

# Biosorption of Lead and Nickel by Biomass of Marine Algae

Z. R. Holan and B. Volesky\*

Department of Chemical Engineering, McGill University, Montreal, Canada  
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Screening tests of different marine algae biomass types revealed a high passive biosorptive uptake of lead up to 270 mg Pb/g of biomass in some brown marine algae. Members of the order Fucales performed particularly well in this descending sequence: *Fucus* > *Ascophyllum* > *Sargassum*. Although decreasing the swelling of wetted biomass particles, their reinforcement by crosslinking may significantly affect the biosorption performance. Lead uptakes up to 370 mg Pb/g were observed in crosslinked *Fucus vesiculosus* and *Ascophyllum nodosum*. At low equilibrium residual concentrations of lead in solution, however, ion exchange resin Amberlite IR-120 had a higher lead uptake than the biosorbent materials. An order-of-magnitude lower uptake of nickel was observed in all of the sorbent materials examined. © 1994 John Wiley & Sons, Inc.  
Key words: lead biosorption • nickel biosorption • brown algae • seaweeds • biosorption screening • biosorption of heavy metals • metal uptake

## INTRODUCTION

There has been ample evidence of passive metal uptake observed with certain types of microbial biomass. Although scattered in a variety of research contributions, it has been summarized in a recently published book<sup>26</sup> which also outlines the potential of this phenomenon termed biosorption. Interest has primarily focused on heavy metals due to their known toxicity as they are discharged in small quantities by numerous industrial activities into the environment, where they tend to accumulate, being concentrated throughout the food chain. This aspect coupled with their persistence results in a serious health hazard threatening water supplies and populations depending on them.

Lead has been known for its toxicity for a long time, and increasing uses of nickel, particularly in metal plating, lead to rising concerns. These and other metals have been detected in some algal populations in different parts of the world.<sup>1,8,24</sup> Studies focusing specifically on nickel are rare.<sup>23,30</sup> Previous work mostly covered the sorption of nickel in a range of other heavy metals.<sup>2,9,13</sup> The information is mostly relevant to the description of metal accumulation by living plants or to the toxic effects of metals on their metabolism. Sometimes the levels of metals found in algal biomass served to detect the water contamination by metallic species. These studies are predominantly of an ecological orientation.<sup>28–30</sup>

\* To whom all correspondence should be addressed.

The potential of some freshwater algae biomass for metal binding has been recognized earlier,<sup>11</sup> leading to the focus on technological aspects of removal and recovery of heavy metals.<sup>7,16</sup> While toxicological studies with heavy metals in marine algae prevail, passive biosorption of heavy metals by seaweed materials has been studied only recently,<sup>14,17</sup> revealing the interesting potential of these abundant natural materials.<sup>26,27</sup>

This work, continuing the exploratory line of studies, compares the sorption of lead and nickel by selected marine algal biomass types abundantly available in the oceans.

## MATERIALS AND METHODS

### Biomass

The origin and treatment of brown algae (Phaeophyta) *Ascophyllum nodosum*, *Fucus vesiculosus*, and *Sargassum natans* were described earlier.<sup>14</sup> *Sargassum fluitans* came from the Caribbean (courtesy of L. Almodovar, University of Puerto Rico); *Sargassum vulgare* and *Padina gymnospora* were collected in Rio de Janeiro (courtesy of A. B. Pacheco, Jardino Botanico). Green alga (Chlorophyta) *Codium taylori* came from Australia (courtesy of H. Mann, on leave from the University of Western Ontario, London, Ontario). Red algae (Rhodophyta) *Chondrus crispus*, *Galaxaura marginata*, and *Palmaria palmata* came respectively from the Caribbean, Rio de Janeiro, and Atlantic Mariculture, Gand Maman, New Brunswick, Canada.

### Chemicals

The origin of the chemicals used was mentioned previously.<sup>14</sup> Analytical grades of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{HNO}_3$  (70%) were purchased from BDH (Toronto, ON), and Fischer Scientific (Fair Lawn, NJ), respectively. Lead (1000 mg/L) and nickel (1005 mg/L) atomic absorption standard solutions were obtained respectively from Fischer Scientific (Fair Lawn, NJ) and Aldrich Chemical Company (Milwaukee, WI).

### Methods

The metal uptake ( $q$ ) was calculated from the initial concentration ( $C_2$ ) and the analyzed final concentration ( $C_f$ ) of

the metal in solution according to the following formula:

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

where  $V$  is the liquid sample volume and  $M$  the starting sorbent weight. Sorption isotherms were constructed from the experimental points by the spline method. The Langmuir sorption model,

$$q = bC_f q_{\max}/(1 + bC_f)$$

was also computer-fitted to the experimental points for comparison, summarized in the tables.<sup>14</sup> Langmuir parameters  $q_{\max}$  (the maximum uptake) and  $b$  (a constant related to energy of adsorption) are useful in quantitatively comparing the sorption performance.

