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Cadmium Uptake by Biosorbent Seaweeds: Adsorption Isotherms and Some Process Conditions

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Cadmium Uptake by Biosorbent Seaweeds: Adsorption Isotherms and Some Process Conditions

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ABSTRACT

Cadmium biosorption was evaluated in 15 samples of heat-inactivated seaweeds collected from the coast of Rio de Janeiro State, Brazil. The classical Langmuir and Freundlich sorption models were fitted to the results in order to test whether these equations could appropriately describe the process of passive biosorption uptake. Depending on the algal sample and on some assumptions, both models could be applied to this study. The possible ion-exchange mechanism associated with the adsorption process was also investigated, as well as the effect of pH on biosorption and re-use of the different biomasses through several biosorption/desorption cycles.

Key Words. Biosorption; Seaweeds; Cadmium adsorption isotherms; Langmuir equation; Freundlich equation

INTRODUCTION

Marine algae have been used as biological indicators of heavy metal pollution in contaminated areas, and such a property is the basis of bio-

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technologies developed for residual metal ion recovery (1, 2). Some studies describe the use of these organisms as passive heavy metal adsorbers, substituting for conventional resins (3–5). However, the mechanism associated with this biosorptive uptake is not completely understood. If one considers that dead algae are not biologically active, their metal uptake can be regarded as a passive adsorption process and, thus, be correlated with such mathematical sorption models as the Langmuir and Freundlich equations.

Cadmium, one of the most toxic metals, is usually present at high concentrations in several kinds of effluents, especially those from metallurgical activities. In view of cadmium's high toxicity, it is of interest to develop a recovery process which may prevent its discharge into water streams.

The purpose of this work was to analyze the cadmium uptake capacity of dry algal samples—including green, red, and brown algae—with the aim of using them as passive cadmium biosorbers, singly or in association with active microbial species.

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Langmuir and Freundlich Equations

Solid–liquid equilibrium can be easily described by adsorption isotherms (6). The Langmuir and Freundlich equations are the mathematical functions most commonly used to describe this process.

The Langmuir isotherm can be expressed as

$$q = kdc/(1 + kc)$$

By plotting q versus c, a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering. The Langmuir equation can also be described by taking the reciprocal value of its terms. Thus:

$$1/q = (1/kd)(1/c) + (1/d)$$

From this form, by plotting $1/q$ versus $1/c$, a straight line is obtained. Parameters k and d can be calculated from the angular and linear coefficients, respectively. The Langmuir isotherm assumes that the adsorption free energy is independent of both the surface coverage and the formation of a monolayer when the solid surface reaches saturation.

By analogy, a similar treatment can be applied to the Freundlich equation. Its general form can be expressed as

$$q = Kc^{1/n}$$

Constants K and n are characteristic of this model and are dependent on different assumptions. This equation can also be linearized by plotting the logarithm of its terms:

$$\log q = (1/n) \log c + \log K$$

By plotting log q versus log c, a straight line is obtained. Therefore, parameters n and K can be predicted from the angular and linear coefficients. The Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, the surface covering being mathematically unlimited.

In this work the experimental results obtained in the laboratory were expressed by adsorption isotherms, which were linearized by simple linear regression to predict the respective constants for each model. The fitting of the models to the data was evaluated taking into account the range of cadmium concentrations tested.

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MATERIALS AND METHODS

Cadmium Solutions

Cadmium solutions were made with analytical grade $3CdSO_4 \cdot 8H_2O$. Concentrations of the metal in solution were determined by atomic absorption spectrometry (Varian Techtron Spectrometer, Model AA6).

Marine Algae

Six different genera of marine algae (seaweeds) collected from the Brazilian Coast and making up a total of 15 algal samples were tested for their cadmium uptake capacities. Sample code, classification (7), and site of collection are listed in Table 1.

Processing of Marine Algal Samples

The algal samples were extensively washed with distilled water to remove particulate material from their surface, and oven-dried at 70°C. Dried biomasses were ground in a mortar with a pestle and then sorted by particle size through a series of Tyler sieves. A fraction (0.503–0.711 mm) was selected for use in the experiments.

Biosorption Experiments

The 15 samples collected were tested for their capacity to sequester cadmium by evaluation of their adsorption isotherms. A series of cadmium solutions was prepared by dissolving cadmium salts in deionized distilled water, with concentrations ranging from 10.0 to 350.0 mg $Cd^{2+} \cdot dm^{-3}$. The contact experiments were performed in 250-mL Erlenmeyer flasks

TABLE 1
Marine Algal Samples—Genera, Sites of Collection, and Classification (7)

Genus	Site of collection	Sample code	Classification[b]
Sargassum[a]	Sepetiba Bay	BS_1	D = Phaeophyta
	Sepetiba Bay	BS_2	C = Cyclosporeae
	Sepetiba Bay	BS_3	O = Fucales
	Grande Island	IGr	F = Sargassaceae
Padina[a]	Sepetiba Bay	BS_1	D = Phaeophyta
	Sepetiba Bay	BS_2	C = Isogeneratae
	Gato Island	IG	O = Dictyotales
			F = Dictyotaceae
Ulva	Sepetiba Bay	BS	D = Chlorophyta
	Guanabara Bay	BG	O = Ulvales
	Vermelha Beach	PV	F = Ulvaceae
Gelidium	Itaipu Beach	IP	D = Rhodophyta
	Itacoatiara Beach	IT	C = Rhodophyceae
			O = Gelidiales
			F = Gelidiaceae
Codium	Vermelha Beach	PV	D = Chlorophyta
	Itacoatiara	IT	O = Siphonales
			F = Codiaceae
Colpomenia	Itaipu Beach	IP	D = Phaeophyta
			C = Heterogeneratae
			O = Chordariales
			F = Punctariaceae

[a] Samples from the same genus and site were collected during different seasons of the year.

