Biosorption Capacity for Cadmium of Brown Seaweed *Sargassum sinicola* and *Sargassum lapazeanum* in the Gulf of California

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Abstract Brown algae *Sargassum sinicola* and *Sargassum lapazeanum* were tested as cadmium biosorbents in coastal environments close to natural and enriched areas of phosphorite ore. Differences in the concentration of cadmium in these brown algae were found, reflecting the bioavailability of the metal ion in seawater at several sites. In the laboratory, maximum biosorption capacity (q_{max}) of cadmium by these nonliving algae was determined according to the Langmuir adsorption isotherm as 62.42 ± 0.44 mg g^{-1} with the affinity constant (b) of 0.09 and 71.20 ± 0.80 with b of 0.03 for *S. sinicola* and *S. lapazeanum*, respectively. Alginate yield was $19.16 \pm 1.52\%$ and $12.7 \pm 1.31\%$, respectively. Although *S. sinicola* had far lower biosorption capacity than *S. lapazeanum*, the affinity for cadmium for *S. sinicola* makes this alga more suitable as a biosorbent because of its high q_{max} and large biomass on the eastern coast of the Baja California Peninsula. *Sargassum* biomass was estimated at 180,000 t, with *S. sinicola* contributing to over 70%.

1 Introduction

Cadmium in the environment has being increasing because of its use in industrial and agricultural activities (Rule et al. 2006). High solubility in water enhances wide distribution in aquatic systems (Lockwood 1976). One of the most important sources of cadmium in aquatic ecosystems is mineral deposits, including phosphorite, in which this element is a common impurity (Mann and Ritchie 1995). One of the largest phosphorite deposits in the world is located in the Baja California Peninsula of Mexico (Riley 1989). A phosphorite mine is located close to the coast, about 50 km northwest of the city of La Paz (COREMI 2000). Previous reports regarding marine sediments and clams sampled near this area showed high cadmium levels at some sites that results upwelling currents, runoff, municipal wastewater and mining (Méndez et al. 1998; 2006). Efficient and affordable technologies to remove cadmium from water effluents include physicochemical and biological methods. Among the biological technologies, biosorp-

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tion processes are useful because they are efficient and relatively inexpensive (Vieira and Volesky 2000).

Biosorption processes use the ability of organisms to absorb heavy metals from water. Bacteria, fungi, yeast, and algae biomass, among other organisms, have high removal capacities for cadmium (Vieira and Volesky 2000). Brown algae *Sargassum* spp. are recognized as an effective biosorbent when their nonliving biomass binds heavy metals from contaminated effluents (Schiewer and Volesky 1999; Davis et al. 2003a, b; Lodeiro et al. 2004). Along the central coast of the Baja California Peninsula, *Sargassum* has the highest biomass in relation to other macroalgae (Pacheco-Ruiz et al. 1998; Casas-Valdez 2009); Huerta-Díaz et al. (2007) determined that *Sargassum* accumulates large amounts of divalent metals, which suggests that *Sargassum* could be used for bioremediation in polluted environments. However, no reports of cadmium levels in macroalgae along the shore of Bahía de la Paz are known.

The algal cell wall plays an important role in metal binding because it contains high concentrations of polysaccharides (Davis et al. 2003b). The main polysaccharide responsible for absorption of metals in brown macroalgae is alginate (Chapman and Chapman 1980; Davis et al. 2003a, b; Mata et al. 2009).

This study measured biosorption capacity of two species of brown seaweeds: *Sargassum sinicola* and *Sargassum lapazeanum* for cadmium in batch processing. Additionally, we measured cadmium concentration in both species close to natural and enriched areas of phosphorite and the concentration of alginate in the two species. Those values were compared with cadmium biosorption capacity.

2 Materials and Methods

2.1 Collection Sites

Sargassum was collected along the rocky shoreline bordering Bahía de La Paz at Califin in the State of Baja California Sur, Mexico in March 2009 (Fig. 1). Large biomasses of both target species were found at this location. Beds of *Sargassum* spp. contained 70% *S. sinicola* and 30% *S. lapazeanum* (Casas-Valdez 2009). The two species were assayed for cadmium biosorption capacity, concentration of alginate, and concentration of cadmium.

2.2 Cadmium Biosorption Capacity and Concentration of Alginate

To analyze cadmium biosorption, the algae were rinsed with fresh water to remove external salt and sand. To remove divalent ions present in the algae and replace them with sodium ions, the biomass was treated by the method described in Hernández-Carmona et al. (1999a) and Patrón-Prado et al. (2010). The algae were washed with 0.1 M nitric acid solution at pH 4 for 15 min under constant agitation. The algal biomass was then filtered and washed with distilled water with slow stirring, while pH 7 was obtained with a solution of 0.1 M NaOH. The algae were filtered and dried until constant weight was reached, then chopped (0.2–0.5-mm fragments), and then stored in polyethylene bags until used. Solutions of cadmium were prepared at concentrations ranging from 5 to 900 mg L^{-1} by dissolving chloride salts (analytical grade) in distilled water. A 50-mL metallic solution (initial pH=4.5) was placed in a propylene tube containing 0.5-g pretreated macroalgae. The mixtures were stirred in an orbital shaker at 100 rpm for 24 h. The metallic solution was then passed through a 400-μm nylon mesh filter. Concentration of cadmium ions in the filtrates was determinate by atomic absorption (AVANTA; GBC Scientific Equipment, Melbourne, Australia) with an air-acetylene flame. All experiments were performed in triplicate.

