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Interference of Aluminum in Copper Biosorption by an Algal Biosorbent

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Cu and Al sorption capacities of NaOH-treated *Sargassum fluitans* biomass were studied using equilibrium methodology. An evaluation of sorption performance and modeling in a two-metal system was carried out using a modified multicomponent Langmuir isotherm. The maximum Cu and Al uptakes calculated from the Langmuir isotherm were 1.54 mmol/g (9.8 weight percent) and 3.75 mmol/g (10.1 weight percent) at pH 4.5, respectively. However, these values were 1.35 mmol/g for Cu and 1.58 mmol/g for Al at pH 3.5. The modified Langmuir model gave the following affinity correlated coefficients: 0.20 for Cu and 6.82 for Al at pH 4.5, and 2.90 for Cu and 3.13 for Al at pH 3.5. The interference of Al in Cu biosorptive uptake was assessed by "cutting" the three-dimensional uptake isotherm surfaces at constant second-metal final concentrations. Equimolar final equilibrium concentrations of Cu and Al of 1 mM at pH 4.5 reduced Cu and Al uptakes by 83.4 and 5.5%, respectively. However, these reductions at pH 3.5 were 53.0 (Cu) and 29.1% (Al).

Key words: **aluminum, copper, biosorption, *Sargassum fluitans* biomass, two-metal system**

Introduction

Passive metal uptake, observed with a broad range of microbial biomass types, has been investigated to remove residual toxic or valuable heavy metals from industrial effluents. The potential of biosorption technology in the treatment of wastewater and environmental pollution control has been outlined earlier by Volesky (1990). Different dead biomass types, such as bacteria, fungi and algae, have been screened for their capability of adsorbing heavy metals from solutions (Volesky and Holan 1995). Considerable work carried out with seaweeds, specially from genera *Sargassum* and *Ascophyllum* (Holan et al. 1993; Kuyucak and Volesky 1988), showed high and even commercially attractive sorbent potential of such organisms for metal removal/recovery from dilute solutions. The presence of a large number of metals in industrial metal-bearing solutions makes it necessary to investigate the effect on the final metal uptake by individual biosorbent materials.

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Although aluminum is not considered a major environmental pollutant, its ubiquitous presence in solutions makes it an obvious target for investigation as to its effect on the biosorbent uptake of many other metals of interest, with copper being of primary interest because of its extensive use and increasing levels in the environment, although it is not acutely toxic (such as cadmium, lead and mercury) to humans.

Simple sorption isotherm curves are usually constructed as a result of studying equilibrium batch sorption behaviour of different biosorbent materials. They enable quantitative evaluation of sorption performance of these materials in conjunction (conventionally only) with one metal (de Carvalho et al. 1994). However, when more than one metal is present in the sorption system, the evaluation of biosorption results, and the interpretation and representation of metals become much more complicated. With two metals in the solution, instead of a two-dimensional biosorption isotherm curve, the system evaluation results in a series of three-dimensional sorption isotherm surfaces (de Carvalho et al. 1995). This representation of cadmium biosorption by *Ascophyllum nodosum* biomass in a two-metal system showed the competitive and inhibitive behaviour of the metals present. In order to facilitate such a study, mathematical models had to be proposed and examined for their suitability (Chong and Volesky 1995). However, the sorption isotherm surfaces have not been smoothed and showed irregularities which may or may not truly reflect the behaviour of the two-metal sorption system. Moreover, the sorption performance of the "virgin" biosorbent studied then was affected by the alginate leached from it (de Carvalho et al. 1994), making it difficult to extrapolate the sorption uptake values over the range of the biosorption studies conducted.

This work illustrates a quantitative approach to an evaluation of the sorption capacity of a well-stabilized NaOH-treated *S. fluitans* biosorbent, prepared from the biomass of the brown marine alga, in conjunction with solutions containing two metals of interest: Al and Cu. The objective of the present work was to evaluate a two-metal biosorption system behaviour, involving copper, aluminum and a generally high metal-sorbing biosorbent material of *Sargassum* seaweed. This is considered a first step in studying multimetal biosorption systems representing more closely industrial effuents.

