ENVIRONMENTAL SCIENCES Vol. 2, No. 1, 1~8
Bulletin of the Korean Environmental Sciences Society

Aluminum Complexation and Precipitation with Seaweed Biosorbent

Hak Sung Lee and Young Tae Kim

Department of Chemical Engineering, University of Ulsan, Ulsan Nam, PO Box 18, Korea 680-749

(Manuscript received on 4 February, 1998)

Biomass of non-living brown seaweed *Sargassum fluitans* pretreated by different methods is capable of taking up more than 10% (11 meq/g) of its dry weight in aluminum at a pH of 4.5. It is indicated that the biomass sequestered the aluminum in the form of polynuclear aluminum species. The fraction of $Al(OH)_3$ precipitated in the aluminum nitrate solution without biomass at pH 4.5 increased as the Al concentration increased. Aluminum-alginate complex precipitated in the solution as alginate was partially released from the biomass. External colloidal precipitate occurring in native and protonated *S. fluitans* biomass sorption systems caused a significant difference in Al sorption isotherms determined by standard and desorption methods, respectively. Sodium ions added for pH adjustment were not sorbed at all in the presence of aluminum ions.

Keywords : aluminum sorption, *Sargassum fluitans* biomass, $Al(OH)_3$, aluminum-alginate complex

1. Introduction

Passive metal uptake, observed with a broad range of microbial biomass types, has been investigated with the aim of using it to remove residual toxic or strategic heavy metals from industrial effluents. This biosorption technology and its potential for the treatment of wastewater and environmental pollution have been outlined recently (Volesky, 1990; Volesky, 1995). Most of the research on biosorption has focussed on uptake of heavy metal by biomass of bacteria, actinomycetes, fungi, and algae (Gadd, 1988). The reported applications of metal-algae interactions include the use of algae as biosorbents for recovery of metals from industrial effluents (Kuyucak, 1988), either to sequester toxic metals (Mann, 1988) or to recover precious metals (Greene, 1986).

Among the huge diversity of biomass available, marine algae have already proven to be the most promising for heavy metal recovery. Brown seaweed of the genus *Sargassum* has been studied for its capacity to bind selectively gold at low pH (Kuyucak, 1989) and also camium, nickel, copper, lead, and zinc cations up to 20% of the biosorbent dry weight (Leusch, 1995). Very little work has been done on biosorption of light metals such as aluminum. The major mechanisms responsible for it include ionic interactions and complex formation between light metal cations and ligands present in the structure of the biomass (Treen-Sears, 1984; Fourest, 1992). While some biomass of brown algae provides an efficient and cheap material for biosorption, there has been an interest in aluminum adsorption particularly because it may interfere with the uptake of heavy metals.

The present work examines the aluminum sorption characteristics and mechanism of *Sargassum fluitans* biomass chemically or physically

pretreated by different methods. The behavior of light metal ions contained in the biomass and their interaction with aluminum were also investigated.

2. Materials and Methods

Biomass and chemical or physical modification: Raw *S. fluitans* biomass was collected sun-dried on the beach near Naples, Florida. Dry raw biomass was treated by soaking in different solutions in flasks shaken gently on a gyrotory shaker: (a) DW-washed *S. fluitans*: The biomass was washed 5 times with distilled water. One point three grams of raw biomass was added to 200 mL of distilled water (pH 6.5 to 7.3, 100 rpm shaking for 2 h at room temperature) then filtered and finally dried overnight at 60℃. The weight loss of raw biomass was approximately 32%. (b) Protonated *S. fluitans*: 1 g of raw biomass was added to 500 mL of 0.1 N HCl (100 rpm shaking overnight at room temperature). Biomass was filtered off and washed with the same volume of distilled water. It was finally dried overnight at 60℃. The weight loss of biomass was approximately 31%. (c) Ca-loaded *S. fluitans*: 1.2 g of raw biomass was added to 200 mL of 0.5 mole/L $Ca(NO_3)_2 \cdot 4H_2O$ (100 rpm shaking overnight at room temperature). Biomass was filtered off and washed with the same volume of distilled water and then dried overnight at 60℃. The weight loss of biomass was approximately 25%. (d) NaOH-treated *S. fluitans*: The procedure was the same as in (c) except for the use of 0.1 N NaOH instead of 0.5 mole/L $Ca(NO_3)_2 \cdot 4H_2O$. The weight loss of raw biomass was approximately 37%. (e) Formaldehyde crosslinking followed a modified procedure of Bullock (1965). Briefly, 5 g of raw biomass were added to a mixture of 33 mL 36% formaldehyde and 67 mL 1 N HCl. The mixture was left at room temperature for 4 hours under gentle mixing. The biomass was then filtered off and washed with distilled water, 3% sodium carbonate, and another distilled water wash. Biomass was dried overnight at 60℃. The weight loss was approximately 39%.