A constant pH for the batch equilibrium sorption experiments was maintained at pH 3.5, 4.5, and 6.0, respectively, by periodically adjusting it with 0.1  $M$   $\text{NH}_4\text{OH}$  or 0.1 to 0.5  $M$   $\text{HNO}_3$  in the case of lead sorption. Constant pH levels of nickel solutions were maintained by adjustments with the same concentration of either  $\text{NaOH}$  or 0.1 to 0.5  $M$   $\text{HCl}$ . The content of  $\text{CaCO}_3$  in calcareous algae (25 g biomass per 750 mL distilled water) was destroyed and estimated titrimetrically with 0.5  $M$   $\text{HCl}$  until constant pH 5. The sorption temperature was kept at approximately 25°C due to the fact that sorption of lead by algae tends to slightly increase in the range 4 to 55°C. The sorption of nickel was temperature independent.<sup>11</sup>

The final equilibrium concentrations of lead and nickel in aqueous samples were determined by a Perkin-Elmer atomic absorption spectrometer (model 3100) at 261.5 and 341.5 nm, respectively. Other methods, including the determination of particle (size >1.0; <1.4 nm) swelling characteristics and methods of crosslinking, have been described earlier.<sup>14</sup>

## RESULTS

### Lead

Equilibrium batch sorption experiments resulted in points of the "biosorption isotherm" which was approximated by the Langmuir model. It is essential to compare the performance of the tested materials at the same equilibrium concentration of the metal in the residual solution. This can be conveniently done from their respective sorption isotherm plots. However, since the biosorption performance may not necessarily follow that predicted by the Langmuir sorption model, the deviation is of interest, as is the maximum metal uptake for each material examined. Both experimental and calculated results of equilibrium sorption experiments are summarized in Tables I and II. The experimental curves represent the best empirical fit through the given experimental points. Metal uptakes at equilibrium residual concentrations ( $C_f$ ) of 10 and 200 mg metal/L were selected for comparison purposes, representing arbitrarily chosen "low" and "high" metal residual concentrations. The Langmuir parameter  $b$  reflects quanti-

tatively the "affinity" between the sorbent and the sorbate. Its informative values are also included in Tables I and II.

Rough screening for metal sorption was performed with 45 algal biomass samples (native and crosslinked) using solutions with the initial ( $C_f$ ) concentration of lead at 250 mg Pb/L. The best performing biomass types were examined in more detail. The comparison of lead sorption by different types of algal biomass (native as well as crosslinked) is summarized in Table I, grouping the biomass types according to their taxonomy. The results show that biosorption of lead by the selected marine algal biomass is considerable, particularly considering that there was no pretreatment of the biomass. In general, the lead biosorbent uptake decreased in the following sequence: Phaeophyta > Chlorophyta > Rhodophyta. Among the Phaeophyta the lead biosorption decreased as follows: *Fucus* > *Ascophyllum* > *Sargassum* > *Padina*. Among the Rhodophyta the decreasing order of lead biosorption was *Galaxaura* > *Chondrus* > *Palmaria*.

There were two calcareous algae examined: *Padina gymnospora* (Phaeophyta) with 4.4% structural limestone and *Galaxaura marginata* (Rhodophyta) with 28.6% aragonite in intracellular spaces. The removal of  $\text{CaCO}_3$  resulted in the 50% drop of lead  $q_{\max}$  in *P. gymnospora*, whereas the same pretreatment resulted in 1277% increase of the lead  $q_{\max}$  in *G. marginata*. The interspecies diversity of biosorption was demonstrated in the genus *Sargassum*, where the lead  $q_{\max}$  decreased as *S. fluitans* > *S. natans* > *S. vulgare*, with only the latter having a significantly lower (by approximately 15%) lead uptake.

The increasing uptake of lead by *F. vesiculosus* and *A. nodosum* with increasing pH is demonstrated in Figures 1 and 2, respectively. The figures also show the pH values established in the sorption systems where pH was not controlled. Obviously, the pH data points in the Figures represent the equilibrium values corresponding to different final concentrations reached in the sorption system, not the time course of the sorption. Individual metal uptake ( $q$ ) data points from these control experiments are not connected because they do not represent the same sorption isotherm since each point was characterized by a different pH value.

Particularly the ends of sorption isotherms for *F. vesiculosus* (Fig. 1) at very high residual metal concentrations are distorted by metal complexes formed as colloids occurring in the solution due to the leaching of water-soluble biopolymers (probably alginates) from the biomass (R. P. de Carvalho, personal communication). The last points of these isotherms were not considered in the calculation of theoretical maximum metal uptakes (Langmuir  $q_{\max}$ ) and coefficient  $b$  because they do not represent the metal removal by sorption but rather due to filtration at the end of the experiment. Consequently, the values of  $q_{\max}$  for those unconventional S-shaped sorption isotherms (Fig. 1 to 3) quoted in Table II ought to be considered only as approximative values. Dry weights of supernatants from control experiments containing only water showed that *F. vesiculosus* biomass gradually released water-soluble

