

Interference of Aluminum in Heavy Metal Biosorption by a Seaweed Biosorbent

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Abstract—Heavy metal and Al sorption capacities of Ca-loaded *Sargassum fluitans* biomass were studied by using equilibrium methodology. An evaluation of sorption performance and modeling in a two-metal system was carried out with a modified multi-component Langmuir isotherm. The maximum uptakes of Cr, Pb, Cu, Cd, Zn and Al calculated from the Langmuir isotherm were 1.74 mmol/g, 1.65 mmol/g, 1.61 mmol/g, 1.15 mmol/g, 0.81 mmol/g, and 2.95 mmol/g at pH 4.5, respectively. The interference of Al in heavy metal biosorptive uptakes was assessed by 'cutting' the three-dimensional uptake isotherm surfaces at constant second-metal final concentrations. The reduction of Pb, Cu, Zn, Cd and Cr uptakes at its final equilibrium concentrations of 1 mM at pH 4.5 was 78.4%, 82.7%, 85.1%, 89.8% and 51.2% in the presence of 1mM Al ion, respectively. The presence of Al ion greatly affected the uptake of all heavy metals tested except Cr.

Key words: Aluminum, Heavy Metals, Biosorption, *Sargassum fluitans*, Ca-Loaded 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 was outlined earlier by Volesky [1990]. Different dead biomass types, such as bacteria, fungi and algae, have been screened for their capabilities of adsorbing heavy metals from solutions [Volesky and Holan, 1995; Lee et al., 1999; Yu and Kaew-sarn, 1999]. Considerable work carried out with seaweeds, especially 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 bio-sorbent materials.

Although aluminum is not considered as 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 toxic metals such as cadmium, lead and chromium.

Simple sorption isotherm curves are usually constructed as a result of studying equilibrium batch sorption behavior of different bio-sorbent materials. They enable quantitative evaluation of sorption performance of these materials in conjunction (conventionally only) with one metal [de Carvalho et al., 1994; Lee and Moon, 2001]. However, when more than one metal is present in the sorption system, the evaluation of biosorption results, their interpretation and representation become much more complicated. With two metals in the solution, instead of a 2-dimensional biosorption isotherm curve, the system evaluation results in a series of 3-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 behavior of the metals present. In order to facilitate such 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 behavior 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 Ca-loaded *S. fluitans* bio-sorbent, prepared from the biomass of the brown marine algae, in conjunction with solutions containing two metals of interest: Al and a heavy metal among Cu, Cd, Pb and Cr. The objective of the present work was to evaluate a two-metal biosorption system behavior involving heavy metals, aluminum and a generally high metal-sorbing biosorbent material of *Sargassum* seaweed. We also assessed the extent of the interference of aluminum ion for the uptake of heavy metals coexistent with it.

EXPERIMENTAL

1. Materials

Raw *S. fluitans* biomass was collected and sun-dried on the beach near Naples, Florida. Dry raw biomass was treated by soaking in 0.5 M CaCl₂ solution in flasks shaken gently on an orbital shaker. Two grams of raw biomass was added to 500 mL of 0.5 M CaCl₂ (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 0.5 M CaCl₂ treat-

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ment.

2. Sorption Experiments

Metal solutions were prepared by dissolving $\text{Al}(\text{NO}_3)_3$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ in distilled deionized water to desired initial concentrations. All sorption experiments were performed by suspending 100 mg of biomass in 100 mL of the metal-bearing solution and shaking on a gyratory shaker for 30 hours. 0.1 N HCl or 0.1 N NaOH was used for pH adjustment. At the end of each experiment, the samples were filtered (Millipore membrane, 0.18 μm) and the filtrate was analyzed by atomic absorption spectrophotometer (Shimatsu AA 680) 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 gyratory 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 $q \text{ (mmol/g)} = V \cdot C_f / M$ 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).

