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Solution and Particle Effects on the Biosorption of Heavy Metals by Seaweed Biomass

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ABSTRACT

Biosorption of cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) by six fractions of particle sizes, ranging from 0.063 to 1.4 mm of dry marine algal biomass of *Sargassum fluitans* and *Ascophyllum nodosum*, is examined. Equilibrium metal uptake by larger particles was higher than that by smaller particles in the order of Pb > Cd > Cu > Co > Zn > Ni for both biomass types, with *S. fluitans* sorbing slightly more than *A. nodosum*. Uptakes of metals ranged from the highest, q_{max} = 369 mg Pb/g (particle size 0.84–1.00 mm), to the low Zn and Ni uptakes, q_{max} = 77 mg/g (size 0.84–1.00 mm) for *S. fluitans*. *A. nodosum* adsorbed metals in the range from q_{max} = 287 mg Pb/g (particle size 0.84–1.00 mm) to q_{max} = 73 mg Zn/g (particle size 0.84–1.00mm). Harder stipe fractions of *S. fluitans* demonstrated generally higher metal uptakes than the softer fractions derived from its blades (leaves). The pH dependence of the Zn uptake by *S. fluitans* exhibited a S-shaped curve between pH 1.5 and pH 7, with 50% of the maximum (pH 7.0) uptake at pH 3.5. Monovalent Na and K ions at higher concentrations inhibited the biosorption of Zn by *S. fluitans*. A significant inhibition started at 50 m*M* potassium chloride or sodium acetate, and at 1*M* the biosorption was completely blocked.

Index Entries: Biosorption; brown algae; *Ascophyllum nodosum*; *Sargassum fluitans*; metal uptake; cadmium; cobalt; copper; nickel; lead; zinc.

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INTRODUCTION

Biosorption, the passive metal uptake by dead biomass, has been observed in a broad range of microbial biomass types. Although other conventional processes, such as chemical precipitation, ion exchange, reverse osmosis, and solvent extraction, remove toxic heavy metals from industrial effluents, biosorption might provide a cheap and efficient alternative process. The use of yeast, bacterial, and fungal biomass for removing metals, particularly from low-concentration solutions, has been explored recently (*1,2*).

Interest has focused on marine biomass, expecially brown algae (*3*), because of its high metal-sorbing potential. It was shown that the marine brown alga *Ascophyllum nodosum* accumulated more than 100 mg Cd/g biomass, outperforming the commercial ion exchange resin Duolite GT-73 (*4*). Other metals are also in the center of environmental concern. The removal of Cu (*5*), Ni (*6*), Pb (*7*), Zn (*8*), and Co (*9*) has been studied.

The main objective of this work was to determine the influence of selected parameters on the accumulation of six different metals by two different types of brown marine algae, *Sargassum fluitans* and *A. nodosum*. Indications that an ion exchange process is of importance in metal ion immobilization make the solution pH and the biosorbent particle size particularly important. Another key parameter is the biomaterial composition. Most brown algae feature a harder stipe and soft blades (leaves), each part chemically and architecturally somewhat different. Metal sorption by these specific seaweed parts was examined. The influence of monovalent ions on the heavy metal uptake also was tested, since industrial effluents very often contain elevated salt levels. The influence of these parameters may be a deciding factor in potential applications of seaweed-derived biosorbent materials in the wastewater cleanup process. Specific observations also contribute to the understanding of the metal biosorption mechanism.

MATERIALS AND METHODS

Biomass and Chemicals

Fresh brown marine alga *A. nodosum* originated from the Atlantic Ocean at Nova Scotia. Another brown alga, *S. fluitans*, was collected from the Gulf of Mexico in Naples, Florida and sun-dried on the beach. Stipes and blades were mechanically separated by rubbing the dried biomass. Particles originating from the filamentous stipe were harder than the particles from the thin flat blades. The native biomass as used consisted of a natural mixture of stipe and blade material particles. The biomass was extensively washed with tap and distilled water and dried at 80°C overnight. Air bladders of *S. fluitans* were separated from the fronds during the washing process and collected from the water surface. They were washed twice in distilled water and dried at 80°C overnight. Washed or unwashed biomass was disintegrated in a laboratory blender and the particles sorted by sieving, using the Canadian Standard Sieve Series. Six different particle size fractions were collected: fraction 1 (#1, particle size d = 0.063–0.105 mm), fraction 2 (#2, d = 0.105–0.295 mm), fraction 3 (#3, d = 0.295–0.500 mm), fraction 4 (#4, d = 0.500–0.840 mm), fraction 5 (#5, d = 0.840–1.00 mm), and fraction 6 (#6, d = 1.00–1.40 mm). The particle size distribution depended on the processing time in the blender.

Analytical grades of HC1, H_2SO_4, NH_4OH (Anachemia, Montreal), anhydrous $CuSO_4$, $ZnSO_4 \times 7 H_2O$ (J. T. Baker, Phillisburg, NJ), $NiC1_2 \times 6 H_2O$, $CdSO_4 \times 8H_2O$, $Pb(NO_3)_2$ (BDH, Toronto, ON), $CoSO_4 \times 7 H_2O$, $CoC1_2 \times 6 H_2O$ (Fisher Scientific, Fair Lawn, NJ), and reagent grade KC1, sodium acetate (Aldrich, Milwaukee, WI), and tetraethylammonium hydroxide (Anachemia, Montreal) were used for metal sorption experiments. Atomic absorption standards (1000 ppm) for all metals were purchased from Fisher Scientific (Montreal).