**Table I.** Experimental and calculated lead uptake by different types of sorbent materials at pH 3.5.

Sorbent type	Experimental		Langmuir parameters <sup>a</sup>				Difference <sup>b</sup>	
	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{max}$ (mg/g)	$b$ ( $\times 10^2$ )	$q_{10}$ (%)	$q_{200}$ (%)
Division Phaeophyta (order Fucales)								
<i>F. vesiculosus</i> <sup>c</sup>	95	174	53	197	229	3.03	79.2	-12.0
<i>F. vesiculosus</i> <sup>d</sup>	11	131	11	131	301	3.87	0	0
<i>F. vesiculosus</i> <sup>e</sup>	63	250	36	250	363	1.10	75	0
<i>A. nodosum</i> <sup>f</sup>	37	251	37	251	359	1.17	0	0
<i>A. nodosum</i> <sup>c</sup>	112	201	46	219	272	2.03	143	-8.2
<i>A. nodosum</i> <sup>g</sup>	41	211	41	213	273	1.79	0	-0.9
<i>A. nodosum</i> <sup>h</sup>	29	189	29	191	271	1.18	0	-1.0
<i>A. nodosum</i> <sup>i</sup>	48	149	48	156	177	3.67	0	-4.5
<i>Sargassum fluitans</i> <sup>c</sup>	47	216	47	215	266	2.14	0	0.4
<i>S. fluitans</i> <sup>g</sup>	88	193	109	193	202	12.82	-19	0
<i>Sargassum natans</i> <sup>c</sup>	52	211	52	213	253	2.61	0	-0.9
<i>Sargassum vulgare</i> <sup>c</sup>	20	149	19	148	228	0.93	5.2	0.7
<i>P. gymnospora</i> <sup>c</sup> (Dictyotales)	22	59	22	59	65	5.26	0	0
<i>P. gymnospora</i> <sup>j</sup>	4.3	23	4	22	31	1.28	7.5	4.5
Division Rhodophyta (order Gigartinales)								
<i>Chondrus crispus</i> <sup>k</sup>	20	142	20	143	209	1.07	0	-0.7
<i>C. crispus</i> <sup>c</sup>	3	65	3	48	195	0.16	0	35.4
<i>G. marginata</i> <sup>j</sup> (Nemalionales)	83	252	75	255	317	2.05	10.7	-1.2
<i>G. marginata</i> <sup>c</sup>	1	11	1	12	25	0.44	0	8.3
<i>P. palmata</i> <sup>c,l</sup> (Palmariales)	—	—	—	—	—	—	—	—
Division Chlorophyta (order Codiales)								
<i>C. taylori</i> <sup>c</sup>	9	130	10	130	376	0.26	-10	0
Urea-formaldehyde complex								
Amberlite IR-120								
Wet	138	283	138	283	299	8.49	0	0
Dry	264	350	70	351	444	1.87	277	-0.3
Duolite GT-73								
Wet	28	114	28	114	136	2.63	0	0
Dry	80	234	80	252	284	3.93	0	-7.1

<sup>a</sup>  $q_{10}$  and  $q_{200}$ , metal uptake at the residual concentrations of 10 and 200 mg/L, respectively.

<sup>b</sup>  $(q_{EXP} - q_{CAL})100/q_{CAL}$ .

<sup>c</sup> Native biomass material.

<sup>d</sup> Crosslinked with formaldehyde and HCl.

<sup>e</sup> Crosslinked with buffered formaldehyde (pH 2).

<sup>f</sup> Crosslinked with bis(ethenyl) sulfone.

<sup>g</sup> Crosslinked with glutaraldehyde.

<sup>h</sup> Crosslinked with formaldehyde and acetic acid.

<sup>i</sup> Crosslinked with formaldehyde and urea.

<sup>j</sup> After removal of  $CaCO_3$ .

<sup>k</sup> Crosslinked with 1-chloro-2,3-epoxypropane.

<sup>l</sup>  $q = 13.5$  mg/g at  $C_f = 243$  mg/L.

material up to 37% of native biomass (not crosslinked) dry weight after 24 h of shaking. This value remained the same for both pH nonadjusted systems and for the controlled pH range 3.5–6.0 (no-metal blanks). The sorption uptake values, however, were always calculated based on the initial mass of the biosorbent. The two equilibrium pH curves for sorption systems without pH control in Figure 1 show slightly lower pH values resulting after 12 h of contact as opposed to 1 h of contact. The bulk of the sorbed metal is sorbed much faster than that as indicated by the preliminary sorption kinetic experiments (not reported here). However, although the sorption equilibrium exists for all practical purposes, leaching of the (polysaccharide) biomass material is slower, and it seems to interact with the residual metal in

the solution, thus disturbing the true sorption equilibrium in the system to a small degree.

Visible precipitate in the sorption suspension was formed above  $C_i = 250$  mg Pb/L in all four series of experiments with *F. vesiculosus*. The formation of precipitate was not entirely due to the formation of lead hydroxides. No formation of precipitate was observed in the range of  $C_i$  up to 250 mg Pb/L where the metal was sorbed by solid biomass preferentially to the soluble biopolymers. Only very light "haze" was observed in the solutions of contact systems with  $C_i$  above 500 mg Pb/L. Increasing values of pH in the contact systems resulted in irregular S-shaped isotherm curves reflecting the sorption "enhancement" by formation of insoluble lead hydroxides. A good comparison

**Table II.** Experimental and calculated lead uptake by different types of native materials at different pH.

Sorbent type	Experimental		Langmuir parameters <sup>a</sup>				Difference <sup>b</sup>	
	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{max}$ (mg/g)	$b$ ( $\times 10^2$ )	$q_{10}$ (%)	$q_{200}$ (%)
Division Phaeophyta (order Fucales)								
<i>F. vesiculosus</i>								
Nonadjusted pH	103 (pH 3.7)	216 (pH 3.5)	—	—	—	—	—	—
pH 3.5	95	174	53	197	229	3.03	79	-12.0
pH 4.5	101	316	70	376	489	1.67	44	-16.1
pH 6.0	114	336	80	453	600	1.55	43	-26.0
<i>A. nodosum</i>								
Nonadjusted pH	115 (pH 4.6)	211 (pH 4)	—	—	—	—	—	—
pH 3.5	112	201	46	218	272	2.03	143	-7.8
pH 4.5	115	219	34	240	354	1.05	238	-8.8
pH 6.0	130	280	77	379	478	1.90	69	-26.1
Amberlite IR-120 (dry)								
Nonadjusted pH	290 (pH 4.4)	393 (pH 4)	—	—	—	—	—	—
pH 3.5	264	350	70	351	444	1.87	277	-0.3
pH 4.5	333	453	106	487	602	2.13	214	-7.0
pH 6.0	408	855	246	895	1039	3.11	66	-4.5

<sup>a</sup>  $q_{10}$  and  $q_{200}$  metal uptake at the residual concentrations of 10 and 200 mg/L, respectively.