Sorption experiments: The aluminum solutions of desired concentrations were prepared by dissolving $Al(NO_3)_3 \cdot 9H_2O$ in distilled and deionized water. All sorption experiments were performed by suspending 100 mg of biomass in 50 mL of metal-bearing solution and shaking on a gyrotory shaker for 30 hours. 0.1 N HCl or 0.1 N NaOH were used for pH adjustments. At the end of each experiment, the samples were filtered (Millipore membrane, 0.45 μm) and the filtrate was analyzed by AAS (Thermo Jarell Ash, model Smith-Hieftje II, Waltham, MA) for the equilibrium metal content. The filtered biomass was washed with distilled water and dried overnight at 60℃ and then weighed for desorption experiments. The metal uptake was calculated as $q\ (mg/g) = V(C_i - C_e) / M$ where: C_i and C_e are the initial and final (equilibrium) metal concentration in the solution, respectively (mg/L), V is the solution volume (L), and M is the initial mass of the biosorbent used (g).

All desorption experiments were performed by suspending 100 mg of metal-loaded biomass in 100 mL of 0.1 N HCl (pH 1.1) and shaking on a gyrotory shaker for 8 hours. At the end of each desorption experiment, the samples were filtered (Whatman No. 1) and the filtrate was analyzed by AAS. The filtered biomass was washed with distilled water, dried overnight at 60℃ and then weighed. The metal uptake was calculated from the results of desorption experiments as $q\ (mg/g) = V * C_f / M$ where: C_f is the final eluted metal concentration in the solution, V is the solution volume, and M is the initial mass of the biosorbent used.

Evaluation of Al precipitation: 50 mL of different concentrations of $Al(NO_3)_3 \cdot 9H_2O$ in distilled deionized water were prepared employing 125 mL Erlenmeyer flasks. After the adjustment of pH to 4.5, the solutions were gently agitated on a gyrotory shaker (120 rpm) for 30 hours at room temperature. At the end of the test period, the solution pH was adjusted and the precipitate filtered off through a Millipore membrane (0.45 μ m). The filtrate was acidified (pH 2.5) with 1 N HCl to avoid further precipitation. Residual dissolved aluminum concentration was determined using AAS. The initial concentration of the starting solutions was determined the same way as in the acidified (pH 2.5) samples.

3. Results and Discussion

3.1. Evaluation of Aluminum precipitation

Aluminum ions tend to precipitate as $Al(OH)_3$ from aluminum nitrate solution at pH 4.5 (Phillips, 1966). Blank tests were conducted over a period of 30 hours with different aluminum nitrate concentrations in order to evaluate the amount of $Al(OH)_3$ precipitate formed (Table 1). The initial pH of the aluminum nitrate solution decreased from pH 3.9 to 3.6 with increasing Al concentrations (20-400 mg/L). These pH values varied after the addition of modified biomass. The fractions of $Al(OH)_3$ precipitated from the aluminum nitrate solution without biomass were determined by the amount of NaOH added for pH control. The precipitation of aluminum-alginate complex and $Al(OH)_3$ was mostly found in the aluminum nitrate solution containing *S. fluitans* biomass.

