



PERGAMON

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SARGASSUM SEAWEED AS BIOSORBENT FOR HEAVY METALS

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Abstract—Six different species of non-living *Sargassum* biomass were compared on the basis of their equilibrium Cd and Cu uptake in order to evaluate potential variability in the sorption performance of different *Sargassum* species. Biosorption uptakes for Cd at the optimal pH of 4.5 ranged from $q_{\max} = 0.90$ mmol/g for *Sargassum* sp. 1 to 0.66 mmol/g for *S. filipendula* I representing a 36% difference. Three species were evaluated for their Cu uptake where $q_{\max} = 0.93$ mmol/g for *S. vulgare*; 0.89 mmol/g for *S. filipendula* I, and 0.80 for *S. fluitans*, representing a 16% difference between the lowest and highest values. Potentiometric titrations were carried out on *S. vulgare*, *S. fluitans* and *S. filipendula* I and yielded the similar results of 1.5 mmol/g weakly acidic sites for *S. vulgare* and *S. fluitans*, and 1.6 mmol/g for *S. filipendula* I. Estimates of 0.3 mmol/g of strongly acidic sites for *S. fluitans* and *S. filipendula* I and 0.5 mmol/g for *S. vulgare* were obtained. The total number of active sites averaged 1.9 ± 0.1 mmol/g. The elution efficiency for Cu-desorption from *S. filipendula* was determined for CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and HCl at various concentrations and solid:liquid ratios (S/L). The highest elution efficiency was >95% for Cu for all elutants at S/L=1 g/l and decreased for both calcium salts with increasing S/L to less than 50% at S/L=10 g/l as a new batch sorption equilibrium was reached quickly. CaCl_2 was chosen to be the most suitable metal-cation desorbing agent. © 2000 Elsevier Science Ltd. All rights reserved

Key words—biosorption, *Sargassum*, metals, heavy metals, metal removal, desorption

INTRODUCTION

Metal mining and metal processing activities inevitably increase the presence of toxic heavy metals in the environment. As a result, removal of these toxins from industrial effluents has become an important priority that is reflected in a tightening and enforcement of environmental regulations. Large volumes of industrial heavy metal-bearing wastewaters require efficient and very cost-effective treatment. While conventional technologies either cannot reliably remove trace metals or they are too costly to implement, biosorption appears to offer a technically feasible and economically attractive approach. *Sargassum* seaweed has been identified for such a purpose (Volesky and Kuyucak, 1988; Volesky and Schiewer, 1999) and is both very effective and easily available.

Biosorption of metals is not based on only one mechanism. It consists of several ones that quantitatively and qualitatively differ according to the

type of biomass, its origin and its processing. Metal sequestration may involve complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural polysaccharide cell wall network (Volesky and Holan, 1995). Due to the common occurrence of the raw biomass material and to its high metal uptake capacity (Kuyucak and Volesky, 1990; Schiewer and Volesky, 1999), recent studies have focused on marine algae otherwise known as seaweeds (Figueira *et al.*, 2000; Kratochvil and Volesky, 1998; Matheickal *et al.*, 1997). The main component responsible for metal sorption is the alginate which is present in a gel form in their cell walls (Fourest and Volesky, 1997). Alginic acid or alginate, the salt of alginic acid, is a characteristic of the brown algae and this common name designates a family of linear polysaccharides containing 1,4-linked β -D-mannuronic and α -L-guluronic acid residues arranged in a nonregular and blockwise order along the chain (Haug *et al.*, 1966). Brown algae cell walls are very porous and easily permeable to small ionic species (Dodge, 1973; Percival and McDowell, 1967a). Furthermore, seaweeds pos-

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sess rigid physical shapes and structures which make their application in biosorption processes particularly suitable. Morphologically, the seaweed thallus particles approximate flat chips rather than having a spherical shape (Yang and Volesky, 1999) which thereby facilitates rapid metal ion mass transfer and effective metal binding.

Cadmium and copper are the focus of this study. Cadmium, one of the "big three" toxic heavy metals (Pb, Hg, Cd), has attracted much attention since it is a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics, and other industrial operations (Forstner and Wittmann, 1979). The presence of ubiquitous copper causes serious toxicological concerns; it is known to deposit in the brain, skin, liver, pancreas and myocardium. The present work investigated the

metal biosorption behavior of several different species of *Sargassum* as a biosorbent material in an attempt to confirm its high metal-sorbing performance as a property of this seaweed genus.

MATERIALS AND METHODS

The biomaterials used in this study consist of two groups of *Sargassum* species. The first group was collected at an earlier date and consists of beach-dried *Sargassum vulgare* and *S. filipendula* I which were collected in Natal, Brazil, and *S. fluitans* which was collected along the Gulf of Mexico coast near Naples, Florida. The second group consists of more recent, commercially obtained *Sargassum* sp. 1 from the Philippines (MCPI Corporation in Cebu) and *Sargassum* sp. 2 collected at the coast of northeastern Australia. These two *Sargassum* samples are awaiting species taxonomical identification. *S. muticum* originated at the South of England and another sample of *S. filipendula* II (Natal, Brazil) was treated slightly differently. Dry biomass of Group 1 was cut with a knife into irregular shaped particles between 1 and 4 mm in size. Biomass from Group 2 was blended and consisted of particles of all sizes smaller than approximately 2 mm. Protonation of the biomass from both groups was carried out by soaking in 0.1 M HCl at a 1:50 (w/v) ratio. The biomass was then washed in distilled water and dried at 50°C overnight.