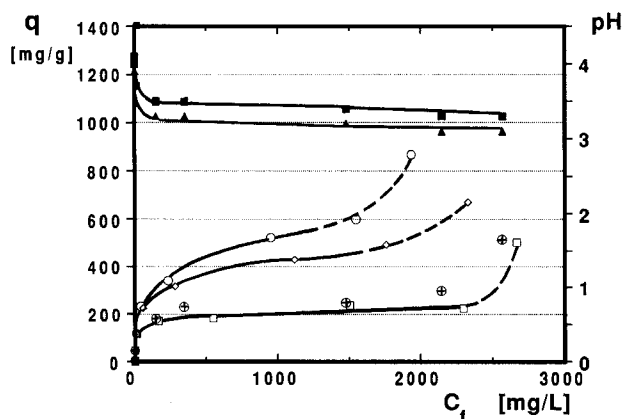
<sup>b</sup>  $(q_{EXP} - q_{CAL}) 100/q_{CAL}$

of sorption performance at  $q_{max}$  cannot be made due to the isotherm anomalies showing at high Pb residual concentrations. More meaningful comparison can be made for values of  $q_{200}$ .

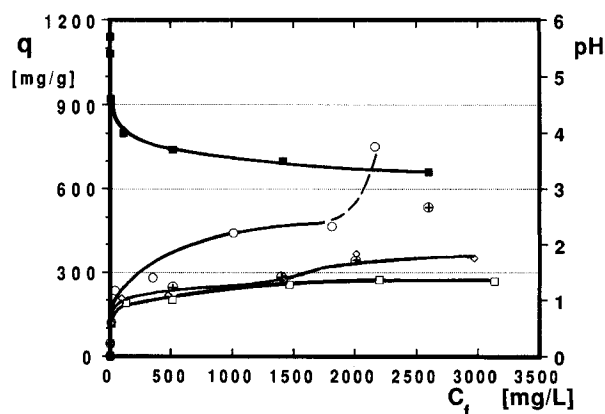
If experimental lead uptake  $q_{200}$  by native biomass of *F. vesiculosus* at pH 6 is considered 100% (336 mg/g), lead  $q_{200}$  values would be 94% and 52% for pH 4.5 and 3.5, respectively. A corresponding comparison for *A. nodosum* would be 78% and 72%. Even though the final difference in pH values between the pH nonadjusted system (final pH 3.8) and that with constant pH 3.5 was only 0.3 pH units, this small difference resulted in 24% higher  $q_{200}$  in the *F. vesiculosus* sorption system with variable pH. There was no such difference for the *A. nodosum* sorption systems. The values of  $q_{10}, q_{200}, q_{max}$ , and  $b$  at different pH values

for native biomass sorption systems are summarized in Table II. Generally, the differences between experimental and calculated values are small for values of  $q_{200}$  but relatively larger for  $q_{10}$ . Experimental values for  $q_{10}$  are usually 2 to 3 times higher in comparison with the ones predicted by the Langmuir model, which obviously was not well followed at low concentrations. The differences between experimental and model-predicted values showed a decreasing tendency with increasing values of metal uptake and pH.

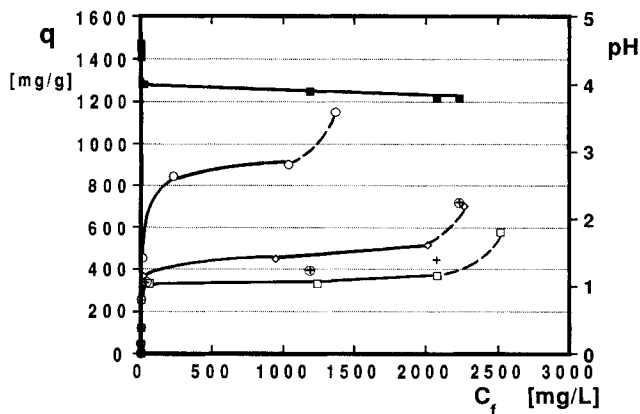
Figure 2 shows the sorption performance of *A. nodosum* native biomass at different constant pH values. The figure also shows the pH decrease in the controls with no pH adjustment. Although the metal solution starting pH was 4.6, it increased immediately as biomass was added to pH 5.7. Further pH decrease in the *A. nodosum* sorption



**Figure 1.** Experimental lead sorption isotherms for dead native biomass of *F. vesiculosus* at different pH: (□) pH 3.5; (◇) pH 4.5; (○) pH 6.0. (-----) Combined biosorption and precipitation metal removal. (⊕) Non-adjusted pH metal uptake values after (■) 1 h and (▲) 12 h of contact (starting pH 4.6).



**Figure 2.** Experimental sorption isotherms for dead native biomass of *A. nodosum* at different pH: (□) pH 3.5; (◇) pH 4.5; (○) pH 6.0. (-----) Combined biosorption and precipitation metal removal. (⊕) Non-adjusted pH metal uptake values after (■) 1 h of contact (starting pH 5.7).



**Figure 3.** Experimental lead sorption isotherms for Amberlite IR-120 at different pH: (□) pH 3.5, (◇) pH 4.5, (○) pH 6.0. (----) Combined biosorption and precipitation metal removal. (●) Nonadjusted pH metal uptake values after (■) 1 h of contact (starting pH 4.6).

system took place within the first hour of the contact and practically did not differ for longer term (12 h) contacts (not specially depicted). There was virtually no precipitation in the *A. nodosum* sorption system and the constant-pH isotherms deviate more only for pH 6 and at  $C_f$  exceeding 1800 mg Pb/L. They follow well the Langmuir model, although the raw native biomass released 27% of water-soluble material independently of the pH value. Again, this weight loss was not considered in the calculations of  $q$  values.