Materials and Methods

Biomass Preparation

Raw *S. fluitans* biomass was collected sun-dried on a beach near Naples, Florida. Dry raw biomass was treated by soaking in 0.1 N NaOH solution in flasks shaken gently on a gyrotory shaker. A sample of 1.5 g of raw biomass was added to 200 mL of 0.1 N NaOH (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 37%. Biomass components such as salt, soluble alginate, pigments and water were removed during 0.1 N NaOH treatment.

Sorption Experiments

Metal solutions were prepared by dissolving $Al(NO_3)_3$ and $Cu(NO_3)_2$ in distilled deionized water to desired initial concentrations. All sorption experiments were performed by suspending 100 mg of biomass in 50 mL of the metal-bearing solution and shaking on a gyrotory shaker for 30 hours. For pH adjustment, 0.1 N HCl or 0.1 N NaOH was used. At the end of each experiment, the samples were filtered (Millipore membrane, 0.18 μm) and the filtrate was analyzed by atomic absorption spectrophotometer (Thermo Jarell Ash, model Smith-Hieftje II, Waltham, Mass.) for the equilibrium metal content. The filtered biomass was washed with distilled water and dried overnight at 60°C, and then weighed for desorption experiments. 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°C and then weighed. 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 (mmol/L), V is the solution volume (L), and M is the initial mass of the biosorbent used (g).

Three-Dimensional Sorption Isotherm Surfaces

The procedure for the equilibrium batch sorption experiments was the same as described above. The 3-D sorption surfaces were obtained by plotting the experimentally determined final (equilibrium) metal concentrations of both metals on the x and y coordinates, respectively, against the Al, Cu or total metal uptakes, respectively, on the z-coordinate. The computer program MATLAB 4.0 was used for this purpose. This program is a high performance interactive software package for scientific and engineering numeric computation capable of plotting a 3-D diagram based on randomly generated experimental data. It can either simply connect the experimental data points using a 3-D interpolating mesh or it can fit a smoothed surface to data. The latter approach, which is more desirable, requires the MATLAB user to input an appropriate equation representing the surface.

Results and Discussion

Single-Metal Sorption

The sorption performance of *S. fluitans* biomass was evaluated through determining the sorption isotherms for the material with Al and

Cu before examining it in solutions containing both metals. As the mechanism of metal uptake by the Sargassum biomass was confirmed to be based on ion exchange (Holan et al. 1993; Schiewer and Volesky 1995), the single-metal sorption behaviour (Fig. 1) of the material was particularly well approximated by a simple Langmuir-type isotherm model:

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

where C_e is the equilibrium metal concentration in the sorption solution. Equation 1 allowed the determination of the maximum metal uptake (q_{max}) and the Langmuir coefficient K ($k_{adsorption}/k_{desorption}$), relating to the "affinity" of the biosorbent for the given metal, both calculated from fitting the Langmuir sorption model to the experimental data.

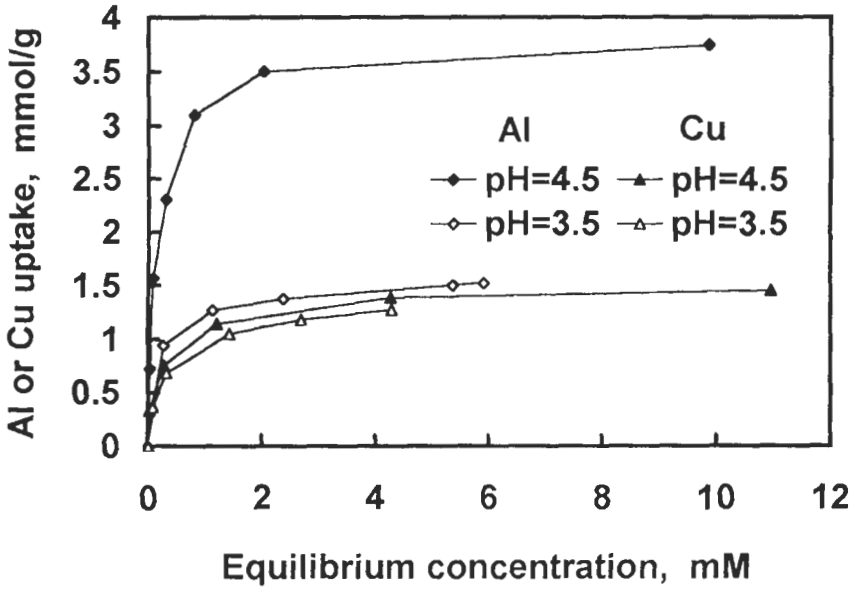

Fig. 1. Effect of pH on the single-metal sorption for the NaOH-treated *S. fluitans* biomass.