The above method of biomass treatment was used for both batch and titration experiments. In the latter, the biomass was acid washed a second time, whereby 500 mg of the biosorbent was resuspended in 100 ml of 0.1 M HCl and rinsed with distilled water until constant conductivity was attained (Cole Palmer model 4070 conductivity meter).

For the potentiometric and conductimetric titrations, the wet biomass was suspended in 1 mM NaCl (100 ml) and 0.5 ml of 0.106 N NaOH was added stepwise until the pH and conductivity values stabilized. Samples were agitated in a rotary shaker at 140 rpm. The titration vessel was purged continually with nitrogen gas to remove inorganic carbon. pH and conductivity measurements were calibrated against Fischer and Oakton calibration standards respectively.

Metal-bearing solutions were prepared by dissolving metal salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salts (from Fisher Scientific and ACP Chemicals, respectively) in distilled water. The chemical equilibrium program MINEQL⁺ (Schecher, 1991) was used to calculate the speciation of copper and cadmium in aqueous solution as a function of total salt concentration and solution pH (Fig. 1). Batch equilibrium sorption experiments were performed in 125 ml Erlenmeyer flasks containing 50 ml of metal-containing solution of a known initial concentration into which 100 mg of specified dry biomass particles were added. The initial concentrations of solutions were (0.16–3.9) mM Cu and (0.09–4.0) mM Cd (Group 1) or (0.25–4.5) mM Cd (Group 2). The suspensions were mildly agitated on a rotary shaker (New Brunswick Scientific) at 2.5 Hz, at room temperature (22°C) for 6 h. The pH was adjusted periodically to pH 4.5 by adding 0.2 M HCl or 0.1 M NaOH as required. By the end of the third hour of contact the pH remained relatively constant at pH 4.5 (± 0.3) for the remaining 3 h of sorption experiments. Following the sorption reaction period, the liquid was separated from the biomass by decanting. Metal free and biosorbent-free blanks were used as controls and the metal concentration of the sample supernatant was determined with an atomic absorption spectrometer (AAS, Thermo Jarrel Ash, model Smith-Hiefje II). Atomic absorption standards (1000 mg/l) were obtained from Fisher Scientific.

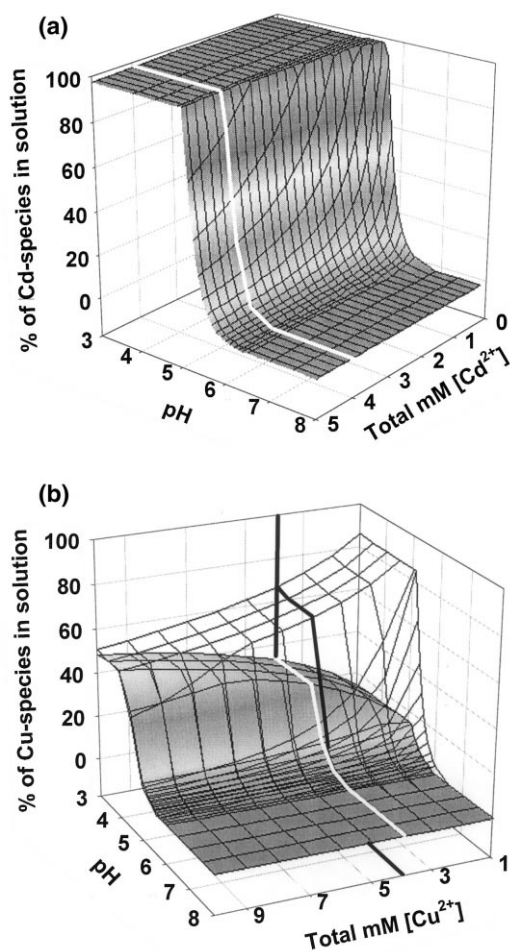


Fig. 1. (a) Uncomplexed cadmium in aqueous solution as a function of total $\text{Cd}(\text{NO}_3)_2$ concentration and pH, calculated with MINEQL⁺ (Schecher, 1991). Shaded surface is Cd^{2+} ; white cut represents a total concentration of 4.0 mM $\text{Cd}(\text{NO}_3)_2$. (b) Speciation of copper in aqueous solution as a function of total CuSO_4 concentration and pH, calculated with MINEQL⁺. Upper surface = Cu^{2+} , shaded surface = $\text{CuSO}_4(\text{aq})$. The cut represents a total concentration of 4.0 mM CuSO_4 .

Biosorption metal uptake (q) was calculated from the sorption system mass balance:

$$q = V(C_i - C_f) / S$$

where V is the solution volume, S is the amount of solids (biomass), and C_i and C_f are the initial and final metal concentrations, respectively.

The Langmuir sorption model was used to fit the isotherm relationship:

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

It uses two parameters (q_{\max} and b) which conveniently reflect the nature of the sorbent material and can be used to compare the biosorption performance. The Langmuir equation was fit to the experimental data points as seen in Figs 2 and 3 using Kaleidagraph software with an internal algorithm based on a least-squares approach. The curves drawn in Figs 2 and 3 use the regressed values for q_{\max} and b shown in the corresponding Tables 1–3. Experimen-

tal errors were estimated for the isotherms and are depicted with error bars.