[b] D = Division, C = Class, O = Order, F = Family.

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(2.0 g·dm^{-3} of biomass, 50 cm^{-3} of cadmium-bearing solution of known initial concentration, 30 ± 0.5°C, 8 hours) on a rotary shaker (Ética, Model 500). After incubation, the eluant solution was separated from the biomass by filtration through an in-line Millipore membrane filter (0.47 μm pore diameter). Final cadmium concentrations were determined by atomic absorption spectrometry. The results presented correspond to the average values obtained.

Release of Alkaline-Earth Elements during Cadmium Biosorption

Release of alkaline-earth elements during cadmium biosorption may indicate the involvement of an ion-exchange mechanism in the recovery of this metal from contaminated solutions. Using adsorption isotherms, the *mg cadmium adsorbed/g dry biomass* ratio can be estimated for each solid–liquid equilibrium, and this ratio can then be associated with the release of alkaline-earth elements from the polysaccharide structure of some algal genera. These elements can act as linkers within the polysaccharide structure, connecting monomeric units or crosslinking adjacent complex molecules. One sample from each algal genus was used in this set of experiments. The alkaline-earth elements were also quantified by atomic absorption spectrometry. Due to the great number of experimental determinations, the data obtained were computer adjusted by power regression.

Cadmium Adsorption and Acid Desorption Cycles

In this set of experiments, 1.0 g of algal sample was added to 250 cm^{-3} Erlenmeyer flasks containing 50.0 cm^{-3} of a 10.0 $mg{\cdot}dm^{-3}$ cadmium solution and incubated for 1 hour in a rotary shaker (30 ± 0.5°C). The content of each flask was then filtered and the filtrate analyzed for its cadmium residual content. Cadmium-laden biomasses were treated with 50 cm^{-3} of 0.5 N HCl to strip the adsorbed metal. The stripped solutions were analyzed for their cadmium content to check the efficiency of the elution. Next, samples were oven-dried (70°C, 24 hours) and reused in successive sorption/desorption cycles, as previously described. It is important to mention that the incubation time for this set of experiments was established as 1 hour on the basis of previous determinations of adsorption equilibrium kinetics carried out for all the algal samples.

Effect of pH on Cadmium Biosorption

Only *Sargassum* sp. (sample BS_1) was used in this set of experiments, due to its outstanding performance as a cadmium biosorbent. 50 cm^{-3} aliquots of a 11.0 $mg{\cdot}dm^{-3}$ cadmium solution were placed into 250 cm^{-3} Erlenmeyer flasks, and the pH of individual aliquots was then adjusted to the desired value with HCl or NaOH (pH range: 2.0 to 12.0). Next, the dried and pulverized biomass of *Sargassum* sp. (sample BS_1) was added to the flasks at a concentration of 2.0 $g{\cdot}dm^{-3}$. The flasks were placed on a rotary shaker at 30 ± 0.5°C and incubated for 24 hours to ensure equilibrium. Biosorbent-free blanks were used as controls to evaluate chemical precipitation (8). The genus *Sargassum* was also selected for its high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it, at least in theory, very liable to the influence of the medium's pH. The experimental determinations reported here correspond to average values.

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RESULTS AND DISCUSSION

Cadmium Adsorption Isotherms and Fitness to Langmuir and Freundlich Equations

The results on cadmium biosorption for each algal sample assayed are presented in Fig. 1 to 6. Together with the experimental data, the corresponding theoretical adjustments of experimental determinations by the Langmuir and Freundlich equations were also plotted.

From the data for *Sargassum* sp. (Fig. 1: B, C, and D) it can be inferred that, according to experimental *q* values, the adsorption process reached saturation in samples BS_2, BS_3, and IGr. For *Sargassum* sp., sample BS_1 (Fig. 1A), the experimental determinations indicate a pattern of increasing *q* values within the range of concentrations tested.

Such behavior shows that this particular sample is a better cadmium adsorber than the other *Sargassum* isolates tested. The constant *q* values observed for samples BS_2, BS_3, and IGr of this genus at equilibrium concentrations greater than 100.0 $mg{\cdot}dm^{-3}$ suggest that, above this level of solute, solid–liquid equilibrium is probably limited by the diffusion of the cadmium ions toward the negatively charged metal-sequestering sites on the surface of the seaweed. That is, the algal surface does not display free sites for metal uptake, being saturated.

There was a good fit between the experimental data for *Sargassum* sp. seaweeds and the Freundlich model, exception made for sample BS_2 (Fig. 1B), although multilayers of adsorbed cadmium ions are expected to exist at equilibrium metal concentrations of around 100.0 $mg{\cdot}dm^{-3}$. One possible explanation for this could be a variation in the chemical structure of surface polysaccharides, as their synthesis may differ between species and may also change as a function of environmental conditions. The Langmuir model, on the other hand, fitted well the experimental data in the case of sample BS_2 (Fig. 1B). With the other *Sargassum* sp. isolates, a good fitting of this model was restricted to low equilibrium concentrations, as expected. Alginates, the main structural polysaccharide of the *Sargassum* seaweeds, can sometimes make up extremely large polymeric chains that might have supplied enough carboxyl sites for cadmium sorption within the metal concentration range studied, thus allowing the formation of a solute monolayer. It must be emphasized that both models consider the solid adsorbing surface as a homogeneous structure with only one type

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FIG. 1 Cadmium adsorption isotherms of *Sargassum* sp. [BS_1-(A)], [BS_2-(B)], [BS_3-(C)], and [IGr-(D)] at 30°C. (■) Experimental, (——) Freundlich isotherm, (- - -) Langmuir isotherm.