Results calculated by equation 1 for NaOH-treated *S. fluitans* are given in Table 1. The maximum Al uptake value obtained at pH 4.5 was much higher than that for the other metal. As shown in Fig. 1, the biosorbent uptake of aluminum was strongly affected by the pH of the solution, while the uptake of copper was only slightly affected by the pH. The total binding sites of light metals displaced by protons when pH was brought down to pH 1.0 was approximately 3.80 meq/g for NaOH-treated *S. fluitans* (Lee and Volesky 1997). However, considering that the binding sites

Table 1. Single-metal sorption constants for NaOH-treated *S. fluitans* biomass

Metal	Equilibrium pH	q_{max} (mmol/g)	K $(mM)^{-1}$
Al	4.5	3.74	6.49
Al	3.5	1.58	3.92
Al	2.5	0.95	2.9
Cu	4.5	1.54	3.82
Cu	3.5	1.35	3.21
Cu	2.5	0.65	2.10

occupied by light metals for the cation exchange capacity were below 34% of q_{max} for Al uptake, the binding site of Al ion at pH 4.5 was below one-per-Al molecule in spite of the ion tri-valence. It was probable that Al ion was bound to biomass in the form of polynuclear aluminum species such as $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$ (Hsu and Bate 1964) and $Al_{13}(OH)_{32}^{7+}$ (Bottero et al. 1980).

Modeling in Two-Metal System at Fixed pH

Creating an interpolated sorption isotherm surface without smoothing the experimental data randomly generated results in surface irregularities. Smoothing of the sorption isotherm surface is possible through assigning a mathematical model to it which can represent the randomly distributed experimental data (Volesky and Holan 1995; Chong and Volesky 1995). This approach makes it possible to eventually derive two-dimensional sorption isotherm curves from the 3-D sorption isotherm surface image by cutting with parallel "iso-concentration" planes for one or the other metal selected concentration values, respectively. The resulting set of sorption isotherm curves depicts either the effect of the second metal on the biosorption of the first one, or vice versa, in an easily understandable manner. These curves reflect then correctly the actual equilibrium biosorption conditions as appropriate (de Carvalho et al. 1995).

In order to propose the most suitable equation to represent the sorption data in a 3-D space, the modified binary Langmuir model was investigated. The model produced an equation with three parameters. These parameters, related to each of the two-metal systems studied, were evaluated by minimizing the sum of squared residuals (residual refers to the difference between experimental metal uptake and that predicted from the model). Again, the MATLAB 4.0 program was used for this purpose.

When equilibrium is established:

$$B + M_1 \Leftrightarrow B\text{-}M_1 \qquad K_1 = k_1/k_{-1} \tag{2}$$

$$B + M_2 \Leftrightarrow B\text{-}M_2 \qquad K_2 = k_2/k_{-2} \tag{3}$$

where [B] is the concentration (number) of unoccupied binding sites, $[B_o]$ is the total concentration (number) of binding sites, M_1 is the metal 1, and M_2 is the metal 2.

Assume:

$$d[B\text{-}M_1]/dt = 0, \qquad d[B\text{-}M_2]/dt = 0 \tag{4}$$

(The sorption system is in equilibrium: there are no net changes of $[B\text{-}M_1]$ and $[B\text{-}M_2]$ with respect to time.)

$$[B_o] = [B] + [B\text{-}M_1] + [B\text{-}M_2] \tag{5}$$

Result:

$$[B\text{-}M_1] = \frac{[B_o]\,[M_1]}{1/K_1 + [M_1] + (K_2/K_1)[M_2]} \tag{6}$$

We define $[B\text{-}M_1]$ as the number of binding sites occupied by M_1 per gram of biosorbent and $[B_o]$ as the total number of binding sites per gram of biosorbent. Then, by multiplying both sides by a value having the units of "mmol M_1 per number of binding sites", we obtain equations 7 and 8, where q_{max} is the maximum uptake of metal sorbed, K_1 and K_2 are the adsorption equilibrium constants ($k_{adsorption}/k_{desorption}$), and $q(M_1)$ is the amount of metal M_1 sorbed at the final equilibrium concentration ($C_e[M_1]$ and $C_e[M_2]$) of metals M_1 and M_2.