RESULTS AND DISCUSSION

Metal uptake by *Sargassum*

Ionic speciation of metals in solution is important in biosorption studies since the metal uptake often depends on the sorption system pH. Higher pH values usually result in higher metal cation uptakes due to lowered metal solubility. Microprecipitation of insoluble metal species may occur close to neutral pH values. This may complicate efforts to elucidate the binding mechanism since typically complexation/coordination dominate.

Figure 1, summarizes calculations made using MINEQL⁺ (Schecher, 1991) for $\text{Cd}(\text{NO}_3)_2$

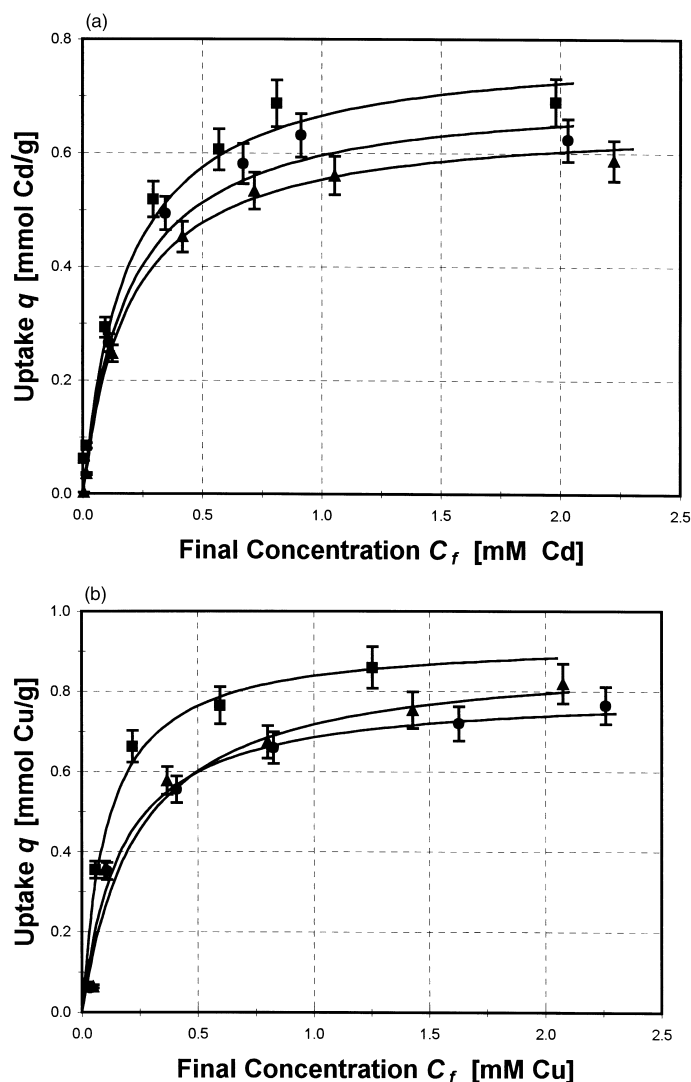


Fig. 2. (a) Cadmium sorption isotherms for Group 1 raw *Sargassum* species at pH=4.5: (■) *S. vulgare*, (●) *S. fluitans*, and (▲) *S. filipendula* I. (b) Copper sorption isotherms for Group 1 *Sargassum* species at pH=4.5: (■) *S. vulgare*, (●) *S. fluitans*, and (▲) *S. filipendula* I.

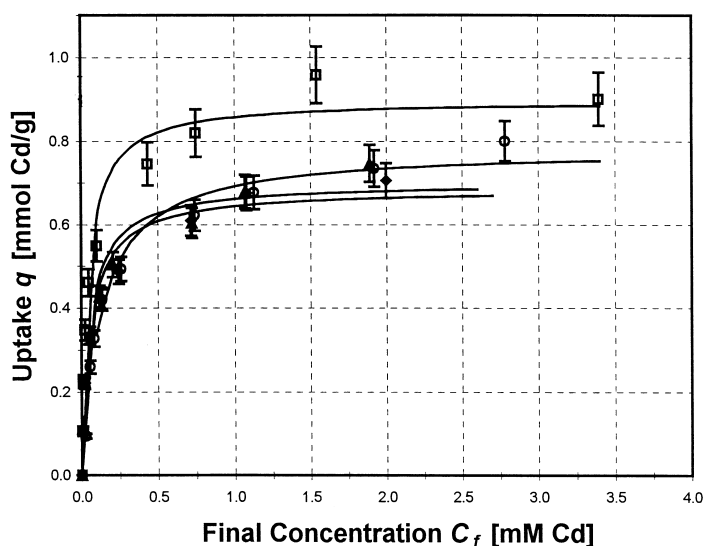


Fig. 3. Cadmium sorption isotherms for Group 2 raw and unsorted (all size fractions) *Sargassum* species at pH=4.5: (□) *Sargassum* sp. 1, Cebu, Philippines, courtesy of MCPI Corporation, (○) *Sargassum* sp. 2, Australia; (▲) *S. filipendula* II; (◆) *S. muticum*, courtesy of W. Farnham, University of Portsmouth, UK.