Metal uptake (q) was determined as:

$$q = \left[V\left(Ci - C_f \right) \right] / S \qquad (1)$$

where q (in milligrams per gram) is the amount of metal ions adsorbed on the sorbent, V (in liters) is the volume of metal-containing solution in contact with the sorbent, C_i and C_f (in milligrams per liter) are the initial and final equilibrium (residual) concentrations of metal ions in the solution, and S (in grams) is the amount of added sorbent on a dry weight basis.

The Langmuir adsorption isotherm estimates the maximum metal adsorption by the biosorbent:

$$q = (q_{max})(b)\left(C_f \right) / \left(1 + \left[b \times C_f \right] \right) \qquad (2)$$

where q_{max} is the maximum biosorption with complete saturation of the surface, b is a constant related to adsorption/desorption energy, which is a measure of the affinity of the biosorbent for a particular metal ion, and C_f is the final equilibrium concentration, as defined in the previous paragraph.

Fig. 1 Study area and sampling sites near La Paz, BCS, Mexico. *1* Tarabillas, *2* San Juan de la Costa, *3* Califin
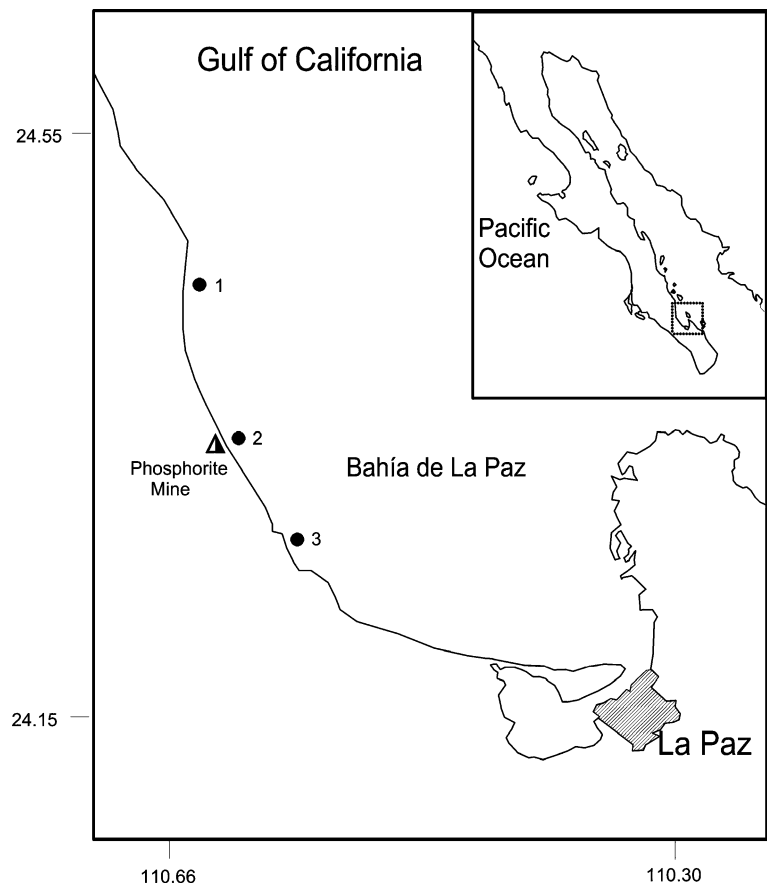
The maximum biosorption capacity (q_{max}) is not the only parameter that needs to be considered in the screening of different biosorbents. The performance of a specific biosorbent is determined by both q_{max} and b; therefore, a better comparison among biosorbents is the following equation (Hashim and Chu 2004).

$$S = \left(C_i - C_f\right)\left(1 + [b \times C_f]\right) / \left([q_{max}][b][C_f]\right)$$

(3)

that combines Eqs. 1 and 2 to estimate the sorbent quantity (*S*) required to achieve a specified level of metal removal in a batch system.

