

# Biosorption of Cr, Cu and Al by *Sargassum* Biomass

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The biosorption and desorption of Cr, Cu and Al were carried out using brown marine algae *Sargassum fluitans* biomass, known as the good biosorbent of heavy metals. The content of alginate bound to light metals could be changed by physical and chemical pretreatment. The maximum uptake of Cr, Cu and Al was independent of the alginate content. The maximum uptake of Al was two times (mole basis) than those of Cu and Cr. The aluminum-alginate complex was found in the sorption solution of raw and protonated biomass. Most of Cu, Al and light metals sorbed in the biomass were eluted at pH 1.1. However, only 5 to 10% of Cr sorbed on Cu biosorption with Ca-loaded biomass. A part of Cr ion was bound to biomass as  $\text{Cr}(\text{OH})_2^+$  or  $\text{Cr}(\text{OH})_2^+$ . Al was also bound to biomass as multi-valence ion and interfered with the desorbed Ca ion. The behavior of raw *S. fluitans* in ten consecutive sorption-desorption cycles has been investigated in a packed bed flow-through-column during a continuous removal of copper from a 35 mg/L aqueous solution at pH 5. The eluant used was a 1%(w/v)  $\text{CaCl}_2/\text{HCl}$  solution at pH 3.

**Key words:** biosorption, *Sargassum fluitans*, Ca-loaded biomass, alginate, multi-valence ion

## 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. Biosorption technology and its potential for the treatment of wastewater and environmental pollution has been outlined recently [1, 2]. Most of the research on biosorption has focussed on uptake of metals by biomass of bacteria, actinomycetes, fungi and algae [3]. Among the huge diversity of biomass available, marine algae have already proved to be promising for heavy metal recovery. The brown seaweed of the genus *Sargassum* has been studied for its capacity to selectively bind gold at low pH [4]. *Sargassum* biomass also binds cadmium, nickel, copper, lead and zinc cations at least up to 20% of the biosorbent dry weight [5]. However, little work has been done on biosorption of metals such as aluminum and chromium. The mechanism of metal biosorption has not been adequately explained, ionic interactions and complex formation between metal cations and ligands contained in the porous structure of the biomaterials are responsible [6]. Recently, it was demonstrated that carboxyl groups from alginate played a major role in the complexation of heavy metals (Cd and Pb) by *Sargassum* seaweed [7]. 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.

Present work examines the characteristics of the sorption of Cr, Cu and Al by *Sargassum fluitans* biomass chemically or physically pretreated by dif-

ferent methods. The behavior of light metal ions contained in the biomass and their interaction with heavy metals were also investigated. The assessment of the long term stability of biosorbent in a packed bed column was carried through many sorption-desorption cycles using copper for sorption process and  $\text{CaCl}_2$  for regeneration.

## MATERIALS AND METHODS

### Biomass Treatments

Raw *S. fluitans* biomass was collected and 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 five times with distilled water. 5 g of raw biomass was added to 1 L of distilled water (pH 6.5 to 7.3, 100 rpm shaking for 2 h at 20°C) then filtered and finally dried overnight at 60°C. (b) Protonated *S. fluitans*: 2 g of raw biomass was added to 1 L of 0.1N HCl (100 rpm shaking overnight at 20°C). Biomass was filtered and washed with the same volume of distilled water. It was finally dried overnight at 60°C. (c) Ca-loaded *S. fluitans*: 5 g of raw biomass was added to 1 L of 0.5 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (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. (d) NaOH-treated *S. fluitans*: The same procedure as for (c) except the use of 0.1N NaOH instead of 0.5 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . (e) Formaldehyde crosslinking (FC or Na-loaded) followed a modified procedure of Bullock [8]. 5 g of raw biomass were added to a mixture of 33 mL 36% formaldehyde and 67 mL 1N HCl. The mixture was left at room temperature for 4 h under gentle mixing. The biomass was then filtered and washed with distilled water, 2% sodium carbonate, and another distilled

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water.