(Fig. 1(a)) and CuSO_4 salts (Fig. 1(b)). The calculations were made based on the thermodynamic data base provided with MINEQL⁺. Both data sets were calculated considering the carbonate system naturally in equilibrium with atmospheric carbon dioxide ($p\text{CO}_2 = 10^{-3.5}$ atm).

For the cadmium nitrate system Cd^{2+} is the dominant specie present at pH lower than approximately pH=5.0 and this depends on the total molarity of the salt in solution. At higher concentrations (calculated to a maximum of 4.0 mM) the Cd^{2+} predominance is shifted to lower pH values. However, it remains the dominant species up to a maximum of pH=5.5. At higher pH values, solid otavite (CdCO_3) is thermodynamically the most stable phase. However, it has been omitted from Fig. 1(a) because it is unlikely to form over the relatively short period during which the experiment was conducted. At pH values greater than 5.0

hydroxides of cadmium may become more dominant. In addition, it is known that small quantities of biomass polysaccharide are leached into solution (Carvalho *et al.*, 1994; Figueira *et al.*, 2000) which may further impede kinetics of precipitation. Although MINEQL⁺ calculations are for a pure aqueous system, and the presence of minute organic material may displace the chemical equilibrium, the predominance of aqueous divalent cadmium should still hold. The pH edge of Fig. 1a should therefore represent the minimum surface which bounds Cd^{2+} as the dominant species.

The copper sulfate system includes two copper species dominant at lower pH values. The upper unshaded surface in Fig. 1(b) is for Cu^{2+} , the lower shaded surface represents $\text{CuSO}_4^0_{(\text{aq})}$. The solids antlerite ($\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$), tenorite (CuO), and brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$) are calculated to be the most stable phases above pH values of 5.0

Table 1. Biosorption isotherm parameters for Cd: different *Sargassum* species (Group 1)^a

	q_{10} [mg/g]	q_{200} [mg/g]	$q_{0.1}$ [mmol/g]	$q_{2.0}$ [mmol/g]	q_{max} [mmol/g]	b [l/mmol]
(a) Cadmium						
<i>S. vulgare</i>	29.3	79.0	0.28	0.72	0.79	5.33
% difference between <i>S. vulgare</i> – <i>S. fluitans</i>	16.2%	10.1%	17%	11%	11%	2.7%
<i>S. fluitans</i>	25.2	71.7	0.24	0.65	0.71	5.19
% difference between <i>S. fluitans</i> – <i>S. filipendula</i> I	8.2%	7.8%	4.3%	8.3%	7.6%	0.2%
<i>S. filipendula</i> I	23.3	66.5	0.23	0.60	0.66	5.20
% difference between <i>S. vulgare</i> – <i>S. filipendula</i> I	25.7%	18.8%	22%	20%	17%	2.5%
(b) Copper						
<i>S. vulgare</i>	35.0	57.5	0.44	0.88	0.93	9.16
% difference between <i>S. vulgare</i> – <i>S. fluitans</i>	41.7%	18.6%	47%	19%	16%	53.7%
<i>S. fluitans</i>	24.7	48.5	0.30	0.74	0.80	5.96
% difference between <i>S. fluitans</i> – <i>S. filipendula</i> I	4.2%	8.6%	15%	8%	11%	43.2%
<i>S. filipendula</i> I	23.7	52.7	0.26	0.80	0.89	4.16
% difference between <i>S. vulgare</i> – <i>S. filipendula</i> I	47.6%	9.1%	69%	10%	4.5%	120%

^a q_{10} q_{200} $q_{0.1}$ $q_{2.0}$: uptakes of metals at chosen respective final concentrations: $C_f = (10; 200 \text{ mg/l})$; $C_f = (0.1; 2.0 \text{ mmol/l})$.

Table 2. Biosorption isotherm parameters for Cd: Group 2 raw and unsorted *Sargassum* species^a

Cadmium	q_{10} [mg/g]	q_{200} [mg/g]	$q_{0.1}$ [mmol/g]	$q_{2.0}$ [mmol/g]	q_{\max} [mmol/g]	b [l/mmol]
<i>Sargassum</i> sp. 1, Cebu, Philippines	66.2	98.3	0.61	0.88	0.90	21.5
<i>Sargassum</i> sp. 2, Australia	35.5	81.9	0.34	0.73	0.78	7.63
<i>S. filipendula</i> II	47.7	76.2	0.44	0.68	0.70	17.4
<i>S. muticum</i>	45.2	74.3	0.42	0.66	0.68	16.1
% difference between <i>S. sp. 1</i> – <i>S. sp. 2</i>	86.5%	20.0%	79%	20%	15%	180%
% difference between <i>S. sp. 1</i> – <i>S. filipendula</i> II	38.8%	29.0%	39%	29%	29%	23.6%
% difference between <i>S. sp. 1</i> – <i>S. muticum</i>	46.5%	32.3%	45%	33%	32%	33.5%

^a q_{10} q_{200} $q_{0.1}$ $q_{2.0}$: uptakes of metals at chosen respective final concentrations: $C_f = (10; 200 \text{ mg/l})$; $C_f = (0.1; 2.0 \text{ mmol/l})$.

