

## Characteristics of Aluminum Biosorption by *Sargassum fluitans* Biomass

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**Abstract:** Biomass of nonliving 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 pH 4.5. There are indications that the biomass hydroxyl groups were involved in sequestering the aluminum in the form of polynuclear aluminum species. Aluminum-alginate complex (like cotton candy) was formed in the aluminum sorption solution as alginate was partially released from the biomass. Aluminum uptake of *S. fluitans* biomass was independent of residual alginate content in the biomass. Sodium ion added for pH adjustment was not adsorbed at all in the presence of aluminum ion.

**Key words:** Aluminum, biosorption, seaweed (*Sargassum fluitans*), biomass, light metals, aluminum-alginate complex.

### 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 has been outlined (Volesky and Holan, 1995). Most of the research on biosorption has focused on uptake of heavy metal by biomass of bacteria, actinomycetes, fungi, and algae (Gadd, 1988). 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 (Fourest

and Roux, 1992; Crist et al., 1994). While some biomass of brown algae provides an efficient and cheap material for biosorption, there has been a particular interest in aluminum adsorption because it may interfere with the uptake of heavy metals. The present work examines the aluminum adsorption characteristics 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.

### MATERIALS AND METHODS

#### Biomass Treatment

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. For DW-washed *S. fluitans*, the biomass

**Table 1.** Chemical and Physical Properties of Pretreated *S. fluitans* Biomass\*

| Biomass type   | Alginate (%) | Light metal (mmol/g) |       |       |       | $q_{\max}$ (mEq/g) | $b$ (mM) <sup>-1</sup> |
|----------------|--------------|----------------------|-------|-------|-------|--------------------|------------------------|
|                |              | Na                   | K     | Mg    | Ca    |                    |                        |
| Native         | 32           | 0.848                | 0.418 | 0.407 | 0.597 | 8.70               | 5.10                   |
| DW-washed      | 31           | 0.205                | 0.188 | 0.461 | 0.963 | 10.02              | 5.40                   |
| Protonated     | 45           | 0.000                | 0.000 | 0.009 | 0.013 | 7.52               | 4.77                   |
| Ca-loaded      | 28           | 0.000                | 0.000 | 0.040 | 1.801 | 8.56               | 5.13                   |
| NaOH-treated   | 36           | 0.490                | 0.031 | 0.461 | 1.180 | 11.18              | 6.38                   |
| Na-loaded (FC) | 4            | 2.291                | 0.000 | 0.007 | 0.010 | 11.59              | 6.44                   |

\*Langmuir isotherm constants ( $q_{\max}$  and  $b$ ) were determined at pH 4.5.

was washed five times with distilled water, and 1.5 g of raw biomass was added to 200 ml of distilled water (pH 6.5–7.3, 100-rpm shaking for 2 hours at room temperature) then filtered and finally dried overnight at 60°C. The weight loss of raw biomass was approximately 32%. For 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°C. The weight loss of biomass was approximately 31%. For Ca-loaded *S. fluitans*, 1.5 g of raw biomass was added to 200 ml of 0.5 mol/L Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O (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°C. The weight loss of biomass was approximately 25%. For NaOH-treated *S. fluitans*, the same procedure was used as for Ca-loaded *S. fluitans* except 0.1 N NaOH was used instead of 0.5 mol/L Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O. The weight loss of raw biomass was approximately 37%. Formaldehyde crosslinking followed a modified procedure of Bullock (1965). The weight loss of biomass throughout the pretreatment was approximately 39%.

### Sorption Experiments

Aluminum solutions of desired concentrations were prepared by dissolving Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O 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. We used 0.1 N HCl or 0.1 N NaOH for pH adjustments. At the end of each experiment, the samples were filtered (Millipore membrane, 0.18 µm) and the filtrate was analyzed by AAS (Thermal Jarell Ash, model Smith-Hieftje II) for the equi-

librium metal content. The filtered biomass was washed with distilled water and dried overnight at 60°C. 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 metal uptake was calculated from the results of desorption experiments as  $q$  (mmol/g) =  $V * C_f/M$ , where  $C_f$  is the final eluted metal concentration in the solution (mM),  $V$  is the solution volume (L), and  $M$  is the initial mass of the biosorbent used (g).

### RESULTS AND DISCUSSION

Table 1 shows the residual alginate contents and total binding sites of light metals eluted by acidic washing of pretreated *S. fluitans* in 0.1 N HCl. Alginate was extracted from the dry biomass using 3% solution of Na<sub>2</sub>CO<sub>3</sub>, according to the method of Percival and McDowell (1967). The concentration of alginate in the crude extracts of biomass was determined according to the method of Kennedy and Bradshaw (1987), using poly(hexamethylene-biguanidinium chloride) (PHMBH<sup>+</sup>Cl<sup>-</sup>) and UV spectrophotometry. These light metals account for about 6.5% of the initial dry weight of the alga, and the calculated ionic content was 2.27 mmol/g, or 3.27 mEq/g. Biomass components including impurities and alginate were extracted in about the same ratio throughout the distilled water washing. Biomass components were extracted during the acidic washing (0.1 N HCl), but little alginate was extracted and concentrated throughout the protonation process (ion exchange between protons and light metals such as Na, K, Mg, and Ca), and

transformed to alginic acid in the biomass. A part of the concentrated alginic acid in the biomass was easily (perhaps proportionately) extracted by the addition of NaOH and also accelerated the formation of external aluminum-alginate complex (like cotton candy) in the Al sorption solution.