3. 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, respectively, on the x and y coordinates against the Al, heavy metals (such as Cd, Pb, Cr and Cu) or total metal uptakes, respectively, on the z-coordinate. The computer program MATLAB 5.0 was used for this purpose. MATLAB (Version 5.0), a high performance interactive software package for scientific and engineering numeric computation, is 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

1. Single-Metal Sorption

The total amount of light metals (such as Na, K, Mg and Ca) displaced by H^+ ions at pH 1.1 was approximately 2.27 mmol/g (6.96 wt%) for native *S. fluitans*. Na^+ and K^+ ions bound to alginate were easily released with it at pH 7. [Lee and Volesky, 1997]. In order to remove the effect of water-soluble alginate and raise the accuracy of sorption experiments, Ca-loaded *S. fluitans* biomass was prepared with 0.5 M CaCl_2 .

The sorption performance of *S. fluitans* biomass was evaluated through determining the sorption isotherms for the material with Al and heavy metals, respectively, before examining it in solutions containing both metals together. As the mechanism of metal uptake by the Ca-loaded biomass was confirmed to be based on ion exchange [Lee and Suh, 2000; Lee and Volesky, 1997], the single-metal sorption behavior (Fig. 1) of the material was particularly well

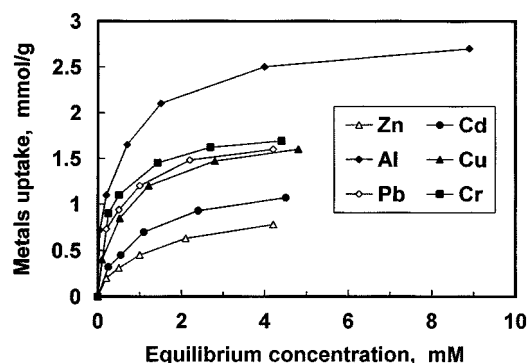


Fig. 1. The amount of single-metal sorption for the Ca-loaded *S. fluitans* biomass at pH 4.5.

Table 1. Single-metal sorption constants for Ca-loaded *S. fluitans* biomass at pH 4.5

Metal	q_{\max} (mmol/g)	$K \text{ (mM)}^{-1}$
Al	2.95	5.41
Cr	1.74	4.52
Pb	1.65	3.29
Cu	1.61	2.32
Cd	1.15	1.91
Zn	0.81	1.16

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. Eq. (1) allowed the determination of the maximum metal uptake (q_{\max}) and the Langmuir coefficient K ($k_{\text{adsorption}}/k_{\text{desorption}}$), relating to the 'affinity' of the biosorbent for the given metal, both calculated from fitting the Langmuir sorption model to the experimental data.

Results calculated by Eq. (1) for Ca-loaded *S. fluitans* are given in Table 1. The affinity of the metal ions towards the biomass shows a tendency to increase with increasing the maximum metal uptake. As shown in Fig. 1, the biosorbent uptake of aluminum was higher than that of other heavy metals. The total binding sites of light metals displaced by H^+ ions when pH was brought down to pH 1.0 was approximately 3.4 meq/g for Ca-loaded *S. fluitans* [Lee and Volesky, 1997]. However, considering that the binding sites occupied by calcium ion for the cation exchange capacity were below 39% of q_{\max} for Al uptake, the binding site of Al ion at pH 4.5 was about 1.2 per Al molecule in spite of tri-valence ion. It was probable that Al ion was bound to biomass in the form of polynuclear aluminum species such as $\{\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}\}^{6+}$ [Hsu and Bate, 1964] and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ [Bottero et al., 1980].

2. Metal Uptake in Two-Metal System at Fixed pH

Creating an interpolated sorption isotherm surface without smoothing the randomly generated experimental data results in surface irregularities. Smoothing of the sorption isotherm surface is possible through assigning a mathematical model to it that can represent the randomly distributed experimental data [Chong and Volesky, 1995]. This approach makes it possible to eventually derive two-dimensional sorption isotherm curves from the 3-D sorption isotherm sur-

Table 2. The model fit for the metal uptake in two-metal system

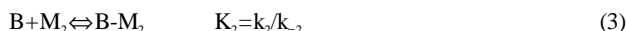
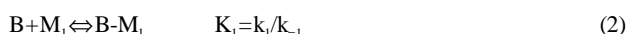
	Al-Cr system			Al-Pb system			Al-Cu system			Al-Cd system			Al-Zn system		
	Total	Cr	Al	Total	Pb	Al	Total	Cu	Al	Total	Cd	Al	Total	Zn	Al
Standard deviation	1.79	1.85	1.71	0.96	0.88	0.99	0.92	0.87	0.94	0.86	0.82	0.93	0.82	0.79	0.85
Standard error	0.62	0.55	0.67	0.53	0.49	0.58	0.49	0.45	0.52	0.42	0.37	0.48	0.37	0.29	0.41
Correlation coeff.	0.84	0.81	0.88	0.89	0.93	0.86	0.92	0.95	0.90	0.93	0.95	0.91	0.95	0.97	0.92

face 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 then correctly reflect 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 5.0 program was used for this purpose.