and occur respectively at successive pH maxima. The cuts of the surfaces in both Fig. 1(a) and (b) represent the maximum initial concentrations used when preparing solutions for metal sorption experiments. In the case of copper, the presence of significant quantities of aqueous copper sulfate may result in a slightly different binding mechanism. However, if assuming divalent copper is sorbed by the biomass and therefore removed from solution, a new equilibrium should form between divalent copper ions and the aqueous copper sulfate complex, whereby divalent copper is favored since at lower total copper concentrations, the complex becomes less significant (see Fig. 1(b)). Furthermore, it can be seen that the presence of the copper sulfate complex becomes much less significant at low total copper sulfate concentrations. In addition, the effect of the influence of low concentrations of sodium and chloride (present from pH adjustment during the sorption experiments) on the speciation of cadmium and copper was negligible. In order to operate at comparable conditions for both metals the sorption experiments were performed at pH 4.5.

When non-protonated biomass of *S. vulgare*, *S. fluitans* and *S. filipendula* I was reacted with Cd and Cu solutions the pH had to be adjusted only with acid to keep it at pH 4.5 during the first 3 h of the sorption process. Especially at lower metal concentrations the pH had a tendency to increase to pH 5.5 between pH adjustments due to the solution protons being preferentially exchanged or bound. The resulting biosorption isotherms are shown in Figs 2 and 3 for all three biomass types.

Tables 1a and 1b summarize the biosorption performance of the Group 1 *Sargassum* species characterized in Fig. 2(a) and (b) isotherm plots which depict the best isotherm model fits. Considering the weight-based uptake, *S. vulgare* had the highest Cd

uptake in the low as well as in the high metal concentration range (Fig. 2). It is useful to select a C_f value at the “low” (e.g. $C_f = 0.1 \text{ mmol/l}$) and “high” end of the range (e.g. $C_f = 2.0 \text{ mmol/l}$) with which to make comparisons of uptake values (q , correspondingly $q_{0.1}$ and $q_{2.0}$, respectively, or alternatively for ease of comparison with previously published results, quoting q_{10} and q_{200} in mg/g). The *S. vulgare* Cd uptake at $C_f = 0.1 \text{ mmol/l}$ was $q_{0.1} = 0.28 \text{ mmol Cd/g}$; that was 17% more than for *S. fluitans* and 22% more than for *S. filipendula* I. The $q_{2.0}$ value of *S. vulgare* (0.72 mmol Cd/g) was 11% higher than that for *S. fluitans* and 20% higher than *S. filipendula* I.

A high value of Langmuir parameter b indicates a steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate. *S. vulgare* had the highest value of $b = 5.33 \text{ l/mmol}$ for Cd. The values for *S. fluitans* and *S. filipendula* I were very close, 5.19 l/mmol and 5.20 l/mmol, respectively.

Table 2 summarizes biosorption performance of the Group 2 *Sargassum* species characterized by Fig. 3. *Sargassum* sp. 1 had the highest Cd uptake in the low and high metal concentration ranges (Fig. 3). The *Sargassum* sp. 1 uptake at $C_f = 0.1 \text{ mmol/l}$ was $q_{0.1} = 0.61 \text{ mmol Cd/g}$. That is comparable to the uptake at $C_f = 2.0 \text{ mmol/l}$ or $q_{2.0} = 0.60 \text{ mmol Cd/g}$ for *S. filipendula* of Group 1. *Sargassum* sp. 1 had $q_{2.0}$ 20% higher than *Sargassum* sp. 2, 29% higher than *S. filipendula* II, and 33% higher than *S. muticum*. All relevant Cd and Cu uptakes, Langmuir b values as well as percent differences among the *Sargassum* species examined are summarized in Tables 1 and 2. In the present experiments, the *Sargassum* metal uptake capacity was predicted within an error-range of 5.3–17.5%.

As indicated in Materials and Methods, the prep-

Table 3. Acidic group content in selected *Sargassum* species (Group 1) in comparison with their heavy metal uptake capacity (Cd and Cu)

	strong acidic groups [mmol/g]	weak acidic groups [mmol/g]	weak acidic groups $\cdot 0.5$ [mmol/g]	q_{\max} cadmium [mmol/g]	q_{\max} copper [mmol/g]
<i>S. vulgare</i>	0.5	1.5	0.75	0.79	0.93
<i>S. fluitans</i>	0.3	1.5	0.75	0.71	0.80
<i>S. filipendula</i> I	0.3	1.6	0.80	0.66	0.89

aration of the biomass in Group 1 and Group 2 was slightly different. The size distribution for the particles in Group 1 (chopped) was different from that in Group 2 (blended) yielding finer particles. As expected, the biomass particle size did not influence the metal (Cd) uptake whereby Group 1 q_{\max} ranges from 0.66 to 0.79 mmol/g and is similar to Group 2, except for *Sargassum* sp. 1 which had a q_{\max} of 0.90 mmol/g. This agrees with the notion that sorption does not take place solely on the biomass particle surface. The cationic metals permeate the particle and the equilibrium attainment rate is governed by interparticle metal ion mass transfer (Yang and Volesky, 1996, 1999).

