3, electrolyte concentration can influence the adsorption capacity of each ion, thereby changing the characteristics of ion selectivity. Among the tested ions,  $\text{Cu}^{2+}$  showed the most dramatic change. As electrolyte concentration was increased from 0.01 mmol to 100 mmol, the adsorption capacity for  $\text{Cu}^{2+}$  was the lowest at 1 mmol. The  $\text{Cu}^{2+}$  adsorption at 1 mmol was only about 10% of that for the  $\text{NO}_3^-$  free system. Within the tested range of electrolyte concentration, the adsorption capacity for  $\text{Pb}^{2+}$  was kept steady at around 3 mmol/g while the adsorption of  $\text{Hg}^{2+}$  was not observed, at except 100 mmol. These results indicate that the effects of electrolyte concentration on  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$

**Table 3. The effects of electrolyte concentration on heavy metal uptake for alginate acid**

Electrolyte concentration (mmol)	$\text{Cu}^{2+}$	$\text{Hg}^{2+}$	$\text{Pb}^{2+}$
0.01	1.48	0	3.28
0.1	0.35	0	3.51
1	0.15	0	2.92
10	0.25	0	3.01
100	2.65	0.28	3.12

\*Unit: mmol/g

**Table 4. Adsorption capacity of polysaccharides for heavy metal in mixture at 1 mmol electrolyte concentration**

	$\text{Cu}^{2+}$	$\text{Hg}^{2+}$	$\text{Pb}^{2+}$
Alginate acid	0.15	0	2.92
Chitosan	0	2.51	0
$\lambda$ -Carrageenan	1.52	0	0.54
Cellulose	0	0	0

\*Unit: mmol/g

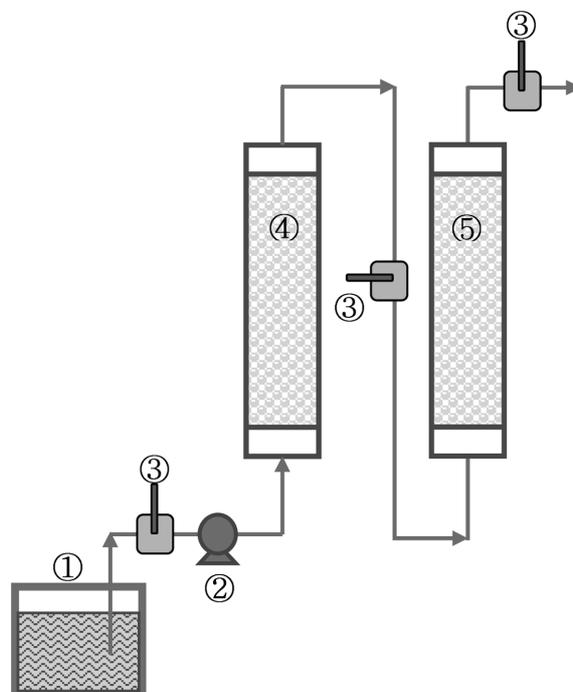
adsorption are insignificant, and these changes of adsorption characteristics, especially  $\text{Cu}^{2+}$ , might be attributed to the difference in ability to form a complex between heavy metal ions and nitrate ions [Volesky, 1990]. For further selectivity studies with other polysaccharides, chitosan,  $\lambda$ -carrageenan, and cellulose, 1 mmol electrolyte concentration, showing the  $\text{Pb}^{2+}$  selectivity with alginate acid, was selected.

The effects of the selected electrolyte concentration to the ion selectivity of polysaccharide were examined. According to the results shown in Table 4, it was possible to sort out the target ion from the mixed heavy metal solution with chitosan, alginate acid, and  $\lambda$ -carrageenan. At the selected electrolyte concentration of 1 mmol, chitosan showed highly specific adsorption to  $\text{Hg}^{2+}$ , but not to  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ . Furthermore,  $\lambda$ -carrageenan showed higher ion selectivity to  $\text{Cu}^{2+}$  than  $\text{Pb}^{2+}$ . Since the presence of electrolyte can alter the characteristics of polysaccharide, the adsorption capacities of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  to  $\lambda$ -carrageenan were slightly higher than those without electrolyte.