### Sorption Experiments

Each metal solution of desired concentrations was respectively prepared by dissolving  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Cr}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$  in distilled and deionized water. All sorption experiments were performed by suspending 100 mg of biomass in 100 mL of metal-bearing solution and shaking on a gyrotory shaker for 30 h. 0.1 N HCl or 0.1 N NaOH were used for pH (=4.5) adjustments. At the end of each experiment, the samples were filtered using 0.45 Millipore membrane and then the filtrate was analyzed by AAS (Shimatsu AA 680, Japan) for the analysis of metal content. The filtered biomass was washed with distilled water, dried overnight at 60°C, and weighed for desorption experiment. Metal uptake was calculated as  $q \text{ (mmol/g)} = V(C_i - C_e)/M$  where:  $C_i$  and  $C_e$  are the initial and equilibrium metal concentration in the solution, respectively (mM),  $V$  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 0.1N 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. 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,  $V$  is the solution volume, and  $M$  is the initial mass of the biosorbent used.

## RESULTS AND DISCUSSION

### Analysis of Light Metals and Alginate Contents for Pretreated Biomass

Alginate was extracted from the pretreated dry biomass using 2% solution of  $\text{Na}_2\text{CO}_3$ , according to the method of Percival and McDowell [9]. The concentration of alginate in the crude extracts of biomass was determined according to the method of Kennedy and Bradshaw [10], using poly(hexamethylene-bisguanidinium chloride) [ $\text{PHMBH}^+\text{Cl}^-$ ] and UV spectrophotometry.

Table 1 shows the residual alginate contents and the amount of light metals eluted by acidic washing of pretreated *S. fluitans* in 0.1N HCl. These light metals account for 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. Those results are compared in Table 1 with the

**Table 1.** Residual alginate and light metal contents

Biomass type	Wt. loss Alginate		Light metal (mmol/g)			
	(%)	(%)	Na	K	Mg	Ca
Native	6	32	0.848	0.418	0.407	0.597
DW-washed	32	31	0.205	0.188	0.461	0.963
Protonated	31	45	0.000	0.000	0.009	0.013
Ca-loaded	25	28	0.000	0.000	0.040	1.801
NaOH-treated	37	36	0.490	0.031	0.461	1.180
Na-loaded(FC)	39	4	2.291	0.000	0.007	0.010
Conc. in sea water (mmol/mL)			0.459	0.0097	0.052	0.010
Concentration ratio (mL/g)			1.847	43.093	7.827	59.700

salt concentration in sea water at place and the date of harvesting. Biomass components including impurities and alginate were extracted in the ratio of about the same throughout the distilled water washing. Biomass components were extracted during the acidic washing (0.1N HCl), but alginate was little extracted and concentrated, and transformed to alginic acid in the biomass.

In case of formaldehyde crosslinked (Na-loaded) *S. fluitans*, 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 2%  $\text{Na}_2\text{CO}_3$  solution and the Na ion was sorbed during this treatment. However, total amount of the biomass binding sites bound to light metals was relatively low. Other ions except Na ion for Ca-loaded *S. fluitans* were almost extracted from the biomass. In case of NaOH-treated biomass, alginate and Ca ion were relatively concentrated and K ion was almost released.