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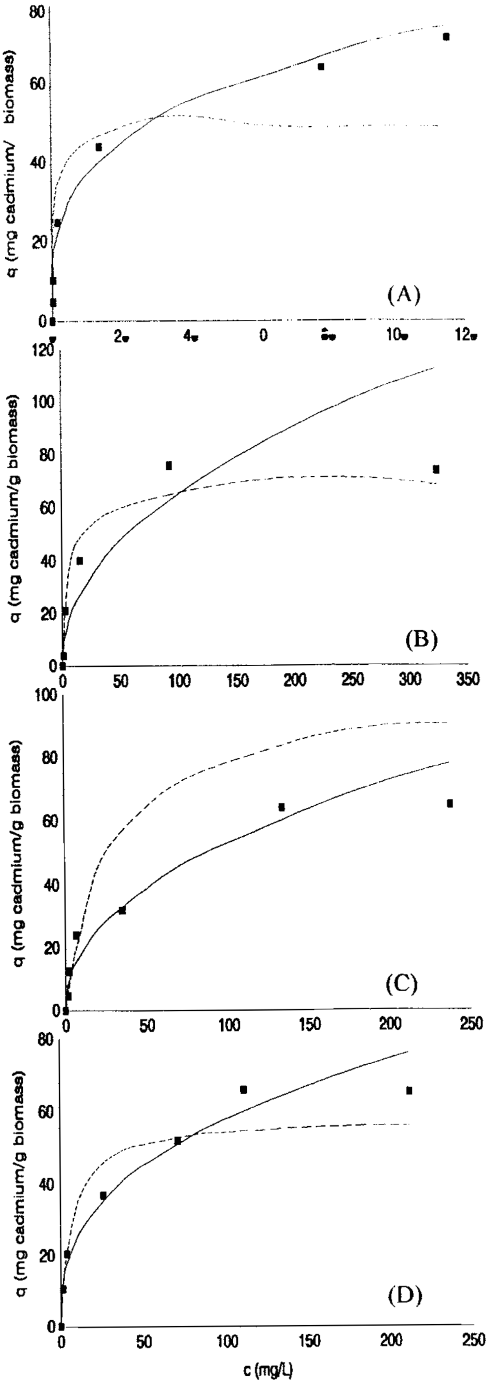

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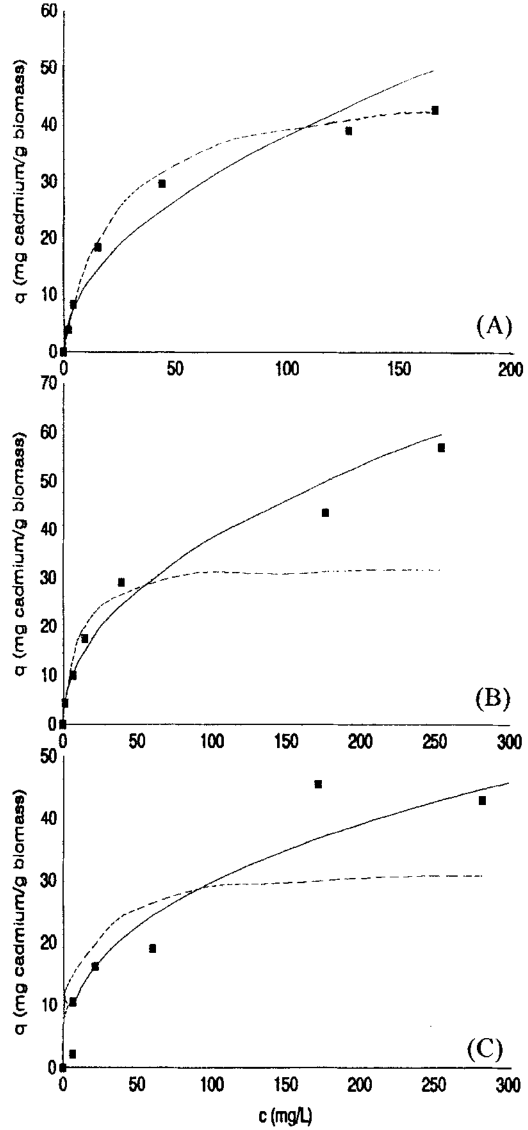

FIG. 2 Cadmium adsorption isotherms of *Padina* sp. [BS_1-(A)], [BS_2-(B)], and [IG-(C)] at 30°C. Same key as in Fig. 1.