In comparison with other biomass types (i.e. fungi, bacteria and other algae) brown algae, especially the *Sargassum* species used in this work, show excellent metal sequestering capabilities. For comparison, the cadmium uptake for biosorption by *Penicillium chrysogenum* biomass was reported as 0.34 mmol/g for $C_f = 0.88$ mmol Cd/g (Volesky, 1994). *S. filipendula* I, binding the least amount of Cd in the present experiments sorbed 0.54 mmol Cd/g at the same C_f level (58% more than *P. chrysogenum*). The bacteria *Pseudomonas testoteroni* bound 0.37 mmol Cd/g as well (at the same C_f level; Rudolph, 1993). The reported copper uptake for *Bacillus subtilis* was 1.24 mmol Cu/g and was treated with alkali to enhance its biosorption behavior. The untreated biomass bound only 0.14 mmol Cu/g (Volesky, 1990).

The unique mixture of polysaccharides, mainly alginate and fucoidan, is largely responsible for the excellent metal sequestering ability of the brown algae. Carboxylate groups of alginate have been identified as the main metal binding site. Other negatively charged functional groups such as the sulphonate groups of fucoidan also contribute to heavy metal complexation (Crist *et al.*, 1990; Four-est and Volesky, 1996). Fucoidan is a branched polysaccharide sulfate ester with L-fucose building blocks which are predominantly $\alpha(1 \rightarrow 2)$ linked (Percival, 1970; Percival and McDowell, 1967b), however it is difficult to evaluate the absolute role these polymers play in determining the ultimate heavy metal uptake.

The variation in the affinity of some divalent metals to alginates was demonstrated early on by Haug (1961). Alginates are often characterized by the proportion of manuronic (M) and guluronic (G) acids present in the polymer. The so called M:G ratio therefore varies among samples. The samples of Haug varied in affinity for divalent metals as a function of their M:G ratio. Furthermore, the affinity for divalent cations such as Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ca^{2+} , etc. increased with the guluronic acid content. The selectivity coefficients for the ion-exchange reaction between sodium and divalent metals were determined for two alginates (Haug and Smidsrod, 1965) and the data further

supported the higher affinity of guluronic acid for divalent metals. This higher specificity is explained by the structure of guluronic acid which can accommodate the Ca^{2+} (and other divalent cations) ion more easily. The rigid and buckled shape of the poly-L-guluronic sections (which is a consequence of being diaxially linked) results in an alignment of two chain sections yielding an array of coordination sites with cavities suitable for calcium (and other metal cations). These cavities are favorable to divalent cations because they are lined with carboxylate and other electronegative oxygen atoms. This configuration is known as the "egg-box" model (Morris *et al.*, 1978; Rees *et al.*, 1982).

Titration of biomass

The results of the potentiometric titration are nearly identical for each biomass examined (Fig. 4). At the beginning of the titration, conductivity, which was also measured, decreases sharply due to the neutralization of free protons from strongly acidic sulphonate groups known to be present. The neutralization of weak acids is characterized by a gentle increase in the solution conductivity. The total amount of strong base used during the titration yields the total number of all functional groups for a given weight of biomass.

The transition between the decreasing and increasing portion of the conductivity curve should correspond to the first equivalence point of the titration (Fig. 4). For *S. fluitans* and *S. filipendula* I the equivalence point, which is more of an equivalent range, is approximately 0.3 mmol/g (± 0.1 mmol/g) whereas the conductivity curve of *S. vulgare* shows an indistinct transition that may be estimated as 0.5 (± 0.1 mmol/g).

The potentiometric curve, however, reveals no clear sign of this equivalence point. On the other hand, the second equivalence point can be seen for

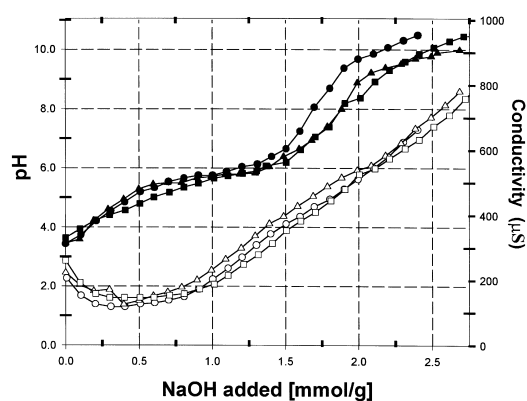


Fig. 4. Potentiometric and conductimetric titration curves of *S. fluitans*, *S. filipendula* I, and *S. vulgare* (Group 1). Potentiometric titration: (●) *S. fluitans*, (▲) *S. filipendula* I, (■) *S. vulgare*. Conductimetric titration: (○) *S. fluitans*, (△) *S. filipendula* I, (□) *S. vulgare*.

all three types of biomass due primarily to the neutralization of the weakly acidic alginic carboxylate groups. The number of equivalents of weak acid was obtained by subtracting the equivalents of strong acid from the total value of strong base used for the titration. This amounts to approximately $(2-0.5)=1.5$ mmol/g for *S. vulgare*, $(1.8-0.3)=1.5$ mmol/g for *S. fluitans* and $(1.9-0.3)=1.6$ mmol/g for *S. filipendula* I. Leaching of alginate was observed during the experiments, possibly introducing a small error in the estimation of the total number of active sites in the (solid) biomass. The solution was clear at the beginning of the titration and became more and more brown toward the end. Table 2 summarizes the data obtained from the isotherms including the Langmuir parameter q_{max} for metal uptake.