The modified binary form of Langmuir was derived as the following equations [Chong and Volesky, 1995].

When equilibrium is established:



where

B=biomass

M₁=metal 1; M₂=metal 2.

$$q(M_1) = \frac{q_{\max} * K_1 C_e(M_1)}{1 + K_1 C_e(M_1) + K_2 C_e(M_2)} \quad (4)$$

$$q(M_2) = \frac{q_{\max} * K_2 C_e(M_2)}{1 + K_1 C_e(M_1) + K_2 C_e(M_2)} \quad (5)$$

where q_{\max} is the maximum uptake of metal sorbed, K_1 and K_2 are the adsorption equilibrium constants ($k_{\text{adsorption}}/k_{\text{desorption}}$), and $q(M_1)$ is the amount of metal M₁ sorbed at the final equilibrium concentration ($C_e[M_1]$ and $C_e[M_2]$) of metals M₁ and M₂.

The fit of the model to the data was assessed by 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:

$$R = \{1 - \sigma_z^2 / \sigma_z^2\}^{0.5} \quad (6)$$

where σ_z is the standard deviation of z given as

$$\sigma_z = [\{\sum (q_i - q_m)^2\} / (n-1)]^{0.5} \quad (7)$$

and σ_w is the standard error given as

$$\sigma_w = [\{\sum (q_i - q_c)^2\} / (n-1)]^{0.5} \quad (8)$$

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 ex-

periments 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 greater than 0.81. These values were decreased as the uptake of heavy metals increased. In the case of Al-Cr system, Cr ion in addition to Al ion is tri-valence and the

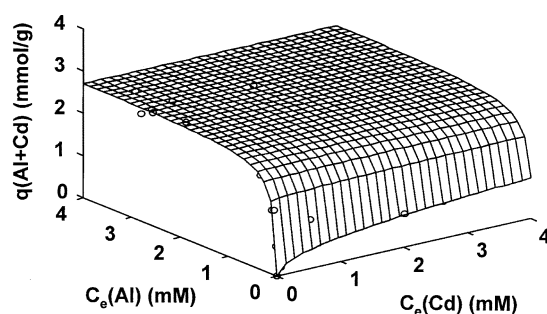


Fig. 2. A 3-dimensional sorption surface for total metal uptake of the Cd-Al biosorption system at pH 4.5.

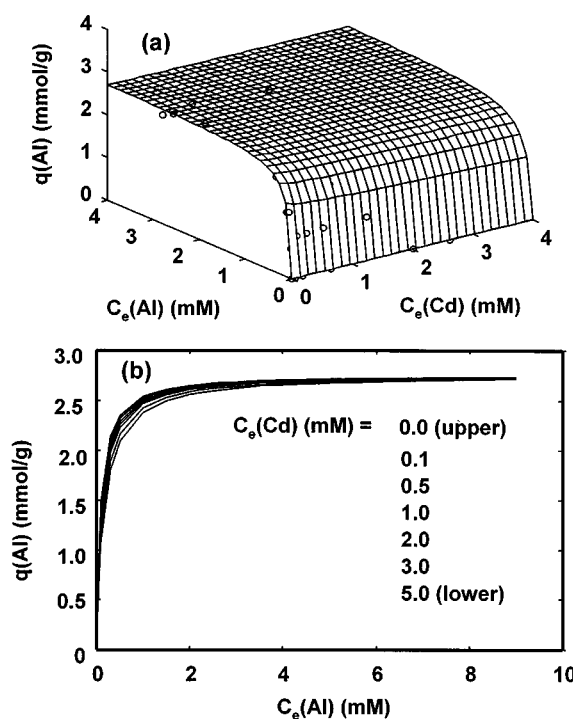


Fig. 3. (a) A 3-dimensional sorption surface for Al uptake of the Cd-Al biosorption system at pH 4.5. (b) Effect of Cd on the equilibrium uptake of Al by Ca-loaded *S. fluitans* biomass at pH 4.5.

model fits are the worst. It seems that a part of Cr ion was bound to the biomass as mono- $(\text{Cr}(\text{OH})_2^+)$ or di-ion $(\text{Cr}(\text{OH})_2^{2+})$ valence.