Table 1. Blank tests for the precipitation of $Al(OH)_3$ on the aluminum nitrate solutions at pH 4.5.

Initial Al concentration (mg/L)	Final Al concentration (mg/L)	Al precipitation (%)
19.2	19.1	0.5
49.0	48.7	0.6
100.5	97.9	2.8
204.8	189.9	7.3
406.3	321.8	20.8

Precipitation of Al for DW-washed *S. fluitans* biomass was observed at Al concentrations higher than 150 mg/L (Figures 1(b)). While no precipitate formed when NaOH-treated *S. fluitans* biomass (Figures 1(e)) was added, the pH of the Al solution increased up to pH 4.1-4.4. As shown in Figures 1(a), 1(c) and 1(d), the difference in the sorption isotherm curves determined by analyses of residual or desorption solutions were mostly caused by the formation of external aluminum-alginate complexes in the sorption solution. $Al(OH)_3$ precipitate formed at high Al concentrations. Higher amounts of NaOH added for pH control were required when protonated *S. fluitans* biomass was used because the pH of Al solution had a tendency to decrease to pH 2.8-3.2 when contacted with the biomass.

3.2. Al biosorption isotherms

Aluminum sorption isotherm curves (Figure 1) were steeper at low final aluminum concentrations than those for heavy metals such as copper and cadmium (Leusch, 1995). This indicates a higher affinity of Al^{3+} toward the biomass than in the case of heavy metals. Lee and Volesky (1997) reported that based on their displacement by protons, light metals demonstrate the following ascending order of affinity toward *S. fluitans* biomass: $Na^{+} \leq K^{+} < Mg^{2+} < Ca^{2+} < Al^{3+}$. The greater the final Al concentration in the solution for each pretreated biomass, the greater was the weight gain of biomass through 30 hours of sorption experiments. Only 3% weight loss was

observed during the sorption experiment at the lowest Al concentration with protonated biomass. Additionally, the greater the weight gain of the sorbent biomass, the higher was the aluminum uptake by the pretreated *S. fluitans* biomass. In the case of a final aluminum concentration higher than 50 mg/L, the weight gain of biomass ranged from 7% to 23% in spite of the fact that the gain attributable to aluminum uptake was approximately 6-10% (Figure 1). The excessive weight gain