### Proton Displacement of Light Metals

A 0.5 g sample was suspended in 500 mL of distilled deionized water. The suspension was brought to pH 7.0 by adding HCl, and a 5 mL sample of the liquid was taken for metal analysis. The process was repeated for each desired pH (down to pH 0.5) with concentrated HCl being used to lower the pH. After filtration and drying, the weight loss of the samples is approximately 31% for native *S. fluitans* and 25% for *S. fluitans* washed with distilled water. Light metals were released upon acidification of algal biomass suspension, initially at pH 7. The total amount of light metals displaced by protons at pH 1.0 was approximately 2.27 mmol/g (3.27 meq/g) for native *S. fluitans* (Fig. 1a) and 1.82 mmol/g (3.24 meq/g) for DW-washed *S. fluitans*, respectively. In the case of native *S. fluitans*, the value was approximately 1.56 mmol/g (2.56 meq/g) when subtracting the amounts of  $\text{Na}^+$  and  $\text{K}^+$  already dissolved at pH 7. However, the amount of light metals released decreased as the pH decreased below pH 1.0. Repeated analyses confirmed that the light metals released were not re-sorbed by the biomass but their AAS analysis was subject to unexpected interference by a high  $\text{Cl}^-$  and/or a high proton concentrations. This phenomenon was confirmed by the AAS analysis of blanks. The fraction of different light metals that remained in the biomass after the washing probably consisted of the metal ions that were chemically bound to the carboxyl, hydroxyl, and/or sulfate groups of the polyuronates and sulfated polysaccharides present in *S. fluitans* [7, 9]. In general, the release of light metals upon acidification reflects binding to carboxylate and sulfate anions which is electrostatic for metals and covalent for protons [6]. Fig. 1 also shows that  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are more abundant in DW-washed biomass than in native biomass. However, the concentration factor of magnesium does not compensate for the biomass weight loss (32%) during DW-washing. As opposed to calcium, a significant fraction of magnesium (approximately 25%) was dissolved during the washing. Consequently, light metals can be arranged in the ascending order of affinity as follows,  $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ . The weight loss of biomass during the acidification process was approximately 31% for native *S. fluitans* and 25% for DW-washed *S. fluitans*, respectively. Therefore, consider-

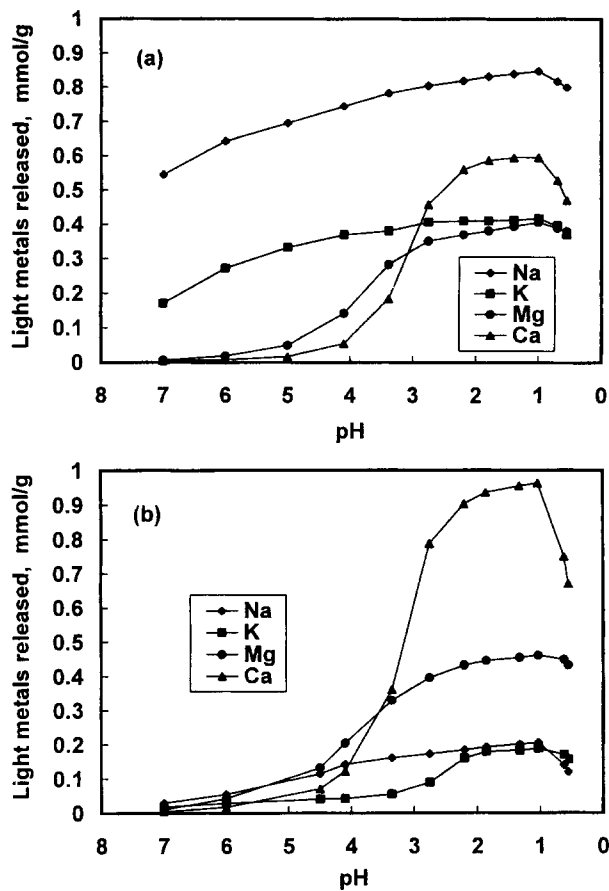


Fig. 1. Proton displacement by light metals in *S. fluitans* biomass: (a) raw, (b) DW-washed.

ing that the stoichiometric weight loss of DW-washed *S. fluitans* due to light metals replacement by the protons was approximately 5.5%, about 19.5% of biomass components were extracted. The weight loss of native biomass during the two steps of treatment (washing with distilled water and acidification process) was more than 49%.