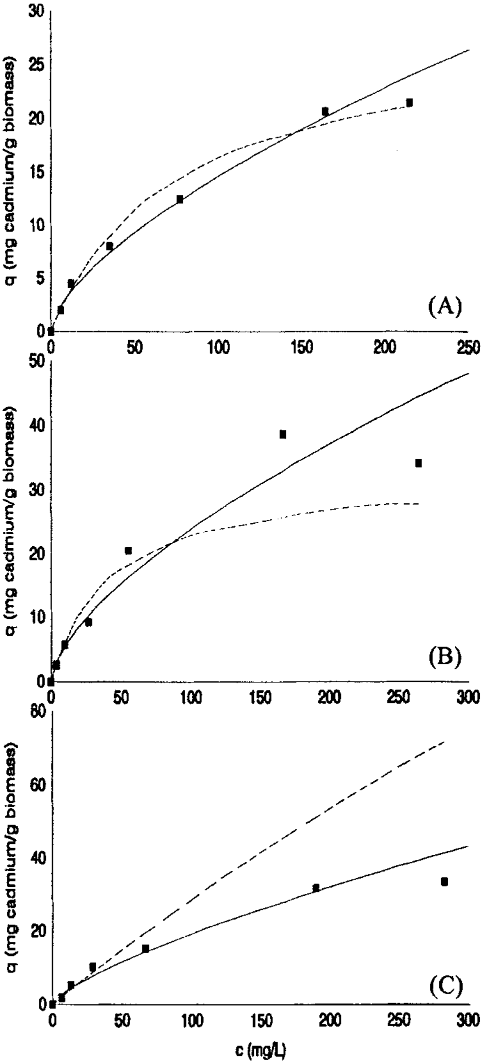

FIG. 3 Cadmium adsorption isotherms of *Ulva* sp. [BS-(A)], [BG-(B)], and [PV-(C)] at 30°C. Same key as in Fig. 1.

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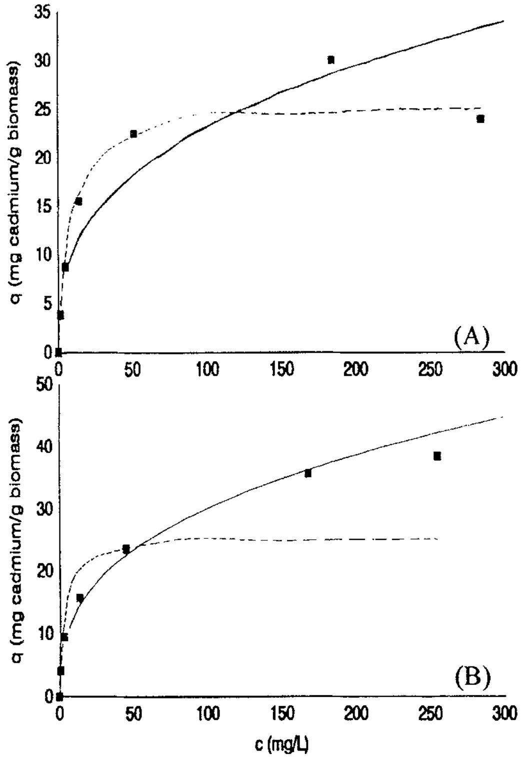

FIG. 4 Cadmium adsorption isotherms of *Gelidium* sp. [IT-(A)] and [IP-(B)] at 30°C. Same key as in Fig. 1.

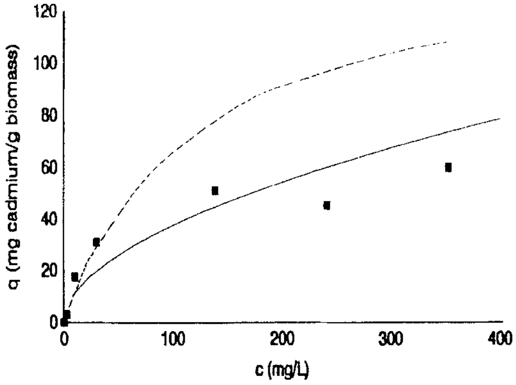

FIG. 5 Cadmium adsorption isotherms of *Colpomenia* sp. [IP] at 30°C. Same key as in Fig. 1.

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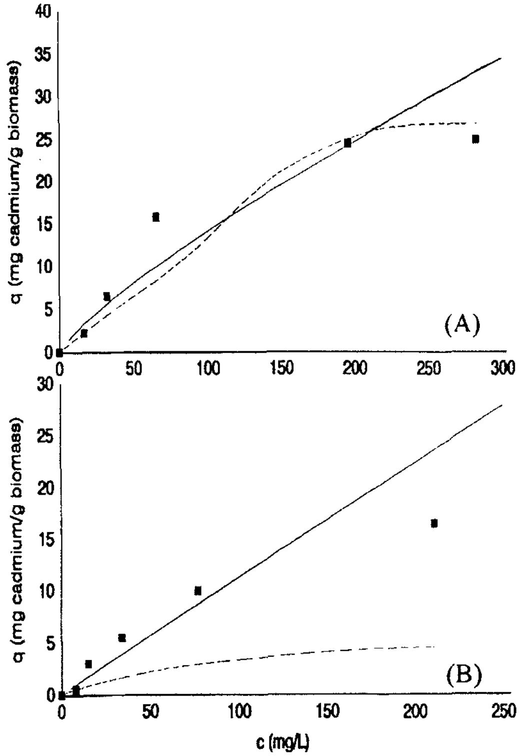

FIG. 6 Cadmium adsorption isotherms of *Codium* sp. [IT-(A)] and [PV-(B)] at 30°C. Same key as in Fig. 1.

of binding site. However, in complex structures like algal polysaccharides, distinct chemical groups of a diverse nature can make up a heterogeneous matrix and contribute differently to the adsorption process.

For all *Padina* samples, the Freundlich equation fitted the data less well than the Langmuir one (Fig. 2).