The substantial difference between *F. vesiculosus* and *A. nodosum* sorption systems was the fact that the latter did not form precipitates up to  $C_i$  values of 2000 to 3000 mg Pb/L. The experimental and predicted values for  $q_{10}$ ,  $q_{200}$ ,  $q_{max}$ , and  $b$  for the two systems are in Table II. The highest experimental value of  $q_{200}$  was about 16.6% lower for *A. nodosum* than that for *F. vesiculosus*. Somewhat higher experimental values of  $q_{10}$  for *A. nodosum* were more favorable than those observed for *F. vesiculosus*, indicating a higher sorption affinity for the metal at low residual concentrations. Large positive differences between the experimental and Langmuir calculated values for  $q_{10}$  (*A. nodosum* in particular) indicate a somewhat lower than

theoretical sorbent-sorbate affinity in the low concentration range.

The natural biomass types examined in this work were crosslinked by various procedures resulting in better physical properties (hardness, swelling characteristics, etc.) of the sorbent material but not necessarily its increased metal uptake (Table I). Only in the following samples did crosslinking result in an improved sorption performance in the higher concentration region, as indicated by the values of  $q_{200}$  (in comparison with the starting native biomass):

1. *F. vesiculosus* crosslinked with formaldehyde at buffered pH 2 (not for  $q_{10}$ ),
2. *A. nodosum* crosslinked with bis(ethenyl)sulfone (not for  $q_{10}$ ), and
3. *C. crispus* crosslinked with 1-chloro-2,3-epoxypropane (also for  $q_{10}$ ).

However, at lower concentration ranges (for  $q_{10}$ ) the first two processed biosorbents (above) performed worse than the native biomass.

The values of swelling characteristics of the biosorbent particles that were not mentioned earlier<sup>14</sup> are in Table III. The swelling of biosorbents decreased with the increasing degree of crosslinking even when this was conducted under very mild conditions in a buffered formaldehyde mixture. The native biomass of *A. nodosum* is more dense than parenchymatous particles of *F. vesiculosus*, and it showed higher differences in values of distention index (DI), swelling ratio (Q), and volume of absorbed solvent (VAS) before and after crosslinking. The volume of swelled native *F. vesiculosus* particles increased about 55% (only 15% when crosslinked) and VAS was only 0.6. The difference between the values of  $W_d$  and  $W_s$  resulted from the fact that 100 mL of dry native particles could absorb 239 mL of water, and only 21 mL after crosslinking. The corresponding values for *A. nodosum* were 230 and 14 mL, respectively. The advantage of crosslinking is more pronounced in *A. nodosum*.

The performance of commercial ion exchange resins was examined by the same procedure as biosorption. Commercially supplied Duolite GT-73 and Amberlite IR-120 contained 54.7% and 42% of water, respectively. Since both

**Table III.** Swelling characteristics of native and crosslinked<sup>a</sup> biomass particles<sup>b</sup> of *F. vesiculosus* and *A. nodosum*.

Type of material	Bulk density dry, $W_d$ (g/mL)	Bulk density wet swollen, $W_s$ (g/mL)	Volume swollen, $V_s$ (mL/g)	Distention index, DI ( $V_s/W_d$ )	Swelling ratio, $Q$ ( $W_s/W_d$ )	Volume of absorbed solvent, VAS [( $W_s - W_d$ )/ $W_d$ ]
<i>A. nodosum</i>						
Native	0.761	3.065	3.15	4.1	4.0	3.0
Crosslinked	0.601	1.042	1.40	2.3	1.7	0.7
<i>F. vesiculosus</i>						
Native	0.478	0.774	1.55	3.2	1.6	0.6
Crosslinked	0.395	0.605	1.15	2.9	1.5	0.5

<sup>a</sup> Crosslinked with buffered formaldehyde at pH 2.

<sup>b</sup> Size of dry particles was (>1.0; <1.4) mm.

resins can withstand temperatures up to 121°C, according to the Rohm & Haas Technical Bulletin, they were dried to a constant weight the same way as the biomass samples so that the sorption comparison can be done on an actual "dry weight" basis (not only calculated). They were contacted with the metal-bearing solution under repeated evacuation in order to assure their rewetting even in the entire micropore surface. Table I indicates that Amberlite IR-120 is an excellent sorbent for lead, better than Duolite GT-73. However, their respective lead uptakes did not increase in proportion to the water removed (dry  $q_{\max}$  increase: 48.5% and 108.8%, respectively).

The sorption of lead by dry Amberlite at different pH as well as the natural decrease of pH values in pH nonadjusted control experiments are illustrated in Figure 3. The experimental and predicted values of  $q_{10}$ ,  $q_{200}$ ,  $q_{\max}$  are in Table II. The sorption isotherms for the ion exchange resin are very steep. The low pH of 3.5 was unfavorable; the value of  $q_{\max}$  was about 43% of  $q_{\max}$  at pH 6.0. The

isotherms at pH 3.5 and 4.5 showed unrealistic increases at values of  $C_f$  higher than 2000 mg/L. The isotherm for pH 6.0 became unconventional already at  $C_f = 1000$  mg Pb/L likely due to the (micro) precipitation of lead hydroxides at higher residual concentrations. Correspondingly, the values of calculated  $q_{\max}$  were adjusted, disregarding the last high-concentration portion of the isotherms.