#### Titration of Protonated *S. fluitans* Biomass

Potentiometric and conductometric titrations were performed with protonated biomass. Titration was carried out by stepwise addition of 0.28 mL of 0.1 N NaOH while 0.2 g of biomass was suspended in 0.1 L of distilled deionized water under a nitrogen atmosphere. The NaOH addition in the initial 'negative' part of the diagrams in Fig. 2 accounts really for the titration of the known amount of HCl initially added to the sample. The conductometric titration curve begins with a decreasing portion, characterizing the repression of the dissociation of the weak acidic groups. This also means the presence of additional free protons from strongly acidic groups, probably sulfonates. In order to distinguish between the strong acids and the beginning of titration of weak acids, a known amount of strong acid (HCl) was added to the suspension prior to titration. The intersection between the linearly decreasing portion and the linear slowly increasing branch, corresponding to the titration of weak acidic groups, yielded a quantitative estimation of equivalents of strong acidic groups in the biomass ( $0.35 \pm 0.05$  mmol/g). The value analyzed by HPLC after the hydrolysis of

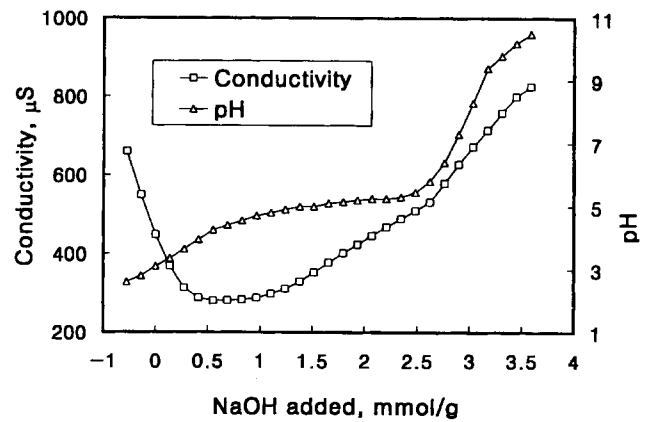


Fig. 2. Potentiometric and conductometric titration of protonated *S. fluitans* biomass.

biomass was approximately 0.25 mmol/g. When all the strong acidic groups were neutralized, the weaker acidic groups began to dissociate and contributed to the measured conductance. In this region, the change attributed to the proton concentration change was low because of the low level of dissociation of the weak acidic groups. When all the weak acids were neutralized, the conductivity increased in the proportion to the excess of NaOH added. This break point corresponds to the second equivalence point of the potentiometric titration curve and gives the amount of weak acidic equivalent groups corresponding to alginic acid (2.27 mmol/g). In the case of the pure alginic acid, the break points of potentiometric and conductometric titrations curves appeared at about 4.5 mmol/g of NaOH addition.

#### Maximum Metal Uptakes and Affinities of Pretreated *S. fluitans* Biomass

The sorption-desorption experiments of Cr, Cu and Al for the pretreated biomass by different methods were investigated at pH 4.5 and the results are summarized in Table 2. Maximum metal uptakes 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,  $K$  is the adsorption equilibrium constant ( $k_{adsorption}/k_{desorption}$ ) representing the affinity between metal and biomass, and  $q$  (mmol/g-biomass) is the amount of metal sorbed at the final equilibrium concentration ( $C_f$ ).

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

The affinity constants for same metal slightly showed an rising trend as the maximum metal uptake increased. However, the maximum metal uptakes were independent of residual alginate content present in the pretreated biomass, as shown in Table 1. This indicates that the binding sites sequestered metals include polyphenol groups in addition to alginate and sulfonate functional groups.

Table 2 shows that the maximum metal uptakes of protonated biomass were the least and the ones of NaOH-treated and Na-loaded biomass stayed the highest levels. Alginate was concentrated in the biomass throughout protonated process (ion-exchange between protons and light metals such as Na, K, Mg and Ca). A part of concentrated alginic acid in the