3. Interference of Al Ion in Heavy Metals Biosorptive Uptake

The total metal uptake sorption surface is the product of adding the two individual metal uptake surfaces. The modified Langmuir model equation can be represented by 3-D sorption isotherm surfaces presented in Fig. 2, 3(a), and 4(a). Fig. 2 shows that, with high levels of overall metal concentration present in the solution, the biosorbent easily reaches the saturation level demonstrated by a wide plateau of the surface for the Cd-Al biosorption system. When both Al and Cd ions were present in the solution together (2-metal experiments), some reduction of the Cd (or Al) uptake could be observed with increasing Al (or Cd) 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 Al [Fig. 3(a)], and

Cd [Fig. 4(a)], respectively. 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. 3(b) and 4(b) at pH 4.5, better reveal the quantitative trends observed in the two-metal systems. The uptake of Cd at pH 4.5 [Fig. 4(b)] was greatly reduced by the presence of Al, whereas the uptake of Al [Fig. 3(b)] remained relatively constant when Cd was present. The effect of the presence of Al ion on the uptake of the Cd ion can be summarized from this plot as seen in Fig. 4(c) for Cd sorption.

The Cd uptake reduction was much more pronounced at pH 4.5 (uptake $q=2.52$ mmol Al/g at $C_{e,\text{Al}}=1.0$ mM was taken as 100%; uptake $q=0.58$ mmol Cd/g was at $C_{e,\text{Cd}}=1.0$ mM was taken as 100%). Equimolar final equilibrium concentrations of Cd and Al of 1 mM at pH 4.5 reduced Cd and Al uptakes to 10.2% and 96.5%, respectively. It was found that the maximum uptake of Al at pH 4.5 [Fig. 3(b) and 4(b)] was much higher than that of Cd, 2.75 mmol/g versus 1.22 mmol/g. These values differed from the ones (2.95 mmol/g for Al and 1.15 mmol/g for Cd) obtained from the respective single-metal systems. The number of binding sites for Al was reduced only marginally in the presence of Cd, while those for Cd slightly increased in the presence of Al. 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 at pH 4.5 [Bottero et al., 1980; Hsu and Bates, 1964].

The curves resulting from the cuts of the 3-D diagrams confirmed well to the modified Langmuir model. The Langmuir parameters, K_1 for Cd 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: 0.09 (mM) $^{-1}$ and 14.62 (mM) $^{-1}$ at pH 4.5.

Comparing K values of Table 1 to K_1 and K_2 values of Table 3, the lower the K value of heavy metal in single-metal system, the higher was found the relative affinity of Al ion and the lower was found the relative affinity of heavy metal ion in two-metal system.

In summary, they showed that when *Sargassum* biosorbent became saturated in the system containing high concentrations of both metals of interest (Al and Cd in this study), the common maximum total metal uptake approached a value of 2.75 mmol/g. The relative affinity of Al towards the biosorbent in the 2-metal (Al+Cd) system also greatly increased in comparison with one-metal system, but that of Cd in the (Al+Cd) system oppositely decreased.

This competitive binding by Ca-loaded *Sargassum* biomass at pH 4.5 was similarly observed in the (Al+Pb), (Al+Cu), (Al+Zn) and (Al+Cr) system. The effects of the Al ion presence on the uptakes of the Pb, Cu, Zn and Cr ions can be summarized from those plots as seen in Fig. 5(a) for Pb, Fig. 5(b) for Cu, Fig. 5(c) for Zn,