Swelling Behavior and Specific Surface

Dry particles were weighted in a cylinder determining the dry bulk density ρ_d (g/mL). The particles were then soaked and swollen in distilled water for 12 h at room temperature. This resulted in a distinct increase of biomass volume, expressed as V_s (mL/g dry wt). The excess water was removed and the wet bulk density ρ_s (g/mL dry wt) was determined. Distention index DI = V_s / ρ_d, swelling ratio Q = ρ_s / ρ_d, and the volume of adsorbed solvent VAS = $(\rho_s - \rho_d) / \rho_d$ were calculated. The amount of water-soluble biopolymers, which were released during the swelling, was determined gravimetrically after washing, filtration, and drying.

The surface area (S_A) was determined by a standard procedure using Quantasorb Surface Area Analyzer model QS-16 (Quantachrome, Syosset, NY) employing N_2-BET adsorption and desorption techniques, with helium as a carrier gas.

Metal Uptake

The sorption methodology, including the construction of isotherms, has been described in detail elsewhere (*2,6,10,11*). A typical equilibrium sorption experiment was carried out in 125 mL Erlenmeyer flasks, applying 100 mg of biomass to 50 mL of metal solution of a known initial concentration C_i. The suspension was agitated on a rotary shaker at 3.5 Hz for 3 h at room temperature. The pH was adjusted several times to pH 3.5 with 0.1*M* NH_4OH, 0.5*M* tetraethylammonium hydrochloride, 0.1*M* HNO_3, 0.1*M* NaOH, 0.1*M* HC1 or 0.1*M* H_2SO_4, depending on the metal, to avoid precipitation. pH 3.5 was selected to avoid the potential effects of microprecipitation of metallic complexes at higher pH levels (above pH 4.5), which interfere with studying the pure sorption phenomenon.

Metal-free and biosorbent-free blanks were used as controls. The solution was separated from the biomass with Millipore membrane filters (0.45 μm) in a 30-mL syringe. The filtrate was either diluted with distilled water (Zn, Cu) or directly analyzed by atomic absorption spectroscopy using AAS (Thermo Jarrel Ash model Smith-Hieftje 11 or Perkin Elmer 3100) at 346.6 nm (Co), 326.1 nm (Cd), 323.3 nm or 341.5 nm (Ni), 216.5 nm or 249.2 nm (Cu), 261.5 nm (Pb), and 213.9 nm or 307.6 (Zn).

The influence of pH was determined for the biosorption of Zn by *S. fluitans* (native biomass, d = 0.5–0.8 mm). The initial concentration C_i was 270 mg Zn/L. The biomass was contacted with the metal solution for 3 h and the pH was adjusted every 30 min to the test value, ranging from pH 1.5 to 7.0. At pH values greater than 7.0, precipitation of $Zn(OH)_2$ occurred excluding this pH region from sorption studies. The influence of monovalent ions was examined using the same biomass. The initial concentration ws $C_i = 250$ mg Zn/L. Different amounts of potassium chloride and sodium acetate from 0.01 to 1.0 mol/L were added to the metal solution before contacting the biomass. The pH was not adjusted during the experiment, to avoid any ionic interferences. The pH after the contacting period ranged from pH 5.2 (0.01*M* NaAc) to pH 5.0 (1.0*M*NaAc).

The metal uptake (q) for the construction of sorption isotherms was calculated using the equilibrium metal concentration values, C_f determined experimentally:

$$(\text{mg metal/g of biomass})\ q = V\,(C_i - C_f)\,/\,m$$

where V is the volume of solution in the batch contact flask (mL), C_i is the initial concentration of metal in the solution (mg/L), and m is the mass of the algal biomass. The Langmuir sorption model (*12*) was chosen for estimation of the maximum sorbate (metal) uptake (q_{max}):

$$q = q_{max}\, b\, C_f\,/\,(1 + b\, C_f)$$

where b is a constant related to the energy of adsorption/desorption. The linearized form of this equation was used to fit the experimental data, allowing the expression of b and q_{max} from the best fit. The q values at C_f higher than 2000 mg/L were not incorporated in the calculation. Metal uptakes q_{10} and q_{200} are those corresponding to the arbitrarily selected equilibrium concentrations (C_f) of 10 and 200 mg metal/L, respectively. They were determined from the smoothed (Langmuir model) experimental isotherms at the respective final concentrations.

RESULTS

Swelling Characteristics and Specific Surface

The key swelling characteristics determined for the two biomass types studied are summarized in Table 1. Both sizes of *A. nodosum* exhibited the highest value of ρ_d, followed by values of ρ_d for *S. fluitans*. The dry

Table 1
Swelling Characteristics of *Ascophylum Nodosum* and *Sargassum fluitans* Particles

Biosorbent	Bulk density dry (ρ_d), g/mL	Bulk density wet (ρ_s), g/mL	Volume swollen (V_s), mL	Distention index (DI), mL/g	Swelling ratio (Q), g/g	Volume of adsorbed area (VAS), mL/g	Surface area (S_A), m^2/g
A. nodosum[a] #5	0.85	5.28	7.4	8.7	6.2	5.2	0.095
A. nodosum[b] #2	0.83	4.48	6.8	8.2	5.4	4.4	0.144
S. fluitans stipes #5	0.35	1.49	1.7	4.9	4.3	3.3	0.298
S. fluitans stipes #2	0.71	3.52	4.5	6.3	5.0	4.0	0.368
S. fluitans blades #5	0.20	1.01	2.2	11.0	5.1	4.1	0.613
S. fluitans blades #2	0.54	2.18	2.7	5.0	4.0	3.0	0.287
S. fluitans native #5	0.40	2.38	5.8	14.5	6.0	5.0	0.527
S. fluitans native #2	0.61	2.92	4.0	6.6	4.8	3.8	0.287

[a] Size of particles was d = 0.841–1.00 mm.
[b] Size of particles was d = 0.105–0.295 mm.

bulk density of the stipe fractions was higher than the density of the blade fraction for the corresponding particle size. *A. nodosum* also had a higher swelling volume (V_s) than *S. fluitans*. Small particles of *S. fluitans* and *A. nodosum* stipe fractions (#2) had higher specific surface (S_A) than big particles (#5). This observation was in contrast to the other fractions (blades and native biomass) of *S. fluitans* possessing the highest values of S_A. This points to the biosorption of metals being based on ionic interactions between ionic groups of the biosorbent and cations rather than simple adsorption to the surface. The release of water-soluble materials (including biopolymers) was observed during the swelling period. The mass loss of small particles was higher than that observed for big particles and following the order: stipe fraction #2 (25%) > blade fraction #2 (22%) > blade fraction #5 (11%) > stipe fraction #5 (8%).