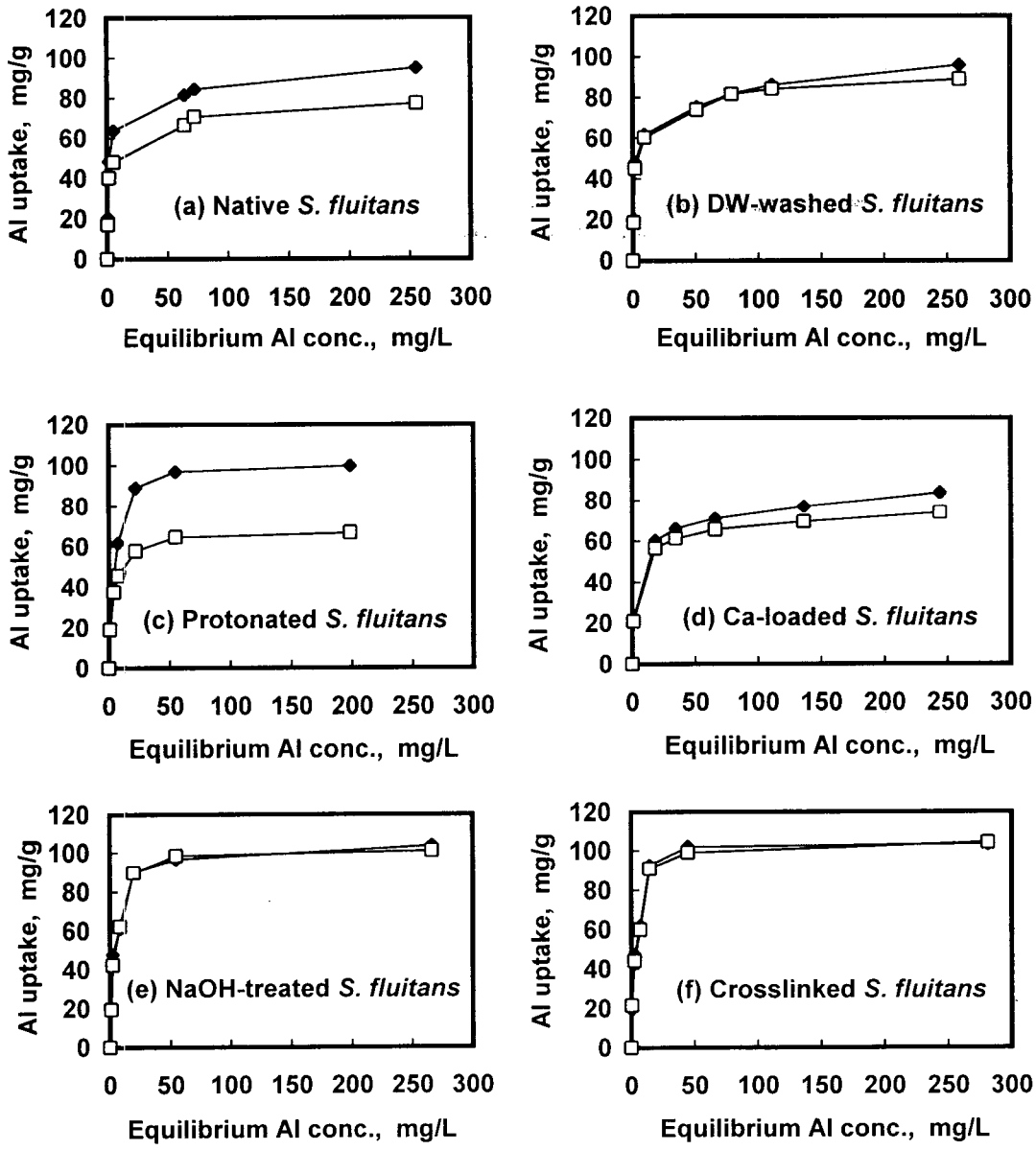

Fig. 1. Biosorption of aluminum on *Sargassum fluitans* biomass pretreated by different methods. Al uptake(pH=4.5) and Al desorption(pH=1.1)
◆ : Filtrate analysis, □ : Elutant analysis.

indicates that aluminum was not sorbed as a simple metal ion but in a complex hydroxyl form readily available from NaOH used for pH adjustment. However, there were net weight losses, approximately 18±4% (based on the initial biomass weight), for each experiment during the subsequent 8 hours of desorption. This means that the biomass components binding aluminum ions were partially extracted from the biomass with aluminum and hydoxyl ions.

Adsorption constants at pH 4.5 were calculated using the Langmuir sorption model in the form of eq. (1), where q_{max} is the maximum uptake of metal sorbed, b is the adsorption equilibrium constant ($k_{adsorption}/k_{desorption}$), and q is the amount of metal sorbed at the final Al equilibrium concentration (C_f).

$$C_f / q = C_f / q_{max} + 1 / (b \cdot q_{max}) \quad (1)$$

Results calculated by eq. (1) for the modified *S. fluitans* are given in Table 2.

As shown in Table 2, the q_{max} for NaOH-treated *S. fluitans* biomass was higher than for other samples. Acid-treated *S. fluitans* biomass had the lowest q_{max} value. The lower the q_{max} value and the higher the Al concentration, the more aluminum-alginate complex was observed forming externally in the Al solution. Moreover, the higher the weight loss of biomass through the pretreatment procedure, the higher is the value of its q_{max}. In case of *S. fluitans* crosslinked by formaldehyde and HCl, the highest q_{max} and weight loss (39%) through the pretreatment procedure was observed. It seems that the crosslinking reaction by formaldehyde and HCl is not effective for immobilizing alginate which is easily extractable by Na_2CO_3. Alginate remaining in the biomass was extracted in the presence of Al^{3+}, forming external aluminum-alginate complex in the solution. The aluminum complexation with alginate in *S. fluitans* biomass does not appear to be the major mechanism of Al biosorption, contrary to the behavior of the Cd and Pb biosorption systems (Fourest, 1996).