$$q(M_1) = \frac{q_{max}{}^{*}K_1C_e[M_1]}{1 + K_1C_e[M_1] + K_2C_e[M_2]} \tag{7}$$

$$q(M_2) = \frac{q_{max}{}^{*}K_2C_e[M_2]}{1 + K_1C_e[M_1] + K_2C_e[M_2]} \tag{8}$$

The fit of the model to the data was assessed using the correlation coefficient R, which indicates how good the fit is. The closer this number is to 1, the better the fit. The correlation coefficient is defined as

$$R = \{1 - \sigma_w{}^2/\sigma_z{}^2\}^{0.5} \tag{9}$$

where σ_z is the standard deviation of z given as

$$\sigma_z = [\{\Sigma\,(q_i - q_m)^2\}/(n - 1)]^{0.5} \tag{10}$$

and σ_w is the standard error given as

$$\sigma_w = [\{\Sigma\,(q_i - q_c)^2\}/(n - 1)]^{0.5} \tag{11}$$

The q_i are the actual data points and the q_c are the calculated values from model for the same value of x and y. The number of experiments is n and the mean of the experimental data is denoted as q_m. The results of the error analysis are tabulated in Table 2. The model fits for two-metal biosorption were well predicted since all the correlation coefficients were more than 0.90.

Table 2. The model fit for two-metal biosorption

	Total uptake		Cu uptake		Al uptake	
	pH 3.5	pH 4.5	pH 3.5	pH 4.5	pH 3.5	pH 4.5
Standard deviation	0.71	0.85	0.48	0.56	0.82	1.12
Standard error	0.20	0.31	0.13	0.19	0.23	0.49
Correlation coefficient	0.96	0.93	0.96	0.94	0.96	0.90

Al-Cu System with NaOH-Treated *S. fluitans*

When both ions were present in the solution (two-metal experiments), some reduction of the Cu uptake could be observed with increasing Al concentrations. This is well indicated in the series of simple isotherm curves generated as "iso-concentration cuts" of the three-dimensional plots whereby the two (equilibrium) metal concentrations are plotted against Cu (Fig. 2), Al (Fig. 3) and total metal uptakes (Fig. 4), respectively. The modified Langmuir model equation can be represented by 3-D sorption isotherm surfaces presented in Fig. 2(a), 3(a) and 4(a). While these 3-D isotherm surfaces represent the summary of the two-metal equilibrium results, the selected cuts through the 3-D diagrams presented in Fig. 2(b) and 3(b) at pH 4.5 and those in Fig. 2(d) and 3(d) at pH 3.5 better reveal the quantitative trends observed in the two-metal systems. Moreover, the effect of the secondary metal presence on the uptake of the primary metal can be summarized from these plots as seen in Fig. 2(c) and 3(c) for Cu and Al sorption, respectively.

The uptake of Cu at pH 4.5 (Fig. 2[b]) was greatly reduced by the presence of Al, whereas the uptake of Al (Fig. 3[b]) remained relatively constant when Cu was present. The Cu uptake reduction was much more pronounced at pH 4.5 (uptake q = 2.72 mmol Al/g at $C_{f,Al}$ = 1.0 mM was taken as 100%; uptake q = 0.95 mmol Cu/g was at $C_{f,Cu}$ = 1.0 mM was taken as 100%). Equimolar final equilibrium concentrations of Cu and Al of 1 mM at pH 4.5 reduced Cu and Al uptakes to 16.6% and 94.5%, respectively. However, these values at pH 3.5 were 47.0% (Cu) and 70.9% (Al) (Fig. 2(d) and 3[d]). It was found that the maximum uptake of Al at pH 4.5 (Fig. 2(b) and 3[b]) was much higher than that of Cu, 3.10 mmol/g versus 1.80 mmol/g. These values differed from the ones (3.75 mmol/g for