Effect of Particle Size

The particle size distribution of washed *S. fluitans* and nonwashed biomass of both algae depended on the processing time in the blender. Harder stipes were faster and more easily disintegrated than the soft blades. Native biomass of *A. nodosum* and *S. fluitans* of six different sizes (from 0.063 to 1.400 mm) and air bladders of *S. fluitans* were used to investigate the influence of particle size on the biosorption of heavy metals. A medium concentration range C_i = (200–266) mg/L metal was applied and the percent metal removal from solution served as an indicator of the sorbent performance by different size particles. Figures 1 and 2 represent the summary of results for *S. fluitans* and *A. nodosum*, respectively. Higher metal uptakes and removals were observed with increasing particle size for all the metals tested. When the w/w metal uptake basis is chosen for the comparison of sorption performance, it favors the heavier metals. However, the weight basis has been adopted here because it is widely used as a quantitative pollution criterion, serving also as a basis for sorption process mass balance calculations. The average weight-based metal uptake observed in the present study decreased in the following order:

Pb > Cd > Cu > Ni > Zn > Co (*S. fluitans*)

and Pb > Cd > Cu > Co ≈ Ni > Zn (*A. nodosum*)

These results can easily be converted to the molar basis relevant to stoichiometric and metal-biosorbent affinity considerations, which, however, have not been addressed in this work. The average molar-based uptakes naturally follow a different order because of different atomic weights of the metals investigated:

Cu > Pb > Ni > Zn > Cd> Co (*S. fluitans*, molar basis)

Cu > Pb > Ni > Co > Zn ≈ Ni (*A. nodosum*, molar basis)

While detailed results are not presented here, biosorption of different metals by *S. fluitans* air bladders can be summarized as follows. The metal

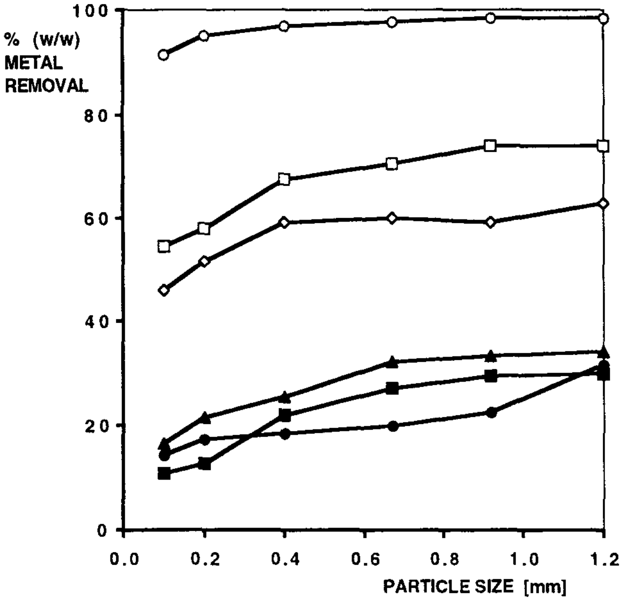

Fig. 1. Size dependence of heavy metal biosorption by particles of *S. fluitans* biomass at pH 3.5: (○) Pb (C_i = 260 mg/L), (□) Cd (C_i = 200 mg/L), (◇) Cu (C_i = 250 mg/L), (●) Co (C_i = 266 mg/L), (▲) Zn (C_i = 255 mg/L), and (■) Ni (C_i = 214 mg/L).

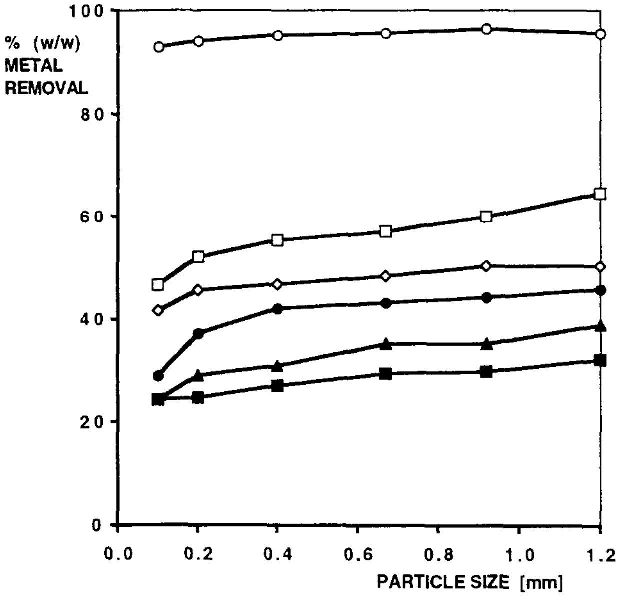

Fig. 2. Size dependence of heavy metal biosorption by particles of *A. nodosum* biomass at pH 3.5: (○) Pb (C_i = 260 mg/L), (□) Cd (C_i = 238 mg/L), (◇) Cu (C_i = 250 mg/L), (●) Co (C_i = 266 mg/L), (▲) Zn (C_i = 275 mg/L), and (■) Ni (C_i = 214 mg/L).

uptake values of S. *fluitans* air bladders were comparable to the uptakes by whole biomass particles of sizes #2 and #3 for Ni, Pb, and Cu; however, their Cd sorption was more comparable to that for biomass particles between sizes #1 and #2. The air bladder material reached Co uptake comparable to size #5 biomass particles. When comparing metal removals by washed and unwashed S. *fluitans*, the former was generally better for all tested metals than the latter. Moreover, the chloride and sulfate ions that were retained in nonwashed biomass after evaporation of seawater caused the formation of a colloid haze of insoluble Pb salts. For this reason, only washed material of S. *fluitans* was used in subsequent experiments. The removal of Co was close to the low values observed for Zn and Ni, which were very close together. Co was therefore not used for the evaluation of biosorption isotherms.