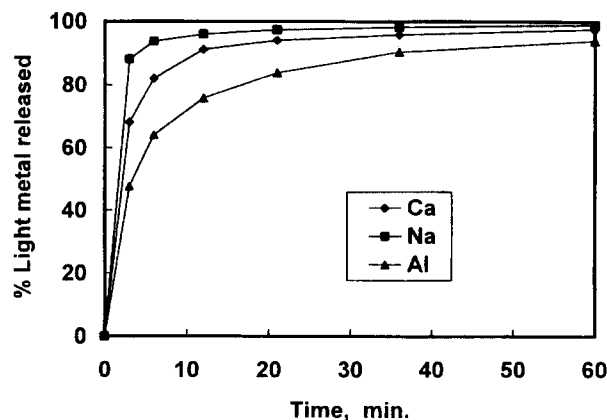
**Table 2.** Maximum metal uptake at pH 4.5 and affinity constant

Biomass type	$q_{max}$ (mmol/g)			K (mmol/L) <sup>-1</sup>		
	Cu	Al	Cr	Cu	Al	Cr
Native	1.29	2.90	1.50	3.10	5.09	5.84
DW-washed	1.44	3.34	1.63	3.79	5.40	5.92
Protonated	1.25	2.51	1.17	3.01	4.77	4.38
Ca-loaded	1.39	2.79	1.59	3.55	5.13	5.76
NaOH-treated	1.51	3.70	1.89	3.86	6.38	6.28
Na-loaded (FC)	1.47	3.86	1.80	3.81	6.44	6.20

biomass was so easily (maybe proportionately) extracted by the addition of NaOH and also caused the decrease of binding sites in the biomass. However, in case of NaOH-treated and Na-loaded biomass, the weight loss of biomass component was not observed after the sorption experiments since the water-soluble alginate had almost dissolved during the pretreatment. The maximum metal uptake of Al was beyond two times those of Cr and Cu. Considering that the binding site of biomass bound to light metals is approximately 3 meq/g, the binding site of Al ion is below one per Al molecule in spite of tri-valence ion. It seems that Al ion bound to biomass in the forms of polynuclear aluminum species such as  $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$  [11] and  $Al_{13}(OH)_{32}^{7+}$  [12]. As shown in Fig. 3, 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 (like cotton candy) in the sorption solution. Aluminum-alginate complex precipitated in the solution as alginate was partially released from the biomass. However, in case of FC and NaOH-treated biomass, this difference in the sorption isotherm curves and any precipitate were not found. The metal-alginate complex (like cotton candy) in the sorption solutions of Cu and Cr was not observed.

**Ion Exchange Between Heavy Metals, Protons and Light Metals**

In order to investigate the affinity between light metals and biomass, desorption rates for light metal-loaded biomass were measured with 0.1N HCl (Fig. 4). DW-washed *S. fluitans* loaded with 9.38 meq/g of Al was used in the Al desorption. About 80% of this Al uptake was sorbed for 10 hours at pH 4.0. The total amounts of