The Langmuir equation fitted almost perfectly the data for sample BS_1 of *Padina* sp. (Fig. 2A), indicating a clear tendency to loading stabilization (q) at around 42 mg cadmium/g biomass. This equation also fitted perfectly the data for sample BS_2 of this genus (Fig. 2B) at cadmium concentrations of up to 50.0 mg·dm^{-3} yet failed to do so at higher concentrations of the metal. Sample IG of *Padina* sp. (Fig. 2C) could be described by the Langmuir model less well than the previous isolates, though still with a reasonable precision at equilibrium concentrations of up to 100.0 mg·dm^{-3}.

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The sorption behavior of *Ulva* sp., sample BS (Fig. 3A), differently from the previously discussed patterns, was in good agreement with both equations in the range of cadmium concentrations tested.

However, samples BG and PV of this genus (Fig. 3B and 3C, respectively) followed the expected behavior for this seaweed; that is, their experimental data fitted the Langmuir equation at low residual metal concentrations and the Freundlich model for the whole cadmium concentration range tested.

Concerning the genus *Gelidium*, sample IT suited well the Langmuir equation (Fig. 4A) and sample IP (Fig. 4B) the Freundlich equation. Structural factors may be responsible for this difference, also observed between other algal genera.

Figures 5 and 6 (*Colpomenia* sp., sample IP and *Codium* sp., samples IT and PV, respectively) show some discrepancies between experimental points and theoretical predictions, despite the obtention of linear regression coefficients within the confidence limits and correlation coefficients at acceptable values (Table 2).

TABLE 2

Langmuir and Freundlich Parameters for the Algal Samples Assayed

	Parameters from the Langmuir equation			Parameters from the Freundlich equation		
Alga sample assayed	k[a]	d[a]	R[c]	K[b]	n[b]	R[c]
Sargassum sp. (BS_1)	131.8	49.3	0.978	18.4	0.29	0.992
Sargassum sp. (BS_2)	15.4	69.4	0.962	7.6	0.46	0.897
Sargassum sp. (BS_3)	3.6	101.0	0.934	6.6	0.45	0.940
Sargassum sp. (IGr)	14.8	57.8	1.003	10.7	0.36	0.984
Padina sp. (BS_1)	4.3	48.3	0.997	3.4	0.52	0.977
Padina sp. (BS_2)	10.4	32.8	0.984	4.1	0.48	0.990
Padina sp. (IG)	7.2	32.4	0.929	4.7	0.39	0.965
Ulva sp. (BS)	1.3	28.6	0.996	0.7	0.64	0.991
Ulva sp. (BG)	2.3	32.4	0.995	1.3	0.64	0.984
Ulva sp. (PV)	0.01	400[d]	0.988	0.6	0.73	0.979
Gelidium sp. (IP)	29.0	25.4	0.987	5.6	0.36	0.991
Gelidium sp. (IT)	12.3	25.7	0.998	4.6	0.35	0.941
Colpomenia sp. (IP)	0.8	144.9	0.991	3.2	0.53	0.927
Codium sp. (IT)	0.2	81.9	0.976	0.3	0.82	0.945
Codium sp. (PV)	0.9	6.8	0.927	0.1	0.97	0.932

[a] Parameters k and d were obtained by simple linear regression with an equation of the type $y = a + a_1 x$, where the coefficients a and a_1 were calculated at statistically significant confidence intervals.

[b] The same as in footnote a, for parameters K and n.

[c] Correlation coefficients, calculated with a 95% confidence limit and corresponding to average values from the experiments.

[d] Theoretical value, mathematically predicted by the Langmuir equation.

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Variations in cadmium biosorption behavior among the various algae tested can be attributed to polysaccharide variability between the genera, between the species, or between strains of a given species. In other words, the degree of heterogeneity among structural polysaccharides may be one of the underlying factors that determine differences in adsorption capacity between the algal isolates.

The values of the Langmuir and Freundlich constants for the different algal samples and the correlation coefficients of the curves used to calculate them are listed in Table 2. These data must be discussed by groups in order to evaluate the samples with the best sorption potential on the basis of the screening conducted and on the information about the parameters of the models tested and their application to the system studied.

As previously mentioned, constant d of the Langmuir equation represents the maximum surface density and constant k the affinity between the adsorbing surface and the solute. Therefore, increasing values of k, obtained from different samples for the same solute and with the same experimental system, indicate increasing affinity for the solute. It can be observed from Table 2 that the affinity of the different algal samples for cadmium was highly variable, as k values ranged from 0.01 to 131.8, indicating that the algae studied clearly differ in their cadmium biosorption behavior. To better illustrate this point, the algal samples from Table 2 may be grouped according to k values. Thus: k values smaller than 1 were obtained for 4 algal samples; k values ranging from 1 to 10 were observed for 5 samples; k values greater than 10 were observed, in increasing order, for the following samples: *Padina* sp. (sample BS_2), *Gelidium* sp. (sample IT), *Sargassum* sp. (sample IGr), *Sargassum* sp. (sample BS_2), *Gelidium* sp. (sample IP), and *Sargassum* sp. (sample BS_1). The distinct k values obtained for samples of the same genus can be attributed to the possible presence of different species or of different strains of the same species. An alternative explanation is that, depending on environmental conditions, different surface structures may have been synthesized. Considering the affinity constants calculated, it can be concluded that samples with $k >$ 10 should be the most suitable cadmium adsorbers.