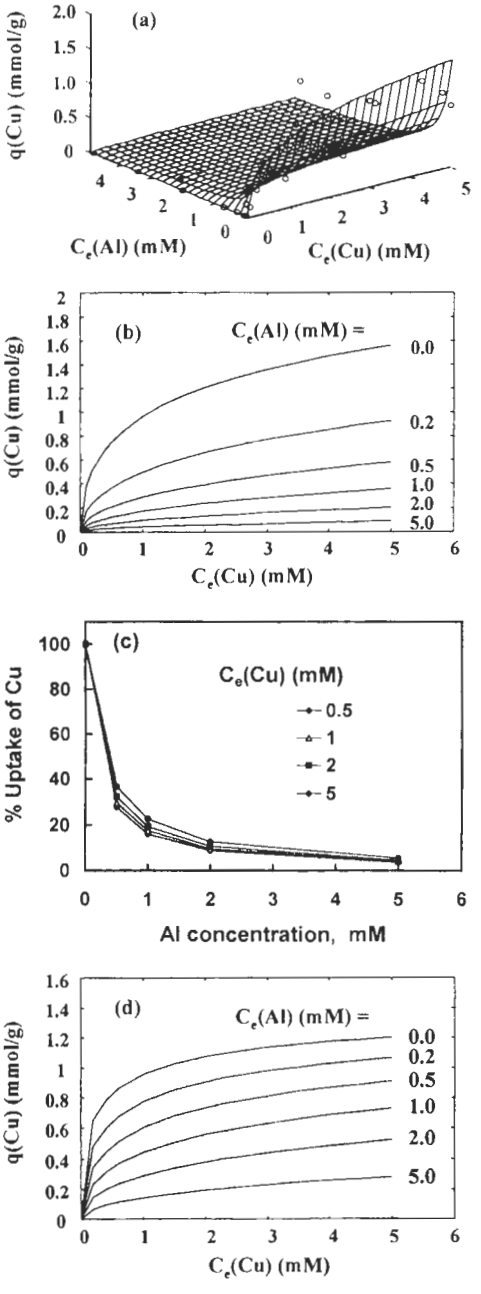

Fig. 2. **(a)** Three-dimensional sorption surface for the Cu-Al biosorption system: copper uptake at pH 4.5. **(b)** Effect of Al on the equilibrium uptake of Cu by NaOH-treated *S. fluitans* biomass at pH 4.5. **(c)** The summary of the effect of Al presence on the Cu uptake NaOH-treated *S. fluitans* biomass at pH 4.5. Equilibrium Cu concentrations arbitrarily selected. **(d)** Effect of Al on the equilibrium uptake of Cu by NaOH-treated *S. fluitans* biomass at pH 3.5.