The correlation between the metal uptake capacity and the amount of acidic groups is related to the number of carboxylic groups (weak acid) occurring in the biomass. These groups play the predominant role in metal binding (Fourest and Volesky, 1997). For *S. fluitans* this relationship is very good when assuming a two-to-one stoichiometric relationship between protons released and divalent metals sorbed. The result is a 6.6% difference in Cu uptake and a 5.3% difference in Cd uptake when comparing half the millimole/gram biomass value of weak acidic groups to q_{max} . The difference for *S. vulgare* is 24% for Cu and 17.7% for Cd, whereas the results for *S. filipendula* I also show a larger deviation for the Cd-uptake (17.5%). The Cu uptake, however, differs much less (11.3%).

Desorption of copper-laden *S. filipendula* I

Sequestered cations have previously been eluted from *Sargassum* biomass (Aldor *et al.*, 1995). The optimal elutant must be effective, non-damaging to the biomass, non-polluting and cheap. Earlier desorption screening tests with Cd-laden *S. fluitans* resulted in the selection of a suitable elutant (Aldor *et al.*, 1995). Different mineral acids and CaCl_2 revealed a metal elution efficiency close to 100%. In this work, the effect of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ on metal elution was examined at different concentrations, initial pH, as well as with different HCl washes. Cu-laden *S. filipendula* I biomass was chosen for the tests. With costs in mind, only technical grades of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ were used, dissolved in tap water. Since these grades contain significant amounts of impurities, the concentration is expressed as mass per volume (w/v %).

Elution efficiency (E) was determined by the ratio of the metal mass in the solution after desorption to the metal mass initially bound to the biomass. The results for the solid:liquid ratio (S:L) of 1 g/l are presented in Fig. 5(a) and (b) for the Ca-salts and in Table 4 for an HCl solution, tap and distilled water. The latter two served as controls.

The elution efficiency is strictly pH dependent. CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ exhibited their best desorption performances at an initial pH of 3. The decrease of metal elution at pH 4 was more pronounced for CaCl_2 than for $\text{Ca}(\text{NO}_3)_2$. The final pH, also illustrated in Fig. 5, indicates the pH at equilibrium. An

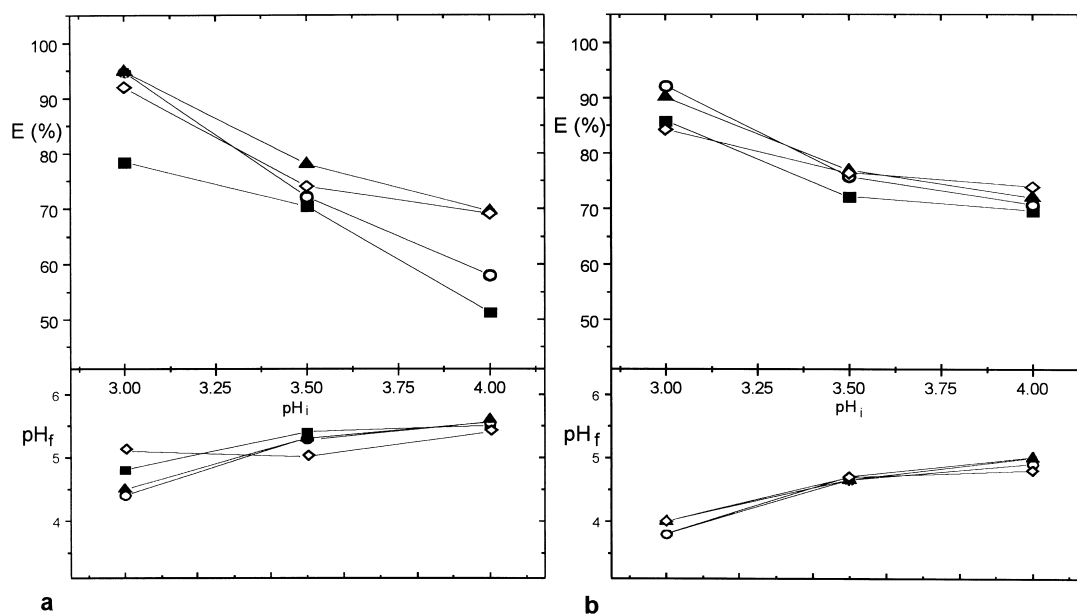


Fig. 5. Effects of the initial pH and calcium concentrations on the Cu elution efficiency and final pH at the S:L ratio of 1 g/l. (a) CaCl_2 : (■) 0.5%, (○) 1%, (▲) 2%, (◇) 3%. (b) $\text{Ca}(\text{NO}_3)_2$: (■) 0.5%, (○) 1%, (▲) 2%, (◇) 3%. (Copper loading on *S. filipendula* I: $q = 0.77$ mmol/g; $C_i = 3.9$ mM, $C_f = 2.4$ mM).

increase of approximately 1.5–2.0 pH units can be seen at every initial pH and at every initial concentration. No correlation with the elution efficiency, however, seems to be apparent.