Table 2. Al sorption constants for modified *S. fluitans* at pH 4.5.

Type of *S. fluitans* biomass	q_{max} (meq/g)	b $(mg/L)^{-1}$
Native *S. fluitans*	8.69	0.189
S. fluitans washed with distilled water	10.02	0.200
Protonated *S. fluitans*	7.52	0.177
Ca-loaded *S. fluitans*	8.36	0.190
S. fluitans soaked in 0.1 N NaOH	11.18	0.236
Formaldehyde crosslinked *S. fluitans*	11.59	0.239

The biosorbent uptake of aluminum was strongly affected by the pH of solution as shown in Figure 2. The aluminum uptake capacity of *S. fluitans* increased with increasing equilibrium pH values. The curves shown in Figures 2(a) and 2(b) indicate a very similar sorption performance in the pH range 3.5-1.5. The Al uptake capacity at pH 4.5 for NaOH-treated *S. fluitans* was higher than that for *S. fluitans* washed with distilled water. This phenomenon is related to biomass components remaining after the biomass modification by pretreatment. The pH of the filtrate decreased from pH 8.0 to 6.5 during five repeated steps of washing *S. fluitans* biomass with distilled water, and components such as alginates and salts were at least partially extracted. The weight loss (39%) resulting from the *S. fluitans* treatment with 0.1 N NaOH was slightly higher than that observed upon washing of *S. fluitans* with distilled water (35%). The pH of the filtrate from NaOH-treated *S. fluitans* was approximately 12.7. Haug and Larsen (1963) reported that the higher the pH of solution for brown algae such as *Laminaria digitata, Laminaria hyperborea and Ascophyllum nodosum*, the higher was the solubility of alginates.

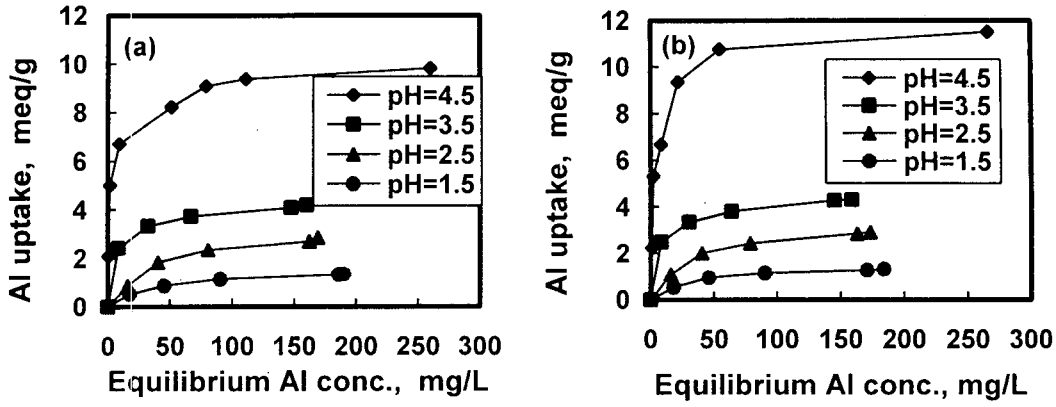

Fig. 2. Biosorption of aluminum on *Sargassum fluitans* biomass.
Effect of pH on the Al uptake for (a) DW-washed S. fluitans; (b) NaOH-treated S. fluitans.