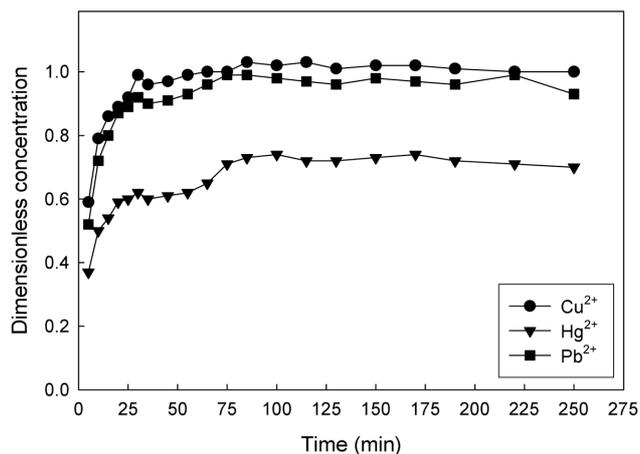
As expected, cellulose with only hydroxyl groups could not adsorb any heavy metal ions. These results suggest that electrolyte can alter the interaction between functional groups of polysaccharide and heavy metal ions and, alginate acid, chitosan, and  $\lambda$ -carrageenan at 1 mmol electrolyte concentration can selectively adsorb  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Cu}^{2+}$ , respectively.

## 3. Selective Biosorption of Heavy Metal Using Packed-Bed Column Reactor

To demonstrate the feasibility of selective biosorption in large scale, two packed-bed column reactors in series containing chitosan and alginate acid beads in each were examined for  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,



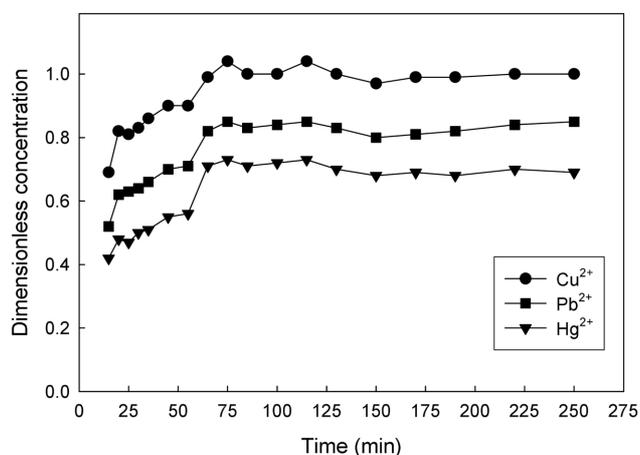
**Fig. 1. Schematic diagram of two packed-bed column reactors (①, feeding water containing  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Cu}^{2+}$ ; ②, pump; ③, sampling port; ④, chitosan bead column; ⑤, alginate acid bead column).**



**Fig. 2.** Breakthrough curve of mercury ion, lead ion and cooper ion mixture using chitosan bead column ( $\text{Hg}^{2+}$ , 1,000 ppm;  $\text{Pb}^{2+}$ , 1,000 ppm;  $\text{Cu}^{2+}$ , 1,000 ppm; bed volume, 50 mL; flow rate, 2 ml/min).

and  $\text{Pb}^{2+}$  adsorption (Fig. 1). The feeding wastewater was composed of 1,000 ppm of  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  respectively. Fig. 2 represents the breakthrough curves of the first reactor containing chitosan beads. Similar to the results shown in the batch system (Table 2), the chitosan column showed the highest adsorption activity to  $\text{Hg}^{2+}$ , maintaining the  $\text{Hg}^{2+}$  adsorption capacity up to 250 min. Its dimensionless concentration of the first column reactor,  $C_{o1}/C_i$  where  $C_{o1}$  is the concentration of the efflux from the first column reactor and  $C_i$  is the concentration of the influx to the first column reactor, leveled off at 0.7, indicating that the chitosan beads were sustainable to absorb 30% of  $\text{Hg}^{2+}$  in inflow up to 250 min. As expected, the dimensionless concentrations of the other two heavy metal ions,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , leveled off at 1.0 even from the beginning, which means that the binding sites for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were saturated at the start and the adsorption capacities of the other two heavy metal ions to chitosan are negligible.