The data in Figs. 1 and 2 were useful for the biosorption performance screening purposes, but an appropriate quantitative comparison of sorption performance by different size particles should be based on complete sorption isotherms.

Biosorption of Five Individual Metals

The comparison of complete biosorption isotherms was done only for particles of sizes #2 and #5, representing large and small particles, respectively. Native S. *fluitans* (Fig. 3) and A. *nodosum* (Fig. 4) biomass particles size #5 sorbed the metals tested in the decreasing order:

on a molar basis: Pb > Cu > Ni > Cd > Zn

on a weight basis: Pb > Cd > Cu > Zn > Ni

Lead was adsorbed best, but its q_{max} uptakes by the two types of biomass tested did not differ substantially. As seen from Table 2, the differences for the respective maximum metal uptakes (q_{max}) determined for the two biomass types were: 0% (Cd), 10% (Cu), 3% (Ni), 8% (Pb), and 5% (Zn). However, in the low concentration range around arbitrarily chosen C_f = 10 mg/L, the corresponding metal uptake q_{10} values differed between 0 and 62% (Table 3).

The Influence of Biomass Composition

S. *fluitans* is composed of a hard stipe and the soft blades. To investigate their respective biosorption capacities for heavy metals, stipes and blades were separated, powderized, and sieved. Fractions of size #2 (small particles) and #5 (big particles) were tested with five different metals. The native, whole biomass was used as a control representing the natural mixture of stipes and blades.

The biosorption of Pb by the stipe (S) and blade (B) fractions of S. *fluitans* is shown in Fig. 5. The stipe fraction exhibited a higher Pb uptake than the blade fraction in the range 0–1500 mg Pb/L (final concentration C_f). The uptake by S was up to 350 mg Pb/g biomass in contrast to the

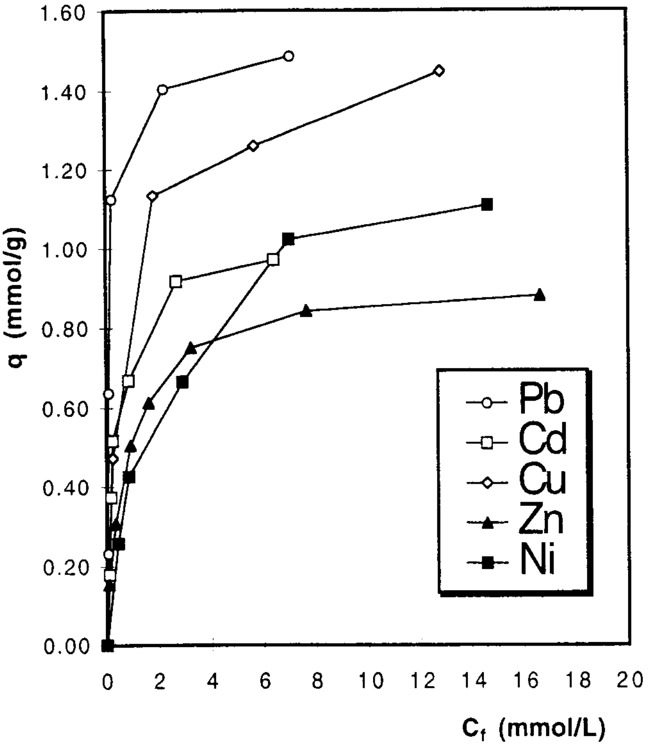

Fig. 3. Biosorption of five heavy metals by biomass of *S. fluitans* biomass at pH 3.5 (particle size #5): (○) Pb, (□) Cd, (◇) Cu, (▲) Zn, and (■) Ni.

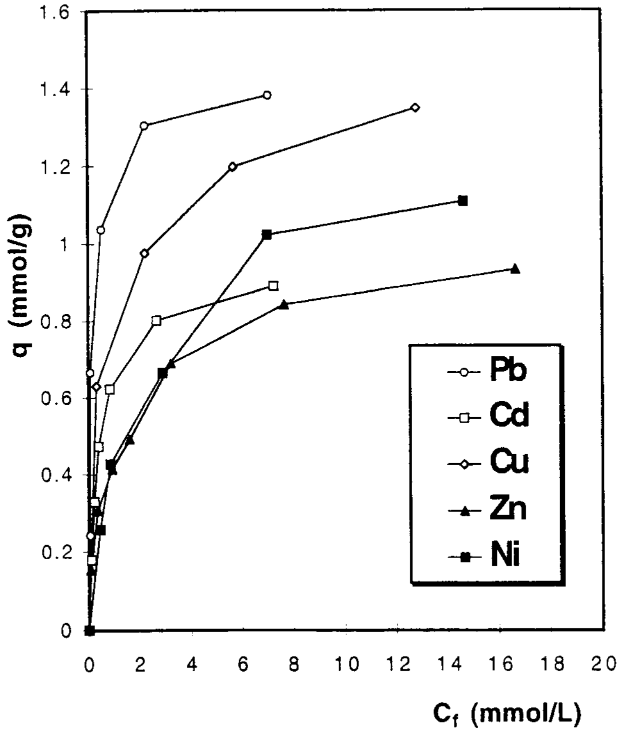

Fig. 4. Biosorption of five heavy metals by biomass of *A. nodosum* biomass at pH 3.5 (particle size #5): (○) Pb, (□) Cd, (◇) Cu, (▲) Zn, and (■) Ni.