Regarding the Freundlich equation, its constants describe the adsorption power of the adsorbent and the distribution of linkages. Constant n is related to the distribution of bindings on the solid surface: if $n < 1$, then the binding energies increase with surface density; if $n > 1$, the surface density—consequently, n values smaller than 1 are observed. It is interesting to mention the results obtained for *Codium* sp. samples: their n values are smaller than 1 yet they approach 1; this indicates that a marked increase in the binding energies as a function of increasing surface density is not occurring. Such values are coherent with *Codium* sp. low performance on cadmium biosorption and are also in accordance with its k values that indicate a low affinity of this algal genus for ionic cadmium.

If we consider n values of up to 0.5, it can be observed that only 8 algal samples could be selected as biosorbents. These samples belong to the genera *Sargassum* (exception made for sample BS_3, with $k = 3.6$), *Padina* and *Gelidium*, which are exactly the ones with high affinity coefficients predicted by the Langmuir equation. In summary, the experimental data can be mathematically correlated with either the Langmuir or the Freundlich equation. Both models were reasonably suitable for fitting the experimental data, even if their assumptions were not strictly respected. The solid surface affinity for the solute and the change in surface density could be predicted by constants k and n from the Langmuir and Freundlich equations, respectively. Based on this assumption, algal samples of the genera *Sargassum*, *Padina*, and *Gelidium* were chosen as those with the highest affinity for divalent cadmium. This theoretical prediction was confirmed by the experimental results that led exactly to the selection of these genera as the most promising adsorbers.

Constants n and k although with different meanings, led to the same conclusion about the correlation of the experimental data with the sorption models. As shown in Fig. 7, increasing k values and decreasing n values indicate a symmetric pattern, in close agreement with the theoretical predictions of both models and, for the most part, with the experimentally based conclusions.

The Langmuir and Freundlich equations impose some basic assumptions for their applicability, and the present experimental data seemed to suit them up to a limit. The Langmuir equation predicts the formation of an adsorbed solute monolayer with no side interactions between the adsorbed molecules/ions. It also assumes that the interaction takes place by adsorption of one molecule/ion per binding site, and that the solid surface is homogeneous and contains only one type of binding site. The Freundlich equation, on the other hand, does not predict surface saturation based on the adsorption process, but mathematically predicts the existence of a multilayered structure. This way, at higher solute concentrations, where multilayers are expected to be formed, the Freundlich model should fit the experimental data with a greater degree of accuracy than the Langmuir model.

Taking an overall view of the results obtained, it could be said that, in general terms, the Langmuir equation fits better the experimental data

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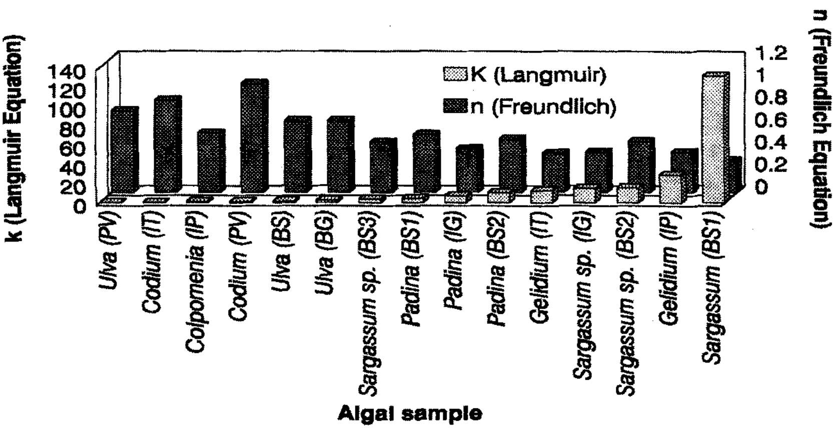

FIG. 7 Comparison between *n* (Freundlich equation) and *k* (Langmuir equation) for different algal samples.

than the Freundlich equation for the range of cadmium concentrations tested. However, it must be pointed out that there was a better fitting to the Langmuir equation at low equilibrium concentrations, as expected, whereas at higher equilibrium concentrations there was an increasing tendency to fit the Freundlich model. The same behavior would probably be predicted at even higher equilibrium concentrations due to the formation of a multilayered network. In the present work, cadmium biosorption was evaluated only within a concentration range representative of the actual cadmium levels found in industrial effluents.

According to the literature, cobalt adsorption has been investigated by uptake evaluation in inactivated algae, fungi, ion-exchange resins, and activated carbon. The main goal of that work seemed to be the screening of biological and non-biological materials for the recovery of cobalt (3). The authors observed that some samples (Resin IRA-400 and the red alga *Porphyra tenera* and *Chondrus crispus*) suited well the Langmuir model while others (Brown alga *Ascophylum nodosum* and *Macrocystis pyrifera*) the Freundlich one.

Some researchers working with fungal and bacterial strains as well as with ion-exchange resins and activated carbon concluded that the Freundlich model described their experimental results with a higher degree of accuracy than the Langmuir model (9). However, the authors did not make theoretical considerations about the mechanism involved, only using the equations as mathematical functions that describe experimental results for a specific metal concentration range.

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Release of Alkaline-Earth Elements during Cadmium Biosorption

Figure 8(A) presents the results for *Sargassum* sp. (sample BS_I), which indicate that ion-exchange is probably associated with cadmium adsorption. The pattern of calcium and magnesium release as a function of *q* confirms the close relationship between these two parameters. The release of the alkaline-earth elements is probably related to the presence of calcium and magnesium alginates and also with crosslinked atoms between polysaccharide chains in brown algae. As observed, a likely ion-exchange in the alginate, the structural macromolecule of these cells, has occurred; the present data allow the conclusion that cadmium replaced magnesium and calcium. Similar ion-exchange properties have already been reported in the literature for alginic acid (10).