After passing the second reactor packed with alginic acid beads,



**Fig. 3.** Breakthrough curve of mercury ion, lead ion and cooper ion mixture using alginic acid bead column ( $\text{Hg}^{2+}$ , 1,000 ppm;  $\text{Pb}^{2+}$ , 1,000 ppm;  $\text{Cu}^{2+}$ , 1,000 ppm; bed volume, 50 mL; flow rate, 2 ml/min).

the dimensionless number of  $\text{Pb}^{2+}$ ,  $C_{o2}/C_i$  where  $C_{o2}$  is the concentration of the efflux from the second column reactor and  $C_i$  is the concentration of the influx to the first column reactor, was maintained at 0.8 up to 300 min, which is lower than the dimensionless number of  $\text{Pb}^{2+}$  of the first reactor with chitosan (Fig. 3). This result means that the alginic acid beads adsorb 20% of  $\text{Pb}^{2+}$  in the effluence from the first reactor. Similar to the results of the batch reactor, the adsorption of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  was insignificant in the alginic acid column. The dimensionless concentration of  $\text{Cu}^{2+}$  reached to 1.0 in the early period and the dimensionless concentration of  $\text{Hg}^{2+}$  was maintained at 0.7, showing that the adsorption of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  to alginic acid was negligible. To increase the adsorption capacity without any change of the selective adsorption characteristics of alginic acid, the packed-bed volume was increased three times the above. The dimensionless concentration of  $\text{Pb}^{2+}$  was observed to be lower than 0.32 up to 250 min, which means that more than 78% of  $\text{Pb}^{2+}$  in the wastewater was removed and shows the possibility to achieve more efficacious adsorption by increasing packed-bed volume (data not shown). These results illustrate the selective adsorption of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  to chitosan and alginic acid, respectively, and suggest that selective adsorption of heavy metal ions can be achieved by polysaccharides with specific functional groups in a consecutive packed-bed column system, and also, it is possible to apply polysaccharide system to remove heavy metal ions in a real wastewater treatment system.

## CONCLUSIONS

The feasibility of adsorbing specific heavy metal ion in a mixed system using polysaccharides with unique functional groups was investigated. Selective adsorption of alginic acid, chitosan, and  $\lambda$ -carrageenan to  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Cu}^{2+}$ , respectively, was observed, and cellulose having only hydroxyl groups showed ineffectiveness on heavy metal ion adsorption. These results are attributed to the functional group difference between the polysaccharides, carboxyl groups for alginic acid, amine groups for chitosan, sulfate group for  $\lambda$ -carrageenan, hydroxyl groups for cellulose. Two packed-bed reactors in series containing chitosan and alginic acid beads in each also showed selective adsorption to  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ , respectively, and the adsorption capacity was increased by increasing bed volume. These results show that it is possible to apply the polysaccharide system to remove specific heavy metal ions in a wastewater treatment system.

## REFERENCES

- Asai, S., Konishi, Y., Tomisaki, H. and Nakanishi, M., "Separation of Mercury from Aqueous Mercuric Chloride Solutions by Onion Skins," *Sep. Sci. Technol.*, **21**, 809 (1986).
- Aspinall, O. G., "The Polysaccharides," Academic Press, New York, Vol. 3 (1985).
- Bailey, S. E. and Trudy, J. O., "A Review of Potentially Low-cost Sorbents for Heavy Metals," *Wat. Res.*, **33**, 2469 (1999).
- Bedell, G. W. and Damall, D. W., in "Biosorption of Heavy Metals" (Volesky, B., ed.), CRC Press, pp. 313 (1990).
- Bræk, G. S., Malnes, A. and Jensen, A., "Heavy Metal Tolerance of Marine Phytoplankton. IV. Combined Effect of Zinc and Cadmium on Growth and Uptake in Some Marine Diatoms," *J. Exp. Mar. Biol.*