Table 2

Langmuir Constants q_{max} and b Resulting from Equilibrium Uptake Studies of Five Metals by Biomass of Marine Algae at pH 3.5

	Cd			Cu			Ni			Pb			Zn		
	q_{max}		b	q_{max}		b	q_{max}		b	q_{max}		b	q_{max}		b
Sorbent type	mg/g	mmol/g	L/mg ×100	mg/g	mmol/g	L/mg ×100	mg/g	mmol/g	L/mg ×100	mg/g	mmol/g	L/mg ×100	mg/g	mmol/g	L/mg ×100
S. fluitans #5[a] stipes	114	1.01	2.65	118	1.86	11.9	75	1.28	0.99	369	1.78	4.38	76	1.16	2.29
S. fluitans #2[b] stipes	111	0.99	2.62	129	2.03	1.61	69	1.18	0.63	341	1.65	4.18	69	1.06	1.99
S. fluitans #5 blades	113	1.01	1.57	112	1.76	5.53	75	1.28	0.67	308	1.49	6.78	73	1.12	2.02
S. fluitans #2 blades	103	0.92	2.07	100	1.57	10.2	72	1.23	0.70	303	1.46	3.93	54	0.83	2.59
S. fluitans #5 native	111	0.99	4.16	110	1.73	6.24	72	1.23	1.04	311	1.50	6.88	77	1.18	1.27
S. fluitans #2 native	108	0.96	1.37	105	1.65	2.5	74	1.27	0.50	289	1.39	3.96	40	0.61	1.92
A. nodosum #2 native	111	0.99	4.16	99	1.57	4.43	70	1.18	1.26	287	1.38	3.37	73	1.12	0.82
A. nodosum #2 native	108	0.96	1.37	89	1.40	3.29	63	1.07	0.75	271	1.31	2.92	71	1.09	0.69

[a] Particle size d = 0.841–1.00 mm.

[b] Particle size d = 0.105–1.295 mm.

Table 3
Experimental Uptakes q_{10} and q_{200} of Five Metals by Marine Algae at pH 3.5

	Cd		Cu		Ni		Pb		Zn	
Sorbent type	q_{10}[a]	q_{200}[a]	q_{10}	q_{200}	q_{10}	q_{200}	q_{10}	q_{200}	q_{10}	q_{200}
S. fluitans #5, stipes[b]	25	86	49	92	9	44	160	281	11	55
S. fluitans #2, stipes[c]	25	84	42	87	5	33	146	264	10	51
S. fluitans #5, blades	21	79	35	83	6	37	134	243	10	54
S. fluitans #2, blades	21	74	46	81	6	39	137	240	10	46
S. fluitans #5, native	29	92	45	85	8	41	151	256	13	47
S. fluitans #2, native	15	62	21	78	5	32	130	226	7	29
A. nodosum #5	20	80	28	77	8	43	139	228	8	44
A. nodosum #2	14	68	20	66	6	34	48	209	9	35

[a] q_{10} and q_{200} represent uptakes (mg metal / g biomass) at equilibrium concentration 10 mg metal/L and 200 mg metal/L, respectively.
[b] Size of particles was d = 0.841–1.00 mm.
[c] Size of particles was d = 0.105–0.295 mm.

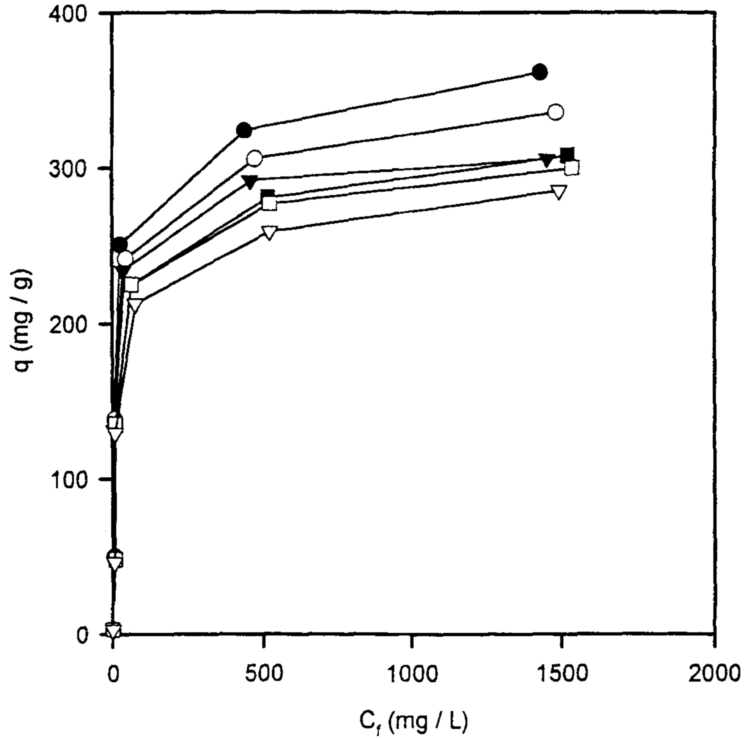

Fig. 5. The effect of biosorbent particle composition on Pb adsorption by *S. fluitans* biomass at pH 3.5, particle size #5, d = 0.84–1.00 mm: (▲) Native biomass, (●) Stipe fraction, and (■) Blade fraction; particle size #2, d = 0.105–0.295 mm: (▽) Native biomass, (○) Stipe fraction, and (□) Blade fraction.

uptake by B, which did not exceed 300 mg Pb/g biomass. The lead uptake by the native biomass did not substantially differ from that observed for the blade fraction. Furthermore, larger particles of stipe fraction size #5 (S5) demonstrated a higher Pb uptake than smaller ones in the stipe fraction of #2 (S2). The same conclusion could be drawn for the blade fractions and for the whole native biomass particles of the two different sizes.