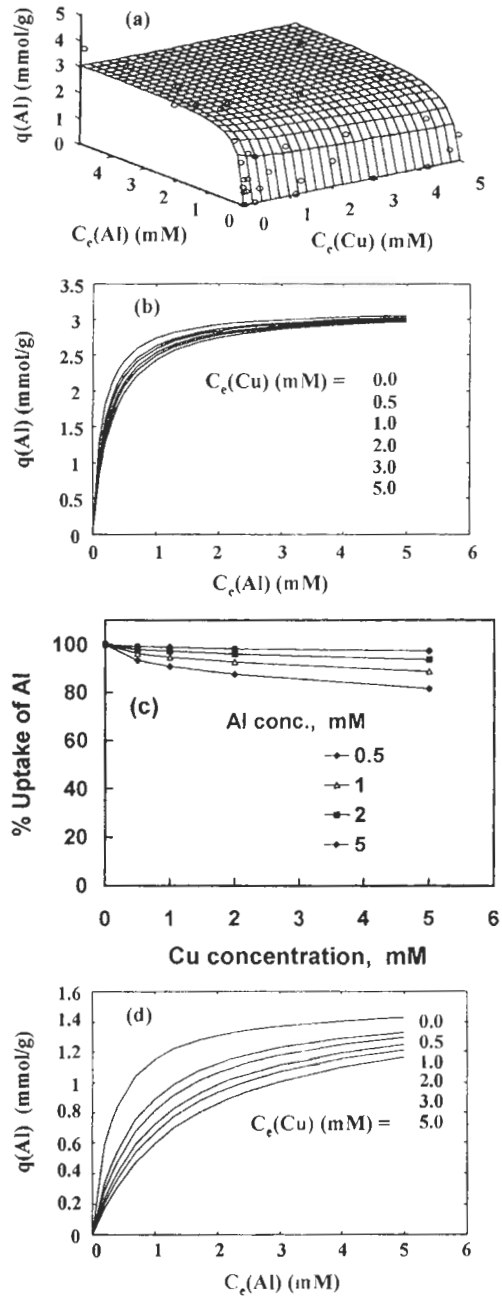

Fig. 3. (a) A three-dimensional sorption surface for the Cu-Al biosorption system: aluminum uptake at pH 4.5. **(b)** Effect of Cu on the equilibrium uptake of Al by NaOH-treated *S. fluitans* biomass at pH 4.5. **(c)** Summary of the effect of Cu presence on the Al uptake NaOH-treated *S. fluitans* biomass at pH 4.5. Equilibrium Al concentrations arbitrarily selected. **(d)** Effect of Cu on the equilibrium uptake of Al by NaOH-treated *S. fluitans* biomass at pH 3.5.

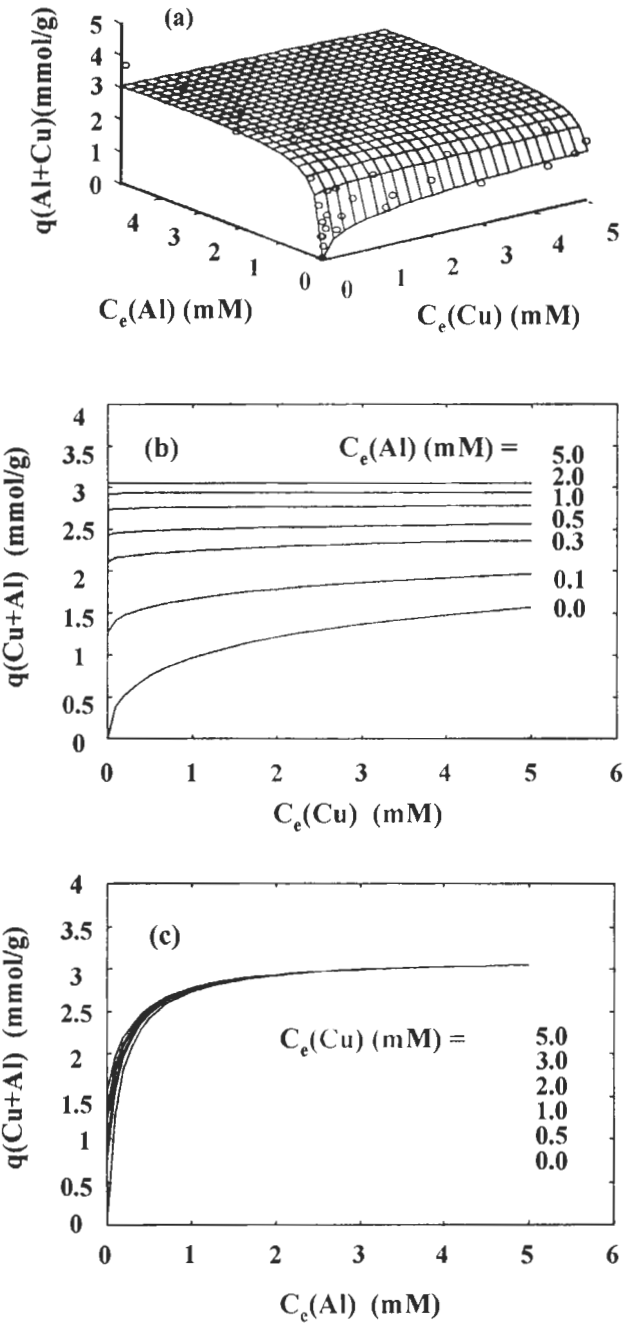

Fig. 4. (a) A three-dimensional sorption surface for the Cu-Al biosorption system: total metal uptake at pH 4.5. **(b)** Effect of Al on the equilibrium total metal uptake by NaOH-treated *S. fluitans* biomass at pH 4.5. **(c)** Effect of Cu on the equilibrium total metal uptake by NaOH-treated *S. fluitans* biomass at pH 4.5.