## Nickel

The best lead biosorbents were also examined for their nickel uptake. In comparison with the biosorption of lead, the biosorption uptake of nickel by the natural materials examined in this work was almost an order of magnitude lower as judged by the values of  $q_{\max}$  (Table IV). The biomass types tested exhibited decreasing affinity for nickel in this sequence: Phaeophyta > Rhodophyta > Chlorophyta. In terms of taxonomic order (represented by limited individual species samples available) the decreasing nickel

**Table IV.** Experimental and calculated nickel uptake by different types of sorbent materials at pH 3.5.

Sorbent type	Experimental		Langmuir parameters <sup>a</sup>				Difference <sup>b</sup>	
	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{\max}$ (mg/g)	$b$ ( $\times 10^2$ )	$q_{10}$ (%)	$q_{200}$ (%)
Division Phaeophyta (order Fucales)								
<i>Sargassum fluitans</i> <sup>c</sup>	5.6	31	5.6	32	44	1.46	0	-3.1
<i>S. fluitans</i> <sup>d</sup>	5.5	21	5.5	21	24	2.94	0	0
<i>S. fluitans</i> <sup>e</sup>	1.4	11	1.2	11	19.8	0.67	17	0
<i>S. natans</i> <sup>d</sup>	2.6	19	2.6	17	24	1.19	0	11.8
<i>S. vulgare</i> <sup>d</sup>	1.7	4.6	1.7	4.6	5	5.26	0	0
<i>F. vesiculosus</i> <sup>f</sup>	3.6	21	3.1	21	31	1.12	16.1	0
<i>F. vesiculosus</i> <sup>d</sup>	5.4	17	5	19	23	2.75	8.0	-11.0
<i>A. nodosum</i> <sup>d</sup>	8.8	34	8.8	34	41	2.79	0	0
<i>A. nodosum</i> <sup>g</sup>	6.8	26	6.8	26	30	2.89	0	0
<i>A. nodosum</i> <sup>h</sup>	4.2	19	4.2	19	24	2.17	0	0
<i>P. gymnospora</i> <sup>d</sup> (Dictyotales)	0.6	5.8	0.6	5.8	10	0.67	0	0
<i>P. gymnospora</i> <sup>i</sup>	2.5	12	2.5	12	14	2.14	0	0
Division Rhodophyta (order Gigartinales)								
<i>C. crispus</i> <sup>d</sup>	4.6	20	4.6	21	26	2.20	0	-4.8
<i>G. marginata</i> <sup>d</sup> (Nemalionales)	0.8	6.9	0.8	6.9	11	0.79	0	0
<i>G. marginata</i> <sup>i</sup>	0.2	3.3	0.2	3.3	11	0.22	0	0
<i>P. palmata</i> <sup>d,j</sup> (Palamariales)	—	—	—	—	—	—	—	—
Division Chlorophyta (order Codiales)								
<i>C. taylori</i> <sup>d</sup>	1.9	5.3	1.9	5.3	5.8	4.95	0	0
Urea-formaldehyde complex								
Amberlite IR-120								
Wet	66	74	66	74	74	8.23	0	0
Dry	79	119	50	130	143	5.89	58	-8.5
Duolite GT-73								
Wet	13	22	13	22	23	12.56	0	0
Dry	28	46	28	46	48	13.91	0	0

<sup>a</sup>  $q_{10}$  and  $q_{200}$  metal uptake at the residual concentrations of 10 and 200 mg/L, respectively.

<sup>b</sup>  $(q_{\text{EXP}} - q_{\text{CAL}})100/q_{\text{CAL}}$ .

<sup>c</sup> Crosslinked with formaldehyde-HCl.

<sup>d</sup> Native.

<sup>e</sup> Crosslinked with epichlorohydrin.

<sup>f</sup> Crosslinked with buffered formaldehyde (pH 2).

<sup>g</sup> Crosslinked with formaldehyde and urea.

<sup>h</sup> Crosslinked with formaldehyde and acetic acid.

<sup>i</sup> After removal of  $\text{CaCO}_3$ .

<sup>j</sup>  $q = 3.9$  mg/g at  $C_f = 236$  mg/L.

affinity would be Fucales > Gigartinales > Dictyotales > Nemalionales > Codiales > Palmariales. The native biomass of species belonging to the order Fucales appeared to be a reasonably good sorbent for many metals. For nickel, however, it did not perform too well, exhibiting the following decreasing sorption ability: *A. nodosum* > *S. fluitans* > *S. natans* > *F. vesiculosus*. The value of  $q_{\max}$  for *C. crispus* was close to that for *S. fluitans*. The differences of nickel sorption were diminished in calcareous algae *P. gymnospora* and *G. marginata* for both native biomass types (before removing  $\text{CaCO}_3$ ) as well as for those with  $\text{CaCO}_3$  removed.

Crosslinking of *S. fluitans* and *F. vesiculosus* with formaldehyde improved their nickel uptake somewhat. Crosslinking with 1-chloro-2,3-epoxypropane or with a formaldehyde-urea mixture resulted in decreased metal uptakes as compared with native materials. However, Table V shows that the nickel sequestering performance ( $q_{\max}$ ) of commercial ionex resin Amberlite IR-120 is 70% higher than that observed for *A. nodosum* at the optimum pH 6.0. The  $q_{\max}$  nickel uptake by hydrated Amberlite was 74.4 mg/g, which can be recalculated to be 164 mg/g on the dry weight basis (Table IV). The same resin actually dried for the sorption test had  $q_{\max} = 143$  mg/g, corresponding to 87% of the calculated value (above).

The sorption of nickel at different controlled pH values is summarized in Figure 4 together with results for sorption systems with nonadjusted pH. These results demonstrate the increasing uptake of nickel with increasing pH values for native biomass *A. nodosum* and in Figure 5 also for commercial resin Amberlite IR 120. Contrary to lead isotherms, nickel isotherms followed the Langmuir model well, and the differences between the experimental and calculated values of  $q_{10}$  and  $q_{200}$  were zero or very small.