Stipes, blades, and the whole native biomass of *S. fluitans* differed in their Cd uptake as well (Fig. 6). The stipe fraction exhibited a higher Cd uptake than the blade fraction. In general, larger-size particles again performed better. Particularly, the blade fraction and the native biomass confirmed the sorption behavior observed with Pb. The quantitative summary of sorption performance observed for each of the five metals tested with the two biomass types is presented in Tables 2 and 3, giving values for q_{max} and b, and for q_{10} and q_{200}, respectively.

Comparing the q_{max} values for Pb, the uptakes were 100% (S5, 369 mg Pb/g biomass), 92% (S2), 83% (B5), 82% (B2), 84% (native #5), and 78% (native #2). The corresponding q_{max} values for Cd uptake were 100% (S5, 114 mg Cd/g biomass), 97% (S2), 99% (B5), 90% (B2), 97% (native #5), and 95% (native #2). These maximum uptake values confirmed more or less

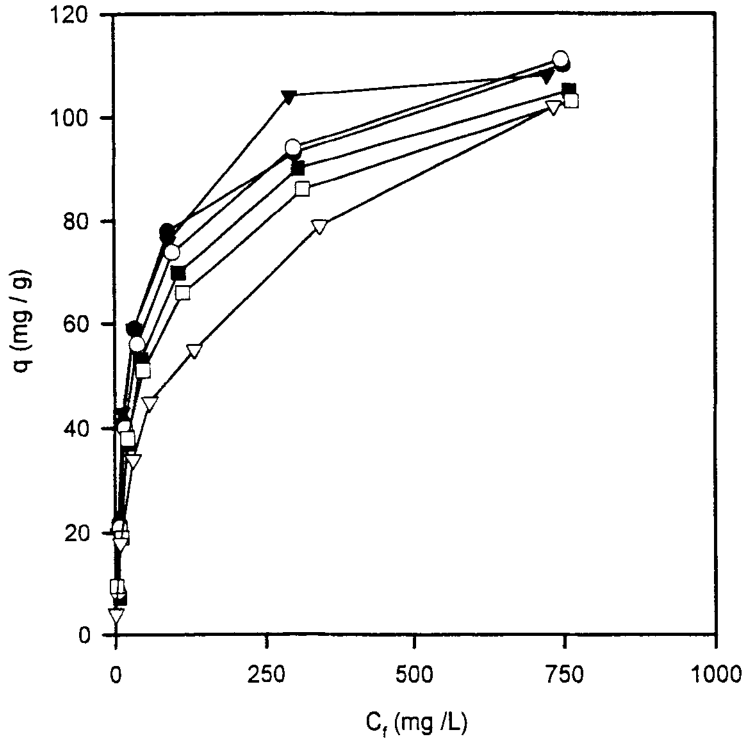

Fig. 6. The effect of biosorbent particle composition on Cd adsorption by *S. fluitans* biomass at pH 3.5, particle size #5, d = 0.84–1.00 mm: (▲) Native biomass, (●) Stipe fraction, and (■) Blade fraction; particle size #2, d = 0.105–0.295 mm: (▽) Native biomass, (○) Stipe fraction, and (□) Blade fraction.

that stipes had a higher uptake than blades and big particles exhibited a higher uptake than small particles.

pH Dependence

The pH dependence was demonstrated with the biosorption of Zn by big particles of *S. fluitans* (native #5) in the pH range 1.5–7.5. The S-shaped curve (Fig. 7) could resemble an overall titration curve if ionic groups were responsible for metal uptake. A 50% uptake was reached at pH 3.5, suggesting that carboxylic groups might be involved. They typically feature pK values between pK 3 and pK 4. No metal uptake was observed at pH 1.5, which could be used for the metal desorption. At pH values above 7, precipitation of $Zn(OH)_2$ occurred; this range cannot be used for evaluation of sorption behavior.

Monovalent Ions

Increasing concentrations of potassium chloride or sodium acetate resulted in suppressed metal sorption. The negative influence of these salts on the biosorption of Zn by *S. fluitans* (native biomass, particle size #5)

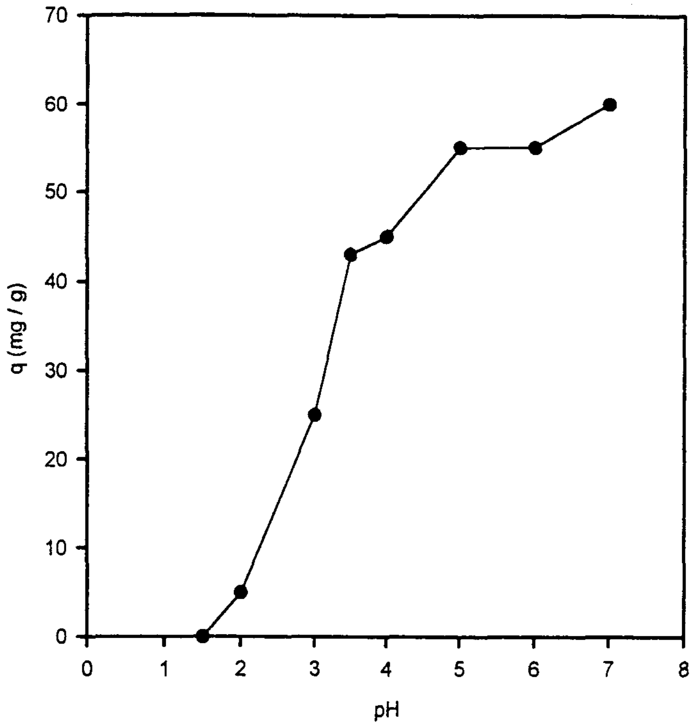

Fig. 7. The effect of pH on biosorption of Zn by particles of *S. fluitans* biomass at pH 3.5 (particle size #5, d = 0.84–1.00 mm).

is shown in a semilogarithmic plot (Fig. 8). A noticeable sorption inhibition started at 50 m*M* concentrations of either sodium acetate or potassium chloride salts. A 1*M* solution inhibited the heavy metal uptake completely. Considering the fact that C_i = 1000 mg/L solutions of heavy metals used in this work represent 17, 16, 15, 9, and 5 m*M* solutions of Ni, Cu, Zn, Cd, and Pb, respectively, concentrations of light metal-containing buffers in biosorption experiments should be kept very low, or such buffers have to be avoided altogether.