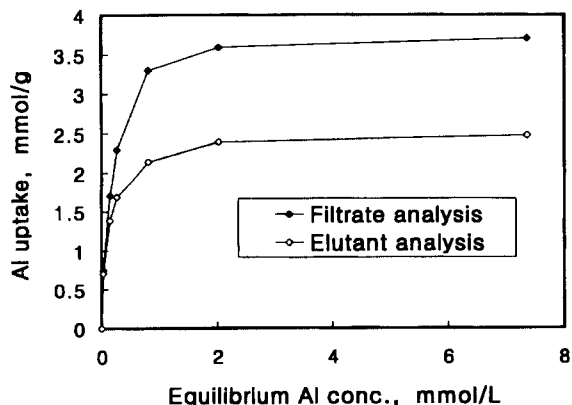


**Fig. 4.** The fraction of light metal displaced by protons at pH 1.1 in metal-loaded *S. fluitans* biomass.

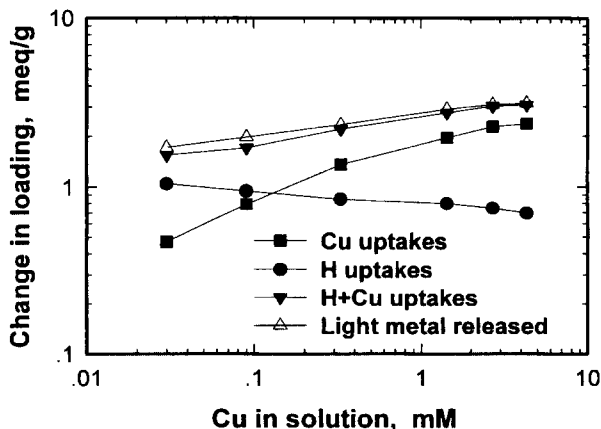
other light metals displaced by protons when the pH was lowered to pH 1.0 was approximately 3.61 meq/g for Ca-loaded *S. fluitans*, and 2.45 meq/g for crosslinked *S. fluitans* loaded with Na, respectively. More than 90% of the total metal sorbed for the three light metals was released within 1 h. The desorption rate of aluminum was the slowest. This observation relates to the binding strength between metal ions and functional groups in the biomass and indicates that the affinity of  $Al^{3+}$  toward the biomass was higher than that of  $Ca^{2+}$ . Since the mobility of protons in the solution is considerably greater than that of other ions, Al was not precipitated in the biomass as  $Al(OH)_3$ , but it became chemically bound to the carboxyl, hydroxyl, and/or sulfate groups of the polyuronides, sulfated polysaccharides and polyphenols present in *S. fluitans* biomass.

Almost Cu, Al and light metals sorbed in the biomass were eluted at pH 1.1. However, only 5 to 10% of Cr sorbed was eluted at pH 1.1. The elution ratio of Cr sorbed did not exceed 20% in 1N HCl or  $HNO_3$  solution. This indicates that the strong bond energy between Cr ion and biomass exists and that ion exchange of Cr sorbed for  $H^+$  and  $Ca^{2+}$  could not easily occur.

Equilibrium experiments were performed to study the sorption of copper on DW-washed *S. fluitans* biomass at pH 3.5 (Fig. 5). The individual flasks containing varying initial concentrations of Cu were adjusted to pH 3.5 using HCl before the biomass was added. Without further pH adjustment, the pH of the solu-



**Fig. 3.** Biosorption of Al for protonated *S. fluitans*: Al adsorption at pH 4.5 and Al desorption at pH 1.1.



**Fig. 5.** Log/Log is isotherm curve of Cu adsorption by *S. fluitans* biosorbent.

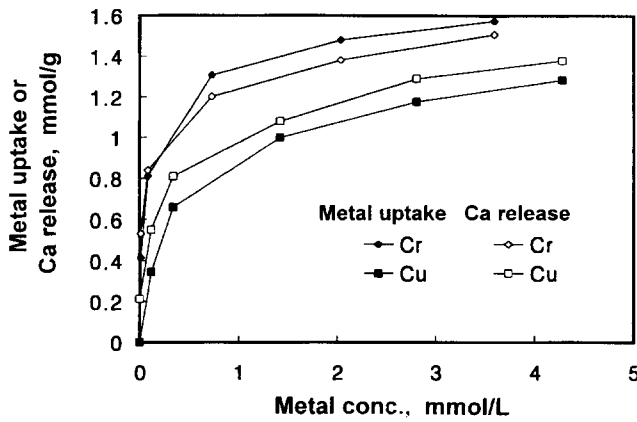


Fig. 6. Ion exchange of metal ions and Ca ion in Ca-loaded biomass.

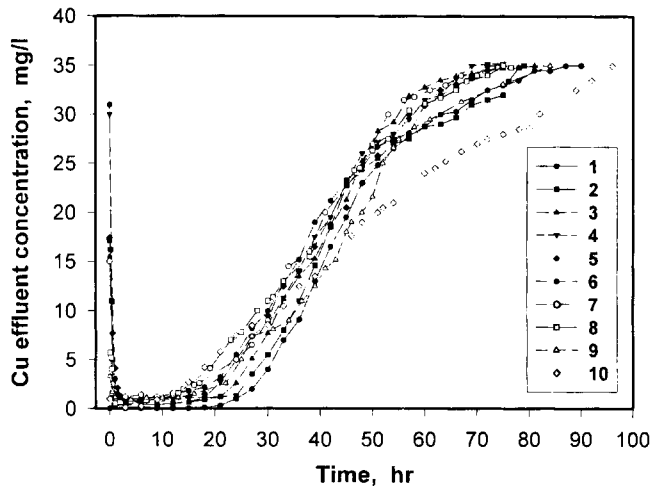


Fig. 7. Breakthrough curve for packed column operation with raw *S. fluitans*.