Padina sp. (BS_I) showed a calcium release pattern similar to that observed for *Sargassum* sp. However, magnesium release was independent of cadmium uptake, probably indicating that the magnesium ions were totally replaced by cadmium ions, even at low equilibrium concentrations (Fig. 8B).

As observed for *Padina* sp. (sample BS_I), the substitution of calcium and magnesium for cadmium was also complete, even at low concentrations, in *Ulva* sp. (sample PV). An explanation for this is probably found in the chemical structure of this algal genus; alkaline-earth elements might be present at very low concentrations, hence the detection of a complete exchange for cadmium within the whole range of metal concentrations tested (Fig. 8C).

The results shown in Fig. 8(D) indicate that red algae of the genus *Gelidium* should have, to a lesser extent than brown algae, an ion-exchange capacity associated with cadmium uptake.

Finally, concerning *Colpomenia* sp., sample IP, a marked release of calcium and magnesium as *q* increases was observed (Fig. 8E).

Of all the algae tested, *Sargassum* sp. and *Gelidium* sp. were those with the lowest release of total alkaline-earth elements. Nevertheless, they presented the highest cadmium uptake capacities if their respective *k* and *n* values are considered. Therefore, it can be concluded that there is more than one mechanism operating during cadmium biosorption in those two genera.

As mentioned before, the structural polysaccharides from the various algal divisions differ in their chemical composition, size, and type. They

FIG. 8 Release of alkaline-earth elements from *Sargassum* sp. [BS_I-(A)], *Padina* sp. [BS_I-(B)], *Ulva* sp. [PV-(C)], *Gelidium* sp. [IP-(D)], and *Colpomenia* sp. [IP-(E)] during cadmium biosorption.

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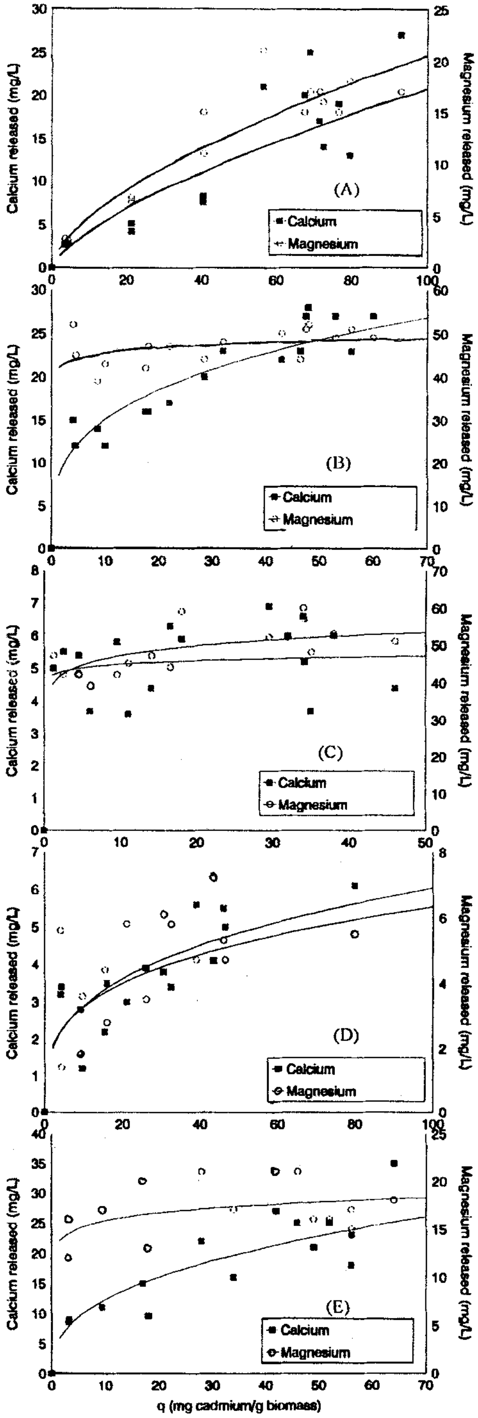

can be sulfated, carboxylated, or aminated, show different structural complexities, and are sometimes stabilized by mono and divalent metals, usually calcium and magnesium.

Cadmium Adsorption and Acid Desorption Cycles

Figure 9 illustrates the cadmium uptake efficiency of different algal genera for 10 subsequent biosorption/desorption cycles.

Overall, the results indicate that some algae kept their ability to recover cadmium for a great number of cycles while others presented a decreased uptake efficiency from cycle to cycle, probably due to some deleterious effects of acid washings on their chemical structures.

Figure 9 also shows that *Sargassum* sp. (sample BS_1) and *Padina* sp. (sample BS_1) were not affected by the acid treatment, as their uptake efficiencies remained constant through all the sorption/desorption cycles. This is a good indication of their potential as biosorbent materials, since they can be reused several times without having to be discarded due to decreased uptake.