## DISCUSSION

This work identified three types of brown marine algae biomass (dead) as excellent sorption materials for binding

lead well in excess of 20% of the material dry weight. According to the maximum lead uptake ( $q_{\max}$ ) the native (raw) biomass types performed in the following order: *F. vesiculosus* > *A. nodosum* > *S. fluitans*. Processing of the biomass by crosslinking can improve its physical properties (strength, hardness, swelling characteristics, etc.) required for column sorption applications without adversely affecting the sorption, which in some cases may even increase. Nickel sorption by the same biomass types was almost an order of magnitude lower.

There is a scientific and practical interest in locating the active sites of the biopolymeric structures of the biomass that are responsible for the sorption. Recently, Kloareg et al.<sup>15</sup> outlined the semispeculative model of the structure of cell walls of brown algae: The cellulose chains formed the structural and rigid network in which four other biopolymers (alginates, xylofucoglucans, xylofucoglycuronans, and homofucans) are embedded. Similarity of fucose-containing polysaccharides of cell walls of several genera of brown algae as well as the variations of the sugar constituents of algal polysaccharides were also described.<sup>18,19</sup> Although the algal species examined in this work for their metal sequestering ability differed taxonomically, their biomass featured two common moieties:

1. Sulfate esters in the cellular polysaccharides including:
  - a. Fucoidans (after removal of alginates) in the division Phaeophyta with  $\text{O}-\text{SO}_3^-$  groups at carbons  $\text{C}_2$  or  $\text{C}_3$  or containing disulfate esters at  $\text{C}_2$  and  $\text{C}_3$  in  $\alpha$ -1,4-linked L-fucopyranosyl residues. Sulfate esters were described in 21 species, including *Fucus vesiculosus*, *Sargassum thurnbergii*, and *Padina arborescens*.<sup>19</sup>
  - b. Carrageenans, agars, porphyrans, furcellarans, funorans, etc. in the division Rhodophyta. They are sulfated galactans at  $\text{C}_2$  or  $\text{C}_4$  or  $\text{C}_6$  (disulfate esters at  $\text{C}_2$  and  $\text{C}_6$  were identified in  $\lambda$ -carrageenan) with different proportions of 1,3- and 1,4-D,L-linked galactosyl residues.<sup>25</sup>

**Table V.** Experimental and calculated nickel uptake by different types of native sorbent materials at different pH.

Sorbent type	Experimental		Langmuir parameters <sup>a</sup>				Difference <sup>b</sup>	
	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{10}$ (mg/g)	$q_{200}$ (mg/g)	$q_{\max}$ (mg/g)	$b$ ( $\times 10^2$ )	$q_{10}$ (%)	$q_{200}$ (%)
<i>A. nodosum</i>								
Nonadjusted pH	10 (pH 5)	64 (pH 4.6)	—	—	—	—	—	—
pH 3.5	11	60	11	60	79	1.56	0	0
pH 4.5	9	64	9	72	117	0.80	0	-11.0
pH 6.0	11	70	7	72	136	0.56	57	-2.8
Amberlite IR-120 (dry)								
Nonadjusted pH	82 (pH 5.5)	127 (pH 5.6)	—	—	—	—	—	—
pH 3.5	79	119	50	130	143	5.38	58	-8.5
pH 4.5	87	119	37	146	173	2.68	135	-18.0
pH 6.0	82	129	24	160	230	1.14	242	-19.0

<sup>a</sup>  $q_{10}$  and  $q_{200}$  metal uptake at the residual concentrations of 10 and 200 mg/L, respectively.

<sup>b</sup>  $(q_{\text{EXP}} - q_{\text{CAL}})100/q_{\text{CAL}}$ .

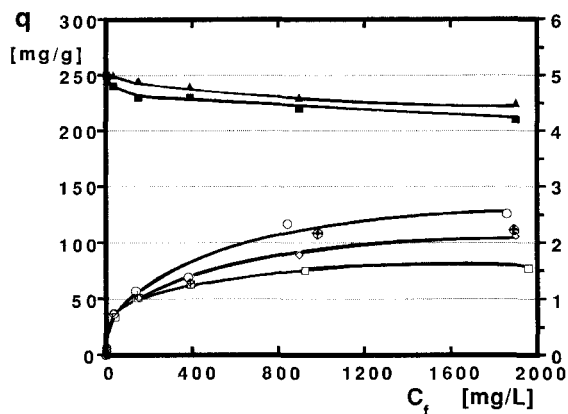


Figure 4. Experimental nickel sorption isotherms for dead native biomass of *A. nodosum* at different pH: (□) pH 3.5; (◇) pH 4.5; (○) pH 6.0. (⊕) Nonadjusted pH metal uptake values after (▲) 1 h and (■) 14 h of contact (starting pH 5.1).

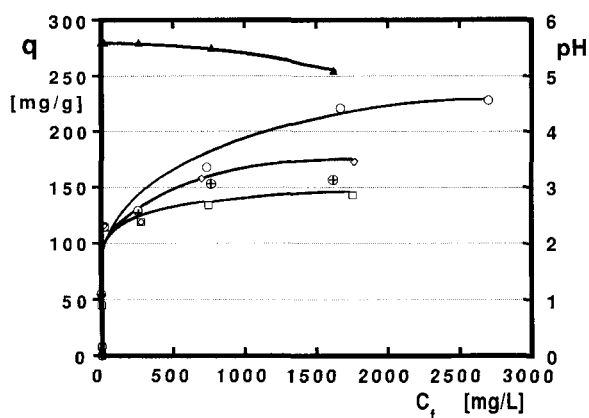


Figure 5. Experimental nickel sorption isotherms for dry Amberlite IR-120 at different pH: (□) pH 3.5; (◇) pH 4.5; (○) pH 6.0. (⊕) Nonadjusted pH metal uptake values after (▲) 1 h of contact (starting pH 4.8).