tion rose after addition of the biomass (not shown). This pH increase was lower for high concentration of metal. For better comparison of the metal uptakes, the pH was subsequently adjusted back to pH 3.5 by addition of HCl, until it was stable. The amount of acid added during this readjustment was assumed to be equal to the proton uptake by the biomass since reactions of the dissolved ions with  $H^+$  or  $OH^-$  are negligible at this low pH. With increasing Cu equilibrium concentrations the uptake of Cu rose as expected. The uptake of protons was the highest for low Cu concentrations and decreased with increasing Cu concentrations, however, it was positive in the concentration range examined. As the heavy metal concentration increased, an increase of light metals K, Na, Ca and Mg released in the solution was observed. The total release on a charge basis (i.e. the release of Ca and Mg multiplied by two) was very close to the total uptake on a charge basis (i.e. the uptake of Cu multiplied by two).

The stoichiometric ion exchange between Cu and Ca ion was observed on Cu biosorption at pH 4.5 with Ca-loaded biomass (Fig. 6). The uptake of Cr was higher than that of Cu and the amount of Ca released with Ca-loaded biomass. The Cr uptake calculated in unit of meq. was 1.5 times and over the amount of Ca released. This observation implies that a part of Cr ion bound to

biomass as  $Cr(OH)_2^+$  or  $Cr(OH)^{2+}$ . The amount of Ca released decreased with increasing Al equilibrium concentrations. Repeated analyses by blank test confirmed that Al ion interfered with the desorbed Ca ion.

### Multiple Sorption-desorption Cycle

The assessment of the long term stability of biosorbent in a packed bed column was carried through ten consecutive sorption-desorption cycles with raw *S. fluitans* (Fig. 7). A copper bearing solution of 35 mg/L at a flow rate of 19 mL/min (3.88 cm/min) was passed through the column. The initial pH of the metal solution was adjusted to about 5. The sorption process was stopped after reaching Cu concentration of 35 mg/L in the effluent and the regeneration solution of 1%(w/v)  $CaCl_2/HCl$  (pH 3) was run through the bed. The breakthrough time decreased from 25.4 h at the first cycle to 12.7 h at the last one. Up to cycle 5, the decrease occurred in approximately 2 h steps. The capacity related to the initial dry weight of biomass (38 g) shows no correlation to the decreasing breakthrough time. The copper uptake obtained in the first sorption cycle (42 mg/g-biomass) corresponds nearly to the uptake obtained from the equilibrium isotherm (43 mg/g) at the residual concentration of 35 mg/L. The capacity at the last cycle (46.5 mg/g) was higher than those of others. This case might be in context with the previous desorption where the usual 15 h  $CaCl_2$ -wash is followed by a 1 h 0.1N HCl-regeneration and again a 15 h  $CaCl_2$ -regeneration. A decreasing breakthrough time and approximately steady capacity is proved by an increasing length of the mass transfer zone and a decreasing slope at the (first) inflection point. A shortened breakthrough time and a broadened mass transfer zone is caused by an unequal packed bed density and unequal flow pattern within the column. The elution efficiency was approximately 95% for 1%(w/v)  $CaCl_2/HCl$  solution and over 99% for 0.1 N HCl. However, 0.1 N HCl-regeneration may cause damage to biomass components. At each cycle, after a short increase, the effluent pH decreases until the breakthrough which lasts approximately 20 h. Then, the pH increases more slightly as the saturation of the bed progresses.

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