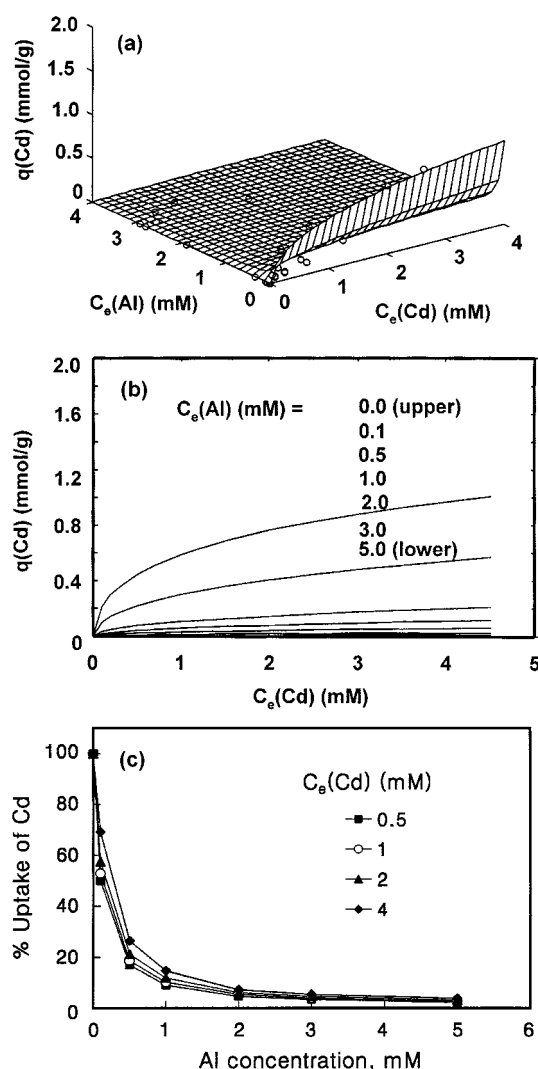


Fig. 4. (a) A 3-dimensional sorption surface for Cd uptake of the Cd-Al biosorption system at pH 4.5. (b) Effect of Al on the equilibrium uptake of Cd by Ca-loaded *S. fluitans* biomass at pH 4.5. (c) Interference of Al ion on the Cd uptake by Ca-loaded *S. fluitans* biomass at pH 4.5.

Table 3. The relative affinity calculated from the modified Langmuir model in two-metal system (K_1 : heavy metal, K_2 : Al)

2-metal system	q_{\max} (mmol/g)	K_1 (mM) $^{-1}$	K_2 (mM) $^{-1}$
Al-Cr	2.92	3.73	6.14
Al-Pb	2.84	0.99	8.20
Al-Cu	2.81	0.58	10.05
Al-Cd	2.75	0.09	14.62
Al-Zn	2.72	0.06	19.38