Al and 1.54 mmol/g for Cu) obtained from the respective single-metal systems. The number of binding sites for Al was reduced only marginally in the presence of Cu, while those for Cu slightly increased in the presence of Al. The maximum uptake of Al at pH 3.5 (1.50 mmol/g) was only slightly higher than that of Cu (1.30 mmol/g). The Al uptake was very sensitive to the pH of the solution as could be expected if Al was sorbed in the form of polynuclear aluminum species.

Figures 4(b) and 4(c) were obtained when the total metal uptake sorption surface was analyzed and viewed in two series of "iso-concentration cuts" by constant Al or Cu concentration planes, respectively. In summary, they showed that when *Sargassum* biosorbent became saturated in the system containing high concentrations of both metals of interest (Al and Cu in this study), the common maximum total metal uptake approached a value of 3.14 mmol/g. It should be noted that the lowest isotherm curves in Fig. 4(b) and (c) represent the one-metal biosorption isotherm for Al and Cu, respectively.

The curves resulting from the cuts of the 3-D diagrams conformed well to the modified Langmuir model. The Langmuir parameters (K_1 for Cu and K_2 for Al), the ratio of the adsorption rate constant to the desorption rate constant, are an indication of the "relative affinity" of the biosorbent towards a metal. K_1 and K_2 values from the modified Langmuir model are as follows: 0.20 $(mM)^{-1}$ and 6.82 $(mM)^{-1}$ at pH 4.5, 2.90 $(mM)^{-1}$ and 3.13 $(mM)^{-1}$ at pH 3.5, 2.39 $(mM)^{-1}$, and 3.51 $(mM)^{-1}$ at pH 2.5.

As shown in Table 1, the maximum uptake and the relative affinity of Al in the one-metal system relatively increased between pH 3.5 and 4.5. Within this pH range, the relative affinity of Al in the (Al+Cu) system also greatly increased, but the relative affinity of Cu in the (Al+Cu) system oppositely decreased.

Quantitative expressions of the preferential Al biosorption in the (Al+Cu) system are greatly dependent on the pH of solution between pH 3.5 and 4.5. This competitive binding by *Sargassum* biomass at pH 4.5 was similarly observed in the (Al+Pb), (Al+Cd), (Al+Zn) and (Al+Cr) system (unpublished work). As described previously in single-metal sorption, Al ion was sequestered to the biomass in the form of polynuclear aluminum species such as $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$ (Hsu and Bate 1964) and $Al_{13}(OH)_{32}{}^{7+}$ (Bottero et al. 1980), and these polymerized aluminum ions prevented other heavy metals from accessing the binding sites.

The initial pH of the aluminum nitrate solution decreased from pH 3.9 to 3.6 with increasing Al concentrations (0.5-5.0 mM). These pH values varied after the addition of NaOH-treated *S. fluitans* 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. While no precipitate was observed when NaOH-treated *S. fluitans* biomass was added to the aluminum nitrate solution, the pH of the Al solution increased up to pH 4.1to 4.4. Within this experimental range of two-metal system, Al ion in the sorption solution still existed in the form of polynuclear aluminum species despite NaOH addition for pH control.

Future work should investigate these phenomena, which are apparently related to the mechanisms of metal biosorption. However, one has to realize the complexity of investigating the mechanisms of biosorption, which could be any or a combination of these processes: complexation, ion exchange, physical adsorption, chelation or inorganic microprecipitation of metals. Sorption preferences observed with NaOH-treated *S. fluitans* biomass and the results of the competition aspects observed will likely have repercussions in the continuous-flow dynamic sorption column system. A net sorption preference for Al uptake over Cu in the relevant concentration range studied (0.0 to 5.0 mM) indicates the possibility of its use in a flow arrangement as a "selective filter" for enrichment of given metallic species. Other authors reported that the use of microbial biosorbent for separation of Pd from Cu (Brierley and Vance 1988) or resins for separation of Cu from Zn (Akita and Takeuchi 1990). It is important to stress that a change in the pH of the sorption system could significantly alter the sorption capacities and preferences in the two-metal sorption system studied.

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