The desorption performance of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ was tested at four different concentrations. Both elutants displayed the highest elution efficiencies for 1% and 2% concentrations at pH 3.0. The observed Cu release at this pH was approximately 95% and 92% respectively for CaCl_2 and $\text{Ca}(\text{NO}_3)_2$. The decrease in elution efficiency at a concentration of 0.5% was steeper for CaCl_2 than for $\text{Ca}(\text{NO}_3)_2$. The difference between them was approximately 8%. On the other hand, the application of a stronger 3% solution resulted in an even more pronounced E decrease for $\text{Ca}(\text{NO}_3)_2$ (down to 86% at pH 3), whereas for CaCl_2 92% desorption was still obtained.

The HCl wash of Cu-laden biomass released all the metal at both concentrations used (0.1 M, 1 M). However, the biomass became more fragile and the color of the biomass turned from brown to black, particularly with the stronger HCl solution. The biomass that was exposed to the calcium solutions turned dark brown but remained soft similar to the treatment with tap or distilled water only.

An important parameter for metal desorption is the solid:liquid ratio (S:L) defined as the mass of metal-laden biosorbent to the volume of the elutant. The smallest possible elutant (liquid) volume is desired (high S:L) so that a highly concentrated metal solution is obtained at the end. Figure 6 illustrates the effect of the S:L ratio on the elution efficiency for 1% CaCl_2 , 1% $\text{Ca}(\text{NO}_3)_2$, and 0.1 M HCl. The elution efficiency for HCl appeared to be nearly independent of the S:L-ratio up to the examined value of 10 g/l. However, elution efficiency decreased with increasing S:L for both calcium-salt solutions. At S:L=2, copper release was less than 80% and dropped to less than 50% at S:L=10 g/l.

Earlier work (Aldor *et al.*, 1995; Kuyucak and Volesky, 1989) indicated the potential of CaCl_2 to be used as an eluting agent for cobalt and cadmium. Copper would not desorb completely, most likely due to the enhanced covalent character of its binding (Crist *et al.*, 1990). The use of calcium salts at pH=3, or HCl, resulted in the best desorption efficiencies. It is clear that protons play a major role

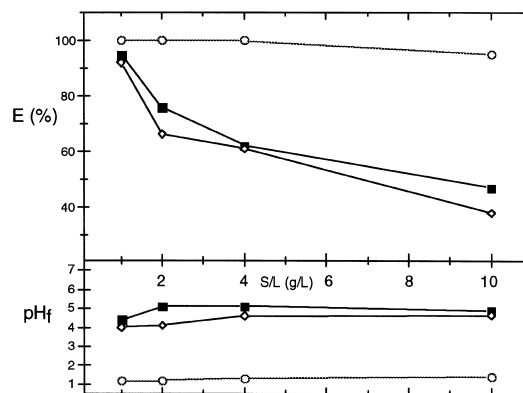


Fig. 6. Effect of the solid:liquid ratio (S:L) on the Cu elution efficiency and final pH for CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ and HCl: (■) 1% CaCl_2 , (◇) 1% $\text{Ca}(\text{NO}_3)_2$, (○) 0.1 M HCl. (Copper loading on *S. filipendula* I: $q = 0.77$ mmol/g; $C_i = 3.9$ mM, $C_f = 2.4$ mM).

in desorption. The increase in the final pH observed in this work indicated that copper was displaced from the biomass by protons. In general, the release of biosorbed metals upon acidification reflects their binding to carboxylate and sulfonate groups in the biomass cell wall material (Crist *et al.*, 1992). Finally, it should be emphasized that batch desorption studies represent just another (two-metal) equilibrium system since the displaced metal from the biomass remains in the solution.

Practical points for the choice of elutant

Ca^{2+} stabilizes the algal biomass by binding alginate and converting it to the gel state. This may prevent excessive weight loss (in the form of matrix polysaccharides) during long-term usage. The present experiments did not reveal any significant difference between the elution efficiency of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$. Furthermore, HCl was found to be a very powerful metal-desorbing agent. However, its use may have damaging effects for the biomass that could result in decreased “next-cycle” metal uptake capacity. (Kuyucak and Volesky, 1989). This aspect may narrow the choice of practical desorbing agents to CaCl_2 or $\text{Ca}(\text{NO}_3)_2$. While residual nitrates in the environment pose dangers, higher levels of chlorides are more easily tolerated (Rudolph, 1993). Furthermore, in industrial quantities (metric tons), the price of CaCl_2 is only approximately half that of $\text{Ca}(\text{NO}_3)_2$. All considered, CaCl_2 appears as the more appropriate metal-cation desorbing agent.

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Table 4. Elution of Cu from *S. filipendula* I at the S:L ratio of 1 g/l^a

Elutant	pH _i	pH _f	E (%)
0.1 M HCl	1.2	1.3	100
1 M HCl	0.9	1.0	100
Tap water	7.5	6.2	6.6
Dist. water	6.6	6.4	1.2

^aCopper loading on *S. filipendula* I: $q = 0.77$ mmol/g; $C_i = 3.9$ mM, $C_f = 2.4$ mM. Elution efficiency: $E = (\text{metal eluted})/(\text{metal biosorbed}) \times 100\%$.

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