- c. Sulfate esters at  $C_2$  and  $C_6$  of  $\beta$ -1,3-galactans are present in *C. taylori* (division Chlorophyta).<sup>4</sup>
2. The presence of polyuronides that are represented by galacturonic, glucuronic, guluronic and mannuronic acids in all three divisions mentioned above.

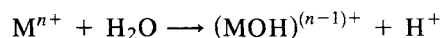
The carboxyl groups, present abundantly in the four mentioned uronic acids, together with sulfate groups, could be considered as ligands mainly responsible for the bulk of metal sorption.<sup>6</sup>

Indications of advantages of morphologically different architecture of algal tissues in relation to increasing the metal biosorbent uptake could be seen in comparing the sorption performance of *F. vesiculosus* and *A. nodosum*. The thallus of the former consists of parenchymatous cells with apical meristems<sup>5</sup> instead of the predominantly filamentous architecture of the latter. The architecture of parenchymatous cells represents a greatly increased surface area which is available for sorption. Comparison of the density of crosslinked particles of *F. vesiculosus* and

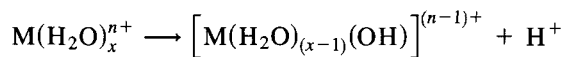
*A. nodosum* indicated a 34% higher density of the latter (Table III). This means that morphological differences existing within the same order can influence the sorption process. Also the structure of alginates present can differ between young and old tissues as well as between different parts of the same plant.<sup>12</sup> The content of sulfate groups as well as uronic acids in the algal biomass examined differ not only between species but even seasonally and geographically within the same species,<sup>21</sup> the variations being responsible for potentially differing sorption capabilities.

To study the sorption of metals which tend to form insoluble (micro)precipitates becomes more complicated due to the fact that the collection of the metal species is not due to the "straight" sequestration mechanism. In the case of lead in particular its solution chemistry is more complex. Addition of NaOH, which may be used to adjust the pH of the solution of lead nitrate,<sup>10,20</sup> likely results in the formation of insoluble  $Pb(NO_3)_2Pb(OH)_2$  and  $Pb(NO_3)_2 \cdot 5Pb(OH)_2$  complexes, which in turn result in distortion of the sorption results. This is a reason to use  $NH_4OH$  for the least interfering pH adjustment of the sorption system. The danger of microprecipitation starts at pH above 5.0 for lead and at pH 6.7 for nickel.<sup>3</sup>

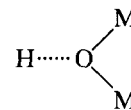
The formation of amphoteric lead hydroxides causes a problem with pH adjustment in the study of sorption systems. Metal ions are coordinated by water molecules that cause a hydrolytic reaction:



or more realistically:



The dissociation of amphoteric hydroxides (which are weak acids) points to the fact that the higher the number of covalent M–O bonds, the more acidic are the hydrogen atoms in the aquated ion, and the following neutralization of protons results in further releasing of protons. Moreover, the hydroxide ion has the ability to form bridges between metal ions. The most common example is the formation of hydroxobridges at an early stage of the precipitation of hydrous metal oxides:



When the solution becomes uncharged, the resulting pH represents an isoelectric point with the lowest solubility of metal ions. Whereas this situation is very favorable for the sorbent deposition of metals, it may make the study of the binding sites more difficult. Another favorable feature of the above-mentioned equation is the fact that the addition of water (or other neutral groups) does not alter the valency, but increases the molecular mass of the complex formed, thus favoring the sorbate deposition. Whereas microprecipitation occurring in the sorption system can complicate the study of sorption, from the process application point of view it may desirably augment the metal immobilization,



thus increasing the apparent overall uptake capacity of biosorbent materials.

There was a conspicuous difference observed in this work between the biosorbent uptake of lead and nickel. Several factors may be responsible for this difference. The lead and nickel sorption follows the general rule that metal sorption increases with increasing valence and atomic number. The lower sorption of nickel in comparison to lead could be related to the fact that nickel has much lower selectivity coefficient for alginates than lead, which features the highest one reflected in the highest values of alginate gel shrinkage.<sup>22</sup> Nickel belongs to the intermediate metals with high affinity not only to ligands like phosphoryl,  $-\text{SO}_3^{2-}$ ,  $\text{R}-\text{NH}_2$ , and  $\text{R}_2-\text{NH}$  but mainly to  $-\text{COO}^-$  groups which it likely shares with lead. The *cis* position of sulfate esters at  $\text{C}_3$  and  $\text{C}_4$  of the branched fucose residue may be instrumental in the covalent binding of lead only to one residue. However, the same site could sequester nickel by an ion exchange mechanism. Sulfate groups at other carbons could assist in forming covalent bonds between adjacent chains of fucoidans and other sulfated polysaccharides. This covalent bond (polysaccharide- $\text{O}-\text{SO}_3-\text{Pb}-\text{SO}_3-\text{O}-$ polysaccharide) practically represents another type of crosslinking worthy of attention in studies of the metal-loaded behavior during desorption.

The higher sorption values observed with several crosslinked types of biomass revealed an additional advantage of crosslinking because the majority of sulfate groups and uronic acids present in the cellular polysaccharides could be covalently attached to the structural polysaccharide network. The crosslinking of *A. nodosum* native biomass with bis(ethenyl)sulfone confirmed the possibility of increasing the sorption capacity of the biosorbent material by incorporation of sulfone groups. Free aldehydic groups originating from dialdehydes used for crosslinking and incompletely anchored at one end only could, after reduction of metal ions and oxidation of aldehydic groups to carboxyl groups, also possibly increase the sorption capacity of a prepared biosorbent.

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