- Ecol.*, **42**, 39 (1980).
- Brierly, C. L., "Bioremediation of Metal Contaminated Surface and Groundwaters," *Geomicrobiol. J.*, **8**, 201 (1990).
- Chen, J. and Yiacoumi, S., "Biosorption of Metal Ions from Aqueous Solutions," *Sep Sci Technol.*, **32**, 51 (1997).
- Gimenez, M. D., Arino, C. and Esteban, M., "Voltammetry of Pb(II), Cd(II) and Zn(II) Ions in the Presence of the Sulphated Polysaccharide  $\lambda$ -Carrageenan," *Analytica Chimica Acta*, **310**, 12 (1995).
- Jang, L. K., Nguyen, D. and Geesy, G. G., "An Equilibrium Model for Absorption of Multiple Divalent Metals by Alginate Gel under Acidic Conditions," *Wat. Res.*, **33**(12), 2826 (1999).
- Jeon, C., Park, J. Y. and Yoo, Y. J., "Removal of Heavy Metals in Plating Wastewater Using Carboxylated Alginic Acid," *Korean J. Chem. Eng.*, **18**, 955 (2001).
- Jeon, C. and Höll, W. H., "Application of the Surface Complexation Model to Heavy Metal Sorption Equilibria onto Aminated Chitosan," *Hydrometallurgy*, **71**, 421 (2004).
- Joseph, D. E., "Industrial Wastewater Treatment (A Guide Book)," Lewis Publishers, CRC Press Inc, CRC Press, Inc., New York (1995).
- Lovely, D. R. and Covas, J. D., "Bioremediation of Metal Contamination," *Curr. Opin. In Biotechnol.*, **8**, 285 (1997).
- Oyrton, A. C., Monteiro, Jr. and Claudio, A., "Some Thermodynamic Data on Copper-Chitin and Copper-Chitosan Biopolymer Interactions," *J. of Colloid Interface Sci.*, **212**, 212 (1999).
- Peniche-Covas, C., Alvarez, L. W. and Argüelle-Monal, W., "The Adsorption of Mercuric Ions by Chitosan," *J. of Appl. Pol. Sci.*, **46**, 1147 (1992).
- Singh, S., Pradhan, S. and Rai, L. C., "Comparative Assessment of Fe(III) and Cu(II) Biosorption by Field and Laboratory-grown *Microcystis*," *Process Biochem.*, **33**, 495 (1998).
- Terry, P. A. and Stone, W., "Biosorption of Cadmium and Copper Contaminated Water by *Scenedesmus abundans*," *Chemosphere*, **47**, 249 (2002).
- Ting, Y. P., "Uptake of Cadmium and Zinc by the Alga *Chlorella vulgaris*: II. Multi-Ion Situation," *Biotechnol. and Bioeng.*, **37**, 445 (1991).
- Udaybaskar, P., Iyengar, L. and Abhakara Rao, A. V. S., "Hexavalent Chromium Interaction with Chitosan," *J. Appl. Polymer Sci.*, **39**, 739 (1990).
- Volesky, B., "Biosorbent Materials," *Biotechnol. Bioeng. Symp.*, **16**, 121 (1986).
- Volesky, B., (ed.) "Biosorption of Heavy Metals," CRC Press, Boca Raton, FL, pp. 318 (1990).
- Yoshinari, B., Koichi, M. and Yoshinobu, K., "Synthesis of a Chitosan Derivative Recognizing Planar Metal Ion and Its Selective Adsorption Equilibria of Copper(II) over Iron(III)," *Reactive Func. Pol.*, **36**, 167 (1998).