3.3. Reaction mechanism of Al biosorption

It has been noted that the major mechanisms responsible for metal biosorption include ionic interactions and complex formation between light metal cations and ligands present in the structure of the biomass (Fourest, 1992; Crist, 1994). It has been noted as well that metal-algae interactions were based on the electrostatic attractions of some metals (Ca, Na) (Crist, 1981) and the covalent-type bonding of others (Cu) (Crist, 1988). The authors also insisted that anions such as carboxylate groups were the most likely sites for electrostatic and covalent-type bonding. Fourest et al. [14] reported that cadmium binding by *S. fluitans* biomass was based on bridging or bidentate complex formation with the carboxyl groups of the alginate. They also reported that this biomass comprised sulfonate groups (0.27 meq/g ± 0.03) and alginate (45% of the dry weight) corresponding to 2.25 mequiv of carboxyl groups per gram of biomass. In parallel, the total amount of light metals displaced by protons when pH is brought down to pH 1.0 was approximately 2.53 meq/g for native *S. fluitans*, 3.05 meq/g for DW-washed *S. fluitans*, 3.61 meq/g for Ca-loaded *S. fluitans*, 3.76 meq/g for NaOH-treated *S. fluitans*, and 2.45 meq/g for crosslinked *S. fluitans*, respectively. The concentration of binding sites occupied by light metals throughout the pre-treatment process increased due to the extraction of biomass components, except for crosslinked *S. fluitans* biomass. However, these values for the cation exchange capacity are much less than those of q_{max} for Al uptake shown in Table 2. The carboxyl binding sites for Cd and Pb in *S. fluitans* biomass can be almost entirely blocked by reacting with propylene oxide (Fourest, 1996). In the case of Al uptake, the q_{max} for *S. fluitans* reacted with propylene oxide was approximately 6.53 meq/g. The difference of q_{max} between native *S. fluitans* and *S. fluitans* reacted with propylene oxide was 2.16 meq/g, corresponding to the amount of carboxyl group binding sites. This indicates that in addition to complexation by carboxyl groups Al biosorption by *S. fluitans* also occurs by another mechanism.

On the other hand, the weight of biomass during Al sorption changed with time and Al concentration. A weight loss of up to 14% was observed at the beginning of Al sorption when protonated *S. fluitans* biomass was used. This

was caused by the extraction of biomass components such as alginic acid, facilitated by the addition of NaOH for the pH adjustment. After an extended sorption period (30 hours), the weight of the biomass slightly increased with Al uptake. Despite the biomass components extraction, a 6% weight gain was observed with protonated biomass when the Al uptake at pH 4.5 was 62 mg/g of dry biomass. With the NaOH treated biomass, the weight gain during the sorption process was up to 23% at 101 mg/g of Al uptake. This indicated that the weight gain due to low Al uptake did not compensate for the weight loss due to the extraction of biomass components. At higher Al concentrations the weight gained through the Al uptake exceeded the biomass extraction losses. During Al sorption experiments, Na^+ ions were not sorbed in the biomass. On the other hand, the amount of NaOH added in order to adjust the pH when protonated biomass was used was higher than required for neutralization of protons released by Al uptake. The mole ratio between NaOH added and Al^{3+} uptake after 1.5 hours of sorption was approximately 4.24 ± 0.16 with protonated biomass. All results indicate that Al was sorbed by the algal biomass in the form of the hydroxide ion. Consequently, different reactions can be suggested for the uptake of Al^{3+} by algal biomass.

- Alginic acid extraction from protonated *S. fluitans* biomass:

$$B\text{-}pUCOOH + pNaOH \rightarrow B^- + pUCOO^-pNa^+ + pH_2O$$

where pU is polyuronic acid with p residues.

- Sorption by carboxyl groups of alginic acid:

* monodentate complexes

$$BCOOH + Al^{3+} + 3OH^- \rightarrow BCOOAl(OH)_2 + H_2O$$

* bidentate complexes

$$2BCOOH + Al^{3+} + 3OH^- \rightarrow (BCOO)_2AlOH + 2H_2O$$

With non-protonated *S. fluitans* biomass, carboxyl groups can be initially occupied by mono or divalent light metals.