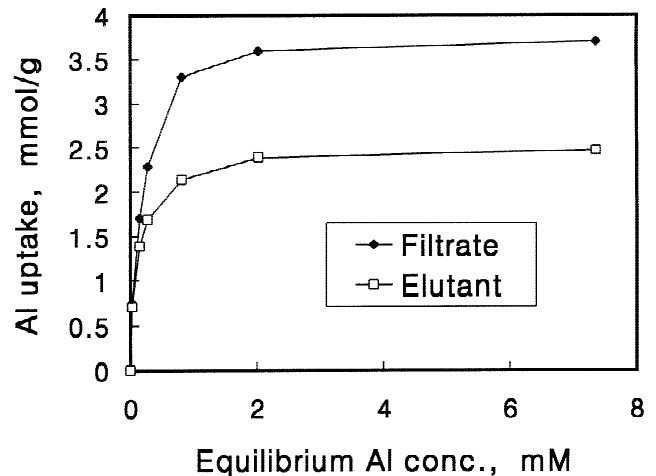
As shown Table 1, considering that the binding sites occupied by light metals for the cation exchange capacity are below 35% of  $q_{\max}$  for Al uptake, the binding site of Al ion is below one per Al molecule despite the trivalence ion. It seems that Al ion bound to biomass in the forms of polynuclear aluminum species such as  $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$  (Hsu and Bates, 1964) and  $Al_{13}(OH)_{32}^{7+}$  (Bottero et al., 1980). The molar ratio between NaOH added and  $Al^{3+}$  uptake after 1.5 hours of sorption was approximately  $4.24 \pm 0.16$  with protonated biomass. 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. This result also suggests that aluminum bound to biomass as hydroxide complexes or polynuclear aluminum species or both.

In the case of formaldehyde-crosslinked (Na-loaded) *S. fluitans*, the crosslinking reaction by formaldehyde and HCl was not effective for immobilizing alginate, which was transformed to alginic acid during the first treatment. This formed alginic acid was almost extracted from the biomass by 3%  $Na_2CO_3$  solution, and the Na ion was sorbed during this treatment. However, the total number of biomass binding sites bound to light metals was relatively low. Binding sites other than alginate still exist in the biomass. Other ions except Ca ion for Ca-loaded *S. fluitans* were almost extracted from the biomass. This result indicates that the affinity of Ca ion toward the biomass is higher than that of other light metals.

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

$$C_e/q = C_e/q_{\max} + 1/(bq_{\max}) \quad (1)$$

Results calculated by equation 1 for the pretreated *S. fluitans* are also given in Table 1. As shown in Table 1, the  $q_{\max}$  values of formaldehyde-crosslinked and NaOH-treated *S. fluitans* biomass were higher than those of others. Acid-treated (protonated) *S. fluitans* biomass had the lowest  $q_{\max}$



**Figure 1.** Aluminum uptake for protonated *S. fluitans* biomass. Filtrate was determined from sorption solution at pH 4.5 as  $q = V \times (C_i - C_e) / M$ . Elutant was determined from desorption solution at pH 1.1.

value. The lower the  $q_{\max}$  value and the higher the Al concentration, the more of aluminum-alginate complex was formed externally in the Al solution. Also, the higher the weight loss of biomass through the pretreatment procedure, the higher is the value of its  $q_{\max}$ . In the case of *S. fluitans* crosslinked by formaldehyde and HCl, the highest  $q_{\max}$  and weight loss (39%) could be observed through the pretreatment procedure despite the lowest binding site.

As shown in Figure 1, the difference between the sorption isotherm curves determined by analyses of residual or desorption solutions was mostly caused by the formation of external aluminum-alginate complex and  $Al(OH)_3$  precipitate in the sorption solution. The weight fraction of the alginate in the filter cake formed at 200 mg/L of Al equilibrium concentration was approximately 30%, based on the alginate analysis by UV spectrophotometry. Higher amounts of NaOH were required for pH control when protonated *S. fluitans* biomass was used because the Al solution tended to decrease to pH 2.8 to 3.2 when in contact with the biomass. Although no precipitate formed when formaldehyde-crosslinked and NaOH-treated *S. fluitans* biomass were added, the pH of the Al solution increased up to pH 4.1 to 4.4.

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 to adjust the pH. After an ex-

tended sorption period (30 hours), the biomass weight slightly increased with Al uptake. At higher Al concentrations, the weight gained through the Al uptake exceeded the biomass extraction losses. During Al sorption experiments, Na ion added for pH adjustment was not sorbed at all in the biomass.

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