The other algae tested, on the other hand, did not behave similarly. Samples of the genera *Ulva*, *Gelidium*, and *Codium* were gradually affected by acid washings from cycle to cycle, as shown by a decreasing cadmium uptake efficiency. Such a decrease was somehow gradual for *Gelidium* sp. and *Ulva* sp., and less so for *Codium* sp. Still, on these genera, it is interesting to note the increase in uptake efficiency from the first to the second biosorption cycle, with probable release of a greater number of cadmium adsorbing sites. It may be that other metals are pres-

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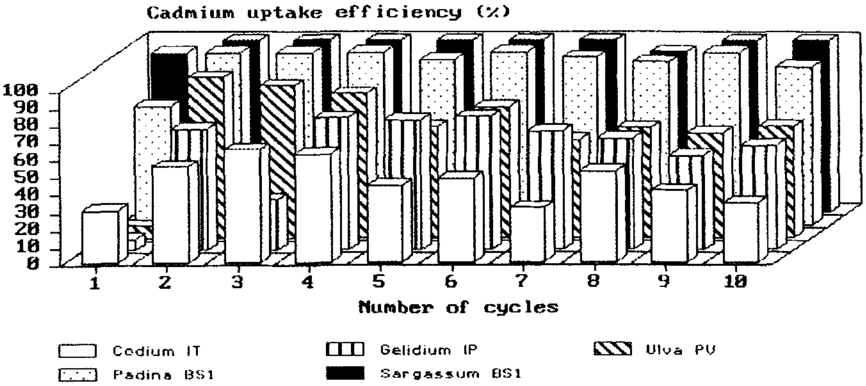

FIG. 9 Repeated cadmium biosorption/desorption cycles.

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ent in these algae and that cadmium was not able, by itself, to release them and be adsorbed into the free sites. HCl treatment can strongly affect ion-exchange properties of the polysaccharides as well as the polysaccharide structure. As the number of uptake cycles increased, the acid washings affected the algal structure, thus causing a detectable gradual decrease in cadmium biosorption from one cycle to the next. Based on this tendency, it can be estimated, for example, that the use of *Ulva* sp. as a cadmium biosorbent would not last for many consecutive cycles.

During copper biosorption by the fungus *Rhizopus arrhizus*, a reversibility of the process was observed after acid washing (11). However, the biomass maintained its sorption capacity for only two sorption/elution cycles. In another example reported in the literature, where the biosorption of cadmium by a regenerated biofilm of *Enterobacter aerogenes* on activated carbon was studied, a decrease in the efficiency of its sorption capacity from cycle to cycle was also detected (12).

One of the main requirements for a biological material to be employed as a heavy metal adsorption agent is its reuse in successive sorption/desorption cycles with no marked effect on structural characteristics; that is, throughout continuous cycles of metal uptake and acid elution, the biomaterial must be able to maintain its metal recovery capacity.

Effect of pH on Cadmium Biosorption

Based on preliminary results, sample BS_1 of *Sargassum* sp. was selected for use in this set of experiments. Cadmium biosorption and cadmium precipitation could be predicted, on the basis of a wide pH range.

Figure 10 shows that cadmium biosorption by *Sargassum* sp. is not markedly affected by pH at the tested values. For example, between pH 3.0 and 8.0, cadmium biosorption was not significantly different. In the alkaline range between pH 8.0 and 10.0, the decreasing residual cadmium concentrations were not exclusively due to biosorption by the seaweed, chemical precipitation having been observed as well. The biosorbent-free control experiments revealed total cadmium precipitation at pH values 11.0 and 12.0. This affected the *Sargassum* sp. biosorption experiments within this extremely alkaline range (pH 11.0 to 12.0), where low residual cadmium concentrations were not just due to metal uptake but also to cadmium precipitation as hydroxyl compounds. At pH 2.0 the equilibrium cadmium concentration was the same as that of the initial solution, indicating the probable nonapplicability of the process following treatment with extremely acid solutions. In this situation, metal desorption through the action of the acid medium outweighs the interaction between anionic surface sites and the ionic species.

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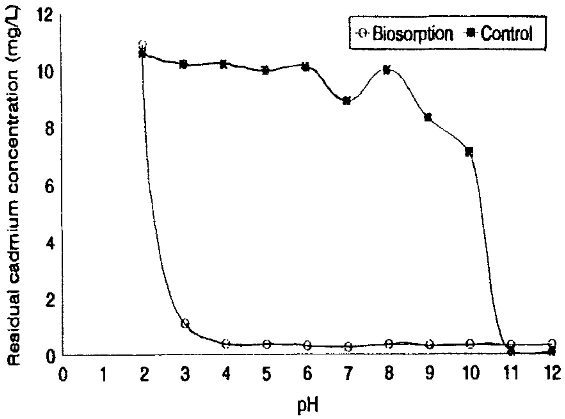

FIG. 10 Effect of pH on cadmium biosorption by *Sargassum* sp. (initial cadmium concentration = 11.0 mg·dm^{-3}).

These results corroborate other findings reported in the literature (10), which describe that, for pH values up to 8.0, cadmium remains in solution in its ionic divalent state (Cd^{2+}). As pH increases, ionic divalent cadmium is gradually substituted by the insoluble hydroxylated forms [$Cd(OH)^+$ and $Cd(OH)_2$], which precipitate out of solution.

The results presented in this work emphasize the potential use of *Sargassum* sp. as a cadmium biosorbent, suggesting its use in continuous units as a treatment system for cadmium-contaminated complex metal solutions.

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NOTATION

c	equilibrium concentration of solute (mg·dm^{-3})
d	constant which represents monolayer covering per unit weight of adsorbent (mg adsorbate/g adsorbent)
k	equilibrium constant (dm^{-3} adsorbent/mg adsorbate)
K	constant related to the strength of the adsorptive bond
n	constant related to bond distribution
q	weight adsorbate/weight adsorbent (mg/g)

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