DISCUSSION

Biomass of two species of brown algae identified earlier for their high heavy metal uptake (*9,13*) has been used in further studies. Both seaweeds, *A. nodosum* and *S. fluitans*, demonstrated an excellent potential for sequestering heavy metals (*3,14*). Especially, the uptake of Cd (*4*) and the uptake of Pb and Ni (*6*) by biomass of marine algae has been examined in more detail. The two seaweeds belong to the same order of Fucales but they exhibit differences in their morphology, cytology, and chemical composition (*15,16*). *S. sluitans* consists of a hard stipe and blades (leaves) with a midrib and wings, lateral branches, and air bladders. Stipes, for

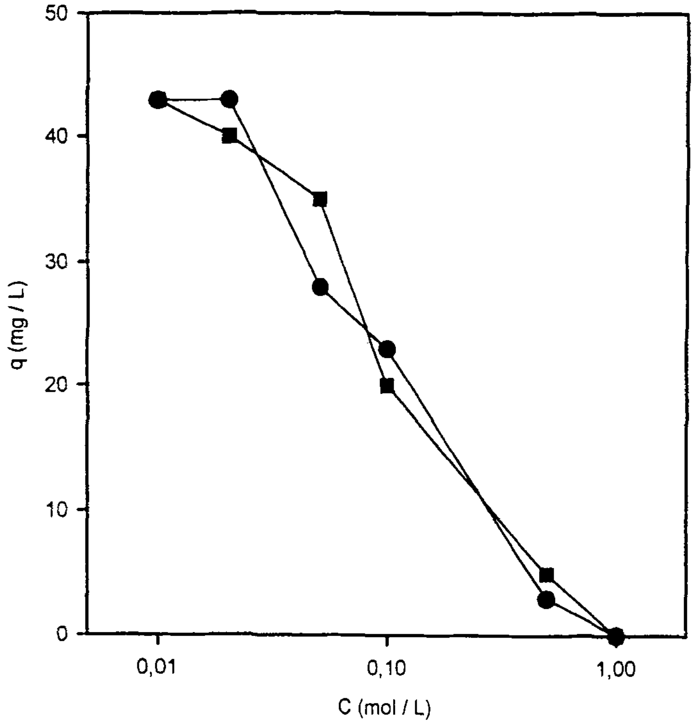

Fig. 8. The influence of monovalent ions on Zn biosorption by particles of *S. fluitans* biomass at pH 3.5 (particle size #5, d = 0.84–1.00 mm): (●) potassium chloride and (■) sodium acetate.

instance, contain 50% more medullary tissues than blades. The thallus of *A. nodosum* consists of a linear, compressed frond lacking a distinct midrib.

The chemical composition of brown algae varies during the seasons and depends on geography and tidal influences as well. It is therefore difficult to relate a specific sorption behavior to a certain chemical composition. *A. nodosum*, for instance, contains a unique mixture of polysaccharides (*17*): 25% L-xylose, 26% D-xylose, 19% D-glucuronic acid, with 13% of sulfate groups, and an additional 12% of protein. Because of the differences in the composition of stipes and blades, it was no surprise that they did not adsorb heavy metals to the same extent. Generally, the stipe fraction demonstrated a better metal uptake. The uptake differences for the stipe fraction, blade fraction, or native biomass were not large; all were well within the same order of magnitude. From a technological point of view concerning the preparation of biosorbent materials, the separation of biomass parts is therefore not important. The differences could be explained by a varying content of polysaccharides or other cell wall constituents bearing metal sorption sites.

The composition of algal polysaccharides has been described in detail (*18*). These compounds are particularly suited for metal sequestering because of their content of carboxylic and sulfate groups. Sulfate esters were found in many species of brown algae (*19*) and carboxylic groups were described as well (*20*). However, other mechanisms than ion exchange can contribute to the sequestering of heavy metals. Covalent bonding of metals to algal cell wall proteins has been reported (*21*). The chelation of cupric ions by chitosan membranes in fungi has been reported (*22*). It was shown that metals could be bound by intra- or intermolecular chelation (*23*).

The influence of pH on metal sorption by fungi (*24,25*) and bacteria (*26*), as well as the influence of ionic strength (*27*), have been demonstrated before. The influence of pH (Fig. 7) and monovalent ions (Fig. 8) on Zn biosorption by *S. fluitans* indicated that ion exchange is at least partly involved. The pH dependence resembled the S-shaped titration curve of chemical groups. Supposing a titration curve for only one chemical group (in reality it is a complex mixture), a value of pK 3 to 4 might be estimated. This is the usual range for carboxylic groups. Furthermore, heavy metal sorption was diminished or suppressed by adding monovalent ions. Cations, such as NA^+, K^+, and heavy metal ions, compete for ionic sorption sites (*39,40*). These two findings suggest that ion exchange plays a major role in metal biosorption by the two biomass types studied here. Native algae in seawater that contains on the order of 30,000 mg/L of light-metal salts would be quite unlikely to sorb heavy metal cations which are present in that environment only in very low concentrations.