- Sorption by additional identified neutral sites:

$$B\text{-}X + Al^{3+} + 3OH^- \rightarrow B\text{-}XAl(OH)_3$$

where, the fraction of carboxyl groups and X sites is approximately 20-35% and 65-80%, respectively.

The proportion of these reactions can vary with the biomass pretreatment.

It seemed that metal-algae interactions for neutral sites were based on the electrostatic attractions of $Al(OH)_3$.

4. Conclusions

Aluminum sorption characteristics and mechanisms of *Sargassum fluitans* biomass chemically or physically pretreated by different methods were studied. In the case of raw and protonated biomasses, the precipitation of aluminum-alginate complex and $Al(OH)_3$ was found in the aluminum nitrate solution. The difference in the sorption isotherm curves determined by analyses of residual or desorption solutions were mostly caused by the formation of external aluminum-alginate complex in the sorption solution. Higher amounts of NaOH added for pH control were required when protonated *S. fluitans* biomass was used.

The excessive weight gain of biomass indicates that aluminum was not sorbed as a simple metal ion but in a complexed hydroxyl form readily available from NaOH used for pH adjustment.

During Al sorption experiments, the amount of NaOH added in order to adjust the pH when protonated biomass was used was higher than required for neutralization of protons released by Al uptake.

Acknowledgement

This work has been supported by University of Ulsan Research Fund in 1997.

References

Bullock, A. L., 1965, DEAE cellulose, In *Methods in Carbohydrate Chemistry*, pp 409-411, Whistler, R. H., ed., Academic Press, NY.

Crist, R. H., J. R. Martin, D. Carr, J. R. Watson, H. J. Clarke, and D. R. Crist, 1994, *Environ. Sci. Technol.*, 28, 1859-1866.

Crist, R. H., K. Oberholser, N. Shank, and M. Nguyen, 1981, *Environ. Sci. Technol.*, 15, 1212-1217.

Crist, R. H., K. Oberholser, D. Schwartz, J. Marzoff, D. Ryder, and D. R. Crist, 1988, *Environ. Sci. Technol.*, 22, 755-760.

Fourest, E., and J. C. Roux, 1992, *Appl. Microbiol. Biotechnol.*, 37, 399-403.

Fourest, E., and B. Volesky, 1996, *Environ. Sci. Technol.*, 30, 277-282.

Gadd, G. M., 1988, In *Biotechnology*, Rehm, H. J., ed., Vol. 6b, Special Microbial Processes, pp 401-433, VCH Verlagesellschaft, Weinheim, Germany.

Greene, B., M. Hosea, M., R. McPherson, M. Henzl, M. D. Alexander, M. D., and D. W. Darnall, 1986, *Environ. Sci. Technol.*, 20, 627-632.

Haug, A., and B. Larsen, 1963, *Acta Chemica Scandinavica*, 17, 1653-1662.

Kuyucak, N., and B. Volesky, 1988, *Biotechnol. Lett.*, 10, 137-142.

Kuyucak, N., and B. Volesky, 1989, *Biorecovery*, 1, 189-204.

Lee H. S., and B. Volesky, 1997, *Water Research*, 31, 3082-3088.

Leusch, A., Z. R. Holan, and B. Volesky, 1995, *J. Chem. Tech. Biotechnol.* 62, 279-288.

Mann, H., W. S. Fyfe, and R. Kerrich, 1988, *Toxic. Assess.*, 3, 1-16.

Phillips, C. S. G., and R. J. P. Williams, 1966, Inorganic Chemistry, Vol. 2, p 265, Oxford Univ. Press, NY.

Treen-Sears, M. E., B. Volesky, and R. J. Neufeld, 1984, *Biotechnol. and Bioeng.*, 26, 123-129.

Volesky, B., 1990, Biosorption and Biosorbents in Biosorption of Heavy Metals B., pp 3-6, Volesky, B., ed., CRC Press, Boca Raton, FL.

Volesky, B. and Z. R. Holan, 1995, *Biotech. Prog.*, 11. 235-250.