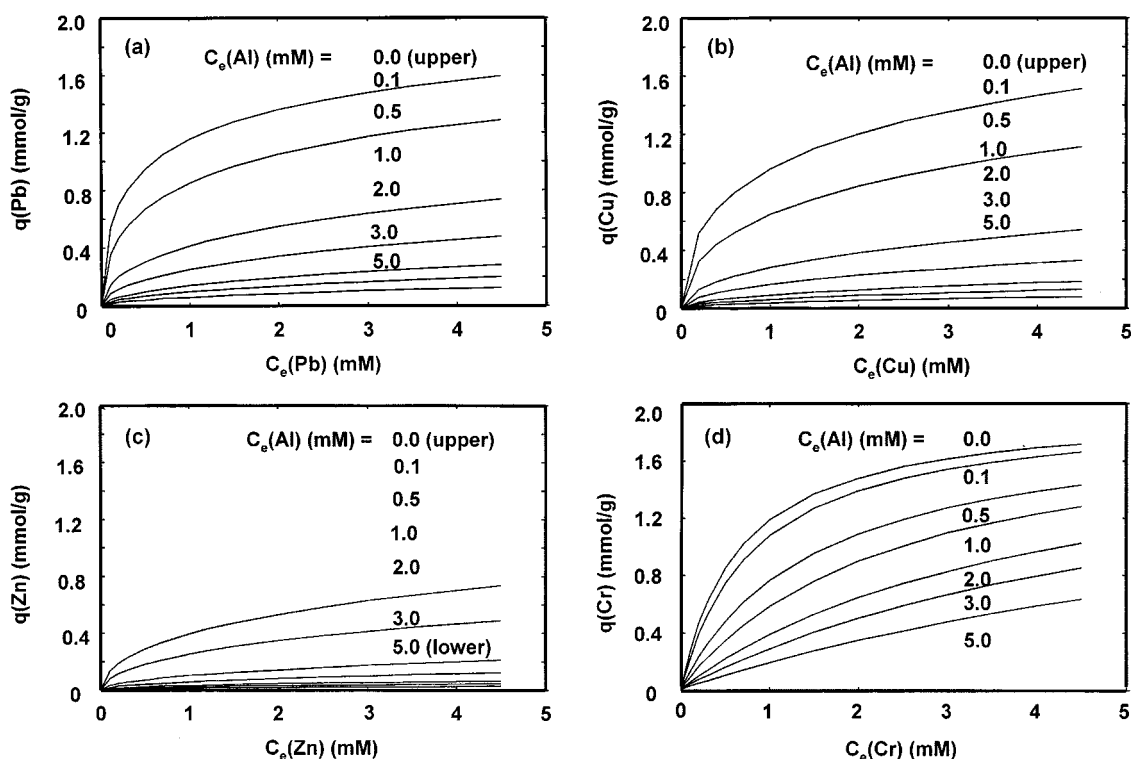


Fig. 5. (a) Effect of Al on the equilibrium uptake of Pb by Ca-loaded *S. fluitans* biomass at pH 4.5. (b) Effect of Al on the equilibrium uptake of Cu by Ca-loaded *S. fluitans* biomass at pH 4.5. (c) Effect of Al on the equilibrium uptake of Zn by Ca-loaded *S. fluitans* biomass at pH 4.5. (d) Effect of Al on the equilibrium uptake of Cr by Ca-loaded *S. fluitans* biomass at pH 4.5.

Fig. 5(d) for Cr sorption. K_1 (heavy metal) and K_2 (Al) values, the relative affinity of the metal towards the biosorbent, from the modified Langmuir model in a two-metal system are summarized in Table 3.

Equimolar final equilibrium concentrations of Pb and Al of 1 mM at pH 4.5 reduced Pb and Al uptakes to 21.6% and 90.5%, respectively. Fig. 5 showed that the reduction of Pb, Cu, Zn and Cr uptakes at its final equilibrium concentrations of 1 mM at pH 4.5 was 78.4%, 82.7%, 85.1% and 51.2% on the presence of Al ion of 1 mM, respectively.

The uptakes of heavy metals except Cr at pH 4.5 were greatly reduced by the presence of Al. Equimolar final equilibrium concentrations of Cr and Al of 1 mM at pH 4.5 reduced Cr and Al uptakes to 48.8% and 80.7%, respectively. As described previously in single metal sorption, Al ion was sequestered to the biomass in the form of polynuclear aluminum species such as $\{\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}\}^{6+}$ [Hsu and Bate, 1964] and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ [Bottero et al., 1980], and these polymerized aluminum ions prevented other heavy metals from accessing to the binding sites. Cr ion represents tri-valence like Al ion at a low pH, but it seems that a part of Cr ion was bound to the biomass as mono- ($\text{Cr}(\text{OH})_2^+$) or di-ion ($\text{Cr}(\text{OH})_2^{2+}$) valence at pH 4.5.

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, or inorganic microprecipitation of metals. Sorption preferences observed with Ca-loaded *S. fluitans* biomass and the results of the competi-

tion aspects observed will likely have repercussions in the continuous-flow dynamic sorption column system. A net sorption preference for Al uptake over heavy metals 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.

CONCLUSION

The interference of Al in heavy metals biosorption was assessed by deriving a three dimensional sorption surface with a modified multi-component Langmuir isotherm. The Langmuir parameters, K_1 for heavy metals 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. The reduction of Pb, Cu, Zn, Cd and Cr uptakes at its final equilibrium concentrations of 1 mM at pH 4.5 was 78.4%, 82.7%, 85.1%, 89.8% and 51.2% on the presence of Al ion of 1 mM, respectively. The uptakes of heavy metals except Cr at pH 4.5 were greatly reduced by the presence of Al. Al ion was sequestered to the biomass in the form of polynuclear aluminum species such as $\{\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}\}^{6+}$ and $\text{Al}_{13}(\text{OH})_{32}^{7+}$, and these polymerized aluminum ions prevented other heavy metals from accessing to the binding sites. 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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