The biosorption of heavy metals was observed to depend also on the sorbent particle size (Figs. 1 and 2). Big particles exhibited a higher metal uptake than small particles. These results are in contrast to the particle size dependence of Cu sorption by chitosan (*28*). The sorption of the smallest (0.282 mm) and the biggest (0.805 mm) particles differed only by 4 mg Cu/g homopolymer and particles of medium size (0.50 mm) exhibited the highest uptake (*28*). In contrast to chitosan, which is a defined homopolymer, biomass of marine algae is composed of many diverse parts and the biomass architecture may play an important role in the binding of heavy metal cations. Next to cellulose and sulfated polysaccharides, alginic acid represents a ubiquitous component in brown algae.

Sulphated polysaccharides, typically ascophyllan, carageenan, fucoidan, and dextransulphate, have not been found very active in binding heavy metals, e.g., Cu (*29*). That leaves alginate as the major metal-binding component. Its poly-L-guluronic acid fragments were found to effectively bind Pb > Cu > Ba > Sr, in that preference sequence (molar basis); its poly-D-mannuronic fragments sorbed well metal cations in the following mole-based preference order: Pb > Cu > Cd > Ba > Ni > Sr > Ca > Mg > Zn = Co = Mn (*29*). The sorption of bivalent ions apparently requires a suitable steric arrangement of the fixed groups on the biopolymer, because the bivalent cation needs to become asociated with more than one negatively charged group. The mechanism of binding of bivalent ions to alginate was proposed early as chelate binding, with the stress on the importance of free hydroxyl groups (*30,31*). If a hydrogen bond between the vicinal OH groups if favored, a substitution of the hydroxyl groups involved becomes very difficult. For alginic acid, the observed mole-based metal affinity sequence was Pb > Ba > Sr > Cu, Cd > Ca, Be, Zn, Co, Ni > Mn, Mn (*31*). The present results are similar, with the exception that on a molar basis Ni was slightly better sorbed than Cd and Zn. They differ from the preference sequence observed by Schweiger for Zn and Ni (*30*). However, it is important to emphasize that there may be many different forms of alginate, depending on the size of mannuronic and guluronic fragment blocks in the polymer (*29*). These variations can be responsible for some discrepancies observed in metal binding by further unspecified alginate bio-polymers.

Another important aspect of metal behavior in biosorption is the metal solution chemistry and behavior. Transition elements are defined as those that contain partially filled d-orbitals and loose 4s2 electrons, not the d-ones. Though Zn and Cd should correspondingly not be included by this definition, they have traditionally been counted among them. Several different aspects may play a role when considering the acid-base equilibria involving metals (as soft acids) and basic ligands: the covalent energy (E_c), Madelung energy (E_M), the electronegativity energy (E_x), and bond length. Examining the Irwing-Williams series from the plot of atomic mass (instead of the original atomic number) for the early transition metals vs the log of the stability constant, the following preference sequence results: Ni < Co < Cu > Zn, which agrees with the present experimental results. The preferred biosorbent deposition of Pb may be promoted by its complex-forming tendencies. Stable hydrate formation, with the next possible formation of oxo/hydroxo species and subsequent dimerization, was already postulated as a factor likely to contribute to formation of increased molecular mass complexes promoting metal deposition (*10*). London dispersion forces, increasing with the size and polarizability, offer a stabilizing factor for the bond between two large and polarizable (soft) atoms, a possible case of Pb-biomass interactions.

Biosorption uptakes of heavy metals reported in different studies, and reviewed recently by Volesky (*10*), showed a considerable variation span. For some metals, certain biomass types can be considered as good biosorbents when compared with other types. For practical (sorption process) reasons, this comparison of metal uptakes was made on a weight basis. Cadmium was equally well sorbed by native *A. nodosum* and *S. fluitans*, with an uptake q_{max} = 111 mg Cd/g biomass (big particles in this study). The Cd uptakes by *Candida tropicalis* (yeast) (*32*) and *Rhizopus arrhizus* (fungus) (*33*) were reported to be q_{max} = 60 mg Cd/g and q_{max} = 30 mg Cd/g, respectively. Nickel, with uptakes of q_{max} = 72 mg Ni/g and q_{max} = 70 mg Ni/g for *S. fluitans* and *A. nodosum*, respectively, was better adsorbed than by many other biomass types tested. Uptakes of q_{max} = 20 mg Ni/g for *C. tropicalis* (*32*) and q_{max} = 18 mg Ni/g for *R. arrhizus* (*24*) were considerably lower than the performance of brown algae. Some brown algae were also excellent biosorbents for Pb (*34*), which, on a weight basis, was sorbed best of all investigated metals. With uptakes of

q_{max} = 311 mg Pb/g and q_{max} = 287 mg/g for *S. fluitans* and *A. nodosum*, respectively, Pb was much better adsorbed than by *Penicillium chrysogenum* (fungus, q_{max} = 122 mg Pb/g) (*35*), or by *Streptomyces longwoodensis* (bacterium, q_{max} = 100 mg Pb/g) (*36*), or some other fungal and bacterial species examined (*34*). However, different types of biomass are known with a much better uptake of Cu and Zu than the two brown algae presently studied. Copper was sorbed by *Bacillus subtilis* with q_{max} = 152 mg Cu/g (*26*), which is higher than both *S. fluitans* or *A. nodosum*. *B. subtilis* also sorbed Zn with the very high q_{max} = 137 mg Zn/g (*37*), which is better than the uptakes by biomass of both seaweeds observed in the present tests. The methodologies of various biosorption studies, however, are apparently still not well standardized (*10*), and considerable margins of possible variations have to be born in mind. The weight-basis for quantifying the sorption performance has been selected in presentation of the current results, since it is more common in pollution-related studies, serving also as a basis for relevant mass balance calculations. The molar basis is preferred in biosorption stoichiometric considerations (*38,39*) and metal-binding site investigations addressed elsewhere (*40*).

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