To assay the concentration of alginate, samples of *S. sinicola* and *S. lapazeanum* were hand-picked and sun-dried (ambient temperature 35–45°C), pulverized to 0.5 mm in a manual mill, and stored in polyethylene bags in a shaded and ventilated location until used. Alginate contents were estimated in the laboratory of a pilot plant for production of alginate at

CICIMAR-IPN, using the following method. Dried and milled algae (10 g) were hydrated with 90 mL 0.1% formaldehyde solution for 12 h. The residual formaldehyde solution was drained, and the algae were washed three times with 150 mL of water, adjusting the pH to 4 with an HCl solution with constant stirring for 15 min during each washing. Alkaline extraction was carried out by placing the algae in 250 mL, adjusting the pH to 10 with 10% Na_2SO_3 solution. The algae were heated in a water bath at 80°C with constant stirring at 800 rpm for 2 h. The paste obtained was diluted with hot water and vacuum-filtered with diatomaceous earth and Whatman filter paper No. 4 (Hernández-Carmona et al. 1999a, b). The alginic acid fibers were precipitated in ethanol water solution (1:1 *v/v*) without conversion to calcium alginate (Haug 1965). The concentration of sodium alginate was calculated on a dry weight basis and was used to compare alginate content of the two species. Results are expressed as mean±standard error.

2.3 Concentration of Cadmium

Concentrations in *Sargassum* were measured from samples collected close to the shore of Bahía de La Paz in March 2009 at three sites: Tarabillas, San Juan de La Costa, and Califin, which are north, at, and south of the waste discharged from the phosphorite mine (Fig. 1). Specimens were collected at low tides, rinsed in seawater collected at their respective locations, and placed in labeled polyethylene bags. In the laboratory, the samples were cleaned of sediments, epiphytes, and animals. The algae were dried at 60°C for 24 h and crushed in a mortar to obtain homogeneous material. Individual samples were then digested in acid-washed Teflon tubes with concentrated nitric acid in a microwave oven (CEM Mars 5 microwave oven, Matthews, NC). Samples were analyzed by atomic absorption (AVANTA, GBC Scientific Equipment, Melbourne, Australia) using an air-acetylene flame. Certified standard reference material (IAEA-392, International Atomic Energy Agency, Vienna, Austria) was used for calibration. Analytical values were within the range of certified values; level of recovery of cadmium was 95% of the detection limit (0.0390 mg kg^{-1}).

3 Results and Discussion

3.1 Cadmium Biosorption Capacity and Concentration of Alginate

The Langmuir adsorption isotherm model is the most widely used to express quantitatively the relationship between the extent of sorption and the residual solute concentration. Although the assumptions of the model are not fulfilled in the case of biosorption processes, the Langmuir model is a valuable tool for describing and comparing data between different biosorbents (Davis et al. 2003a, b). For *S. sinicola*, the maximum biosorption capacity (q_{max}) of cadmium was 62.42± 0.44 mg g^{-1} with an affinity constant (b) of 0.09. For *S. lapazeanum*, q_{max} was 71.2±0.80 mg g^{-1}, b=0.03 (Fig. 2). This difference in affinity for cadmium is attributed to the number and chemical nature of the metal-binding sites, such as carboxyl, ether, alcohol, and amino groups of the biosorbent structure (Williams et al. 1998; Sheng et al. 2004). Sulfonate groups do not play an important role in binding of bivalent ions (Sheng et al. 2004). Both species had lower q_{max}
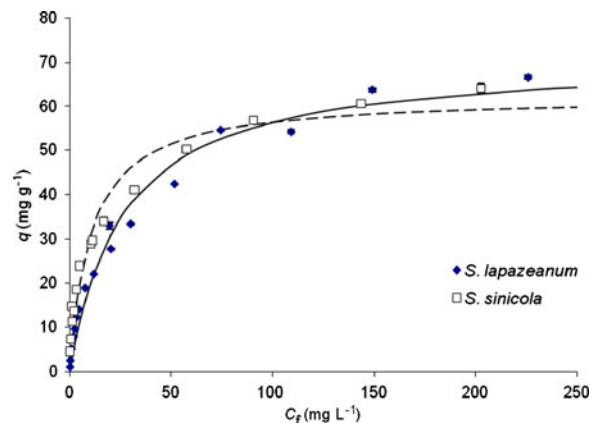

Fig. 2 Sorption isotherm for cadmium (Cd^{2+}). *Line* shows results calculated using the Langmuir model (Eq. 2); *S. sinicola* (*solid line*) and *S. lapazeanum* (*dotted line*)

values than other brown algae, such as *Fucus spiralis*, but higher than some green algae, such as *Chaetomorpha linum* and *Ulva* sp., and red algae, such as *Asparagopsis armata* (Table 1). The q_{max} values were lower than values reported for other species of *Sargassum*, such as *Sargassum baccularia*, *Sargassum filipendula*, and *Sargassum fluitans* (Davis et al. 2000, 2004; Hashim and Chu 2004).

Applying the data from the Langmuir model (Eq. 2) for *S. sinicola* and *S. lapazeanum*, the biosorbent quantity required to produce a final concentration (C_f) of 1 mg L^{-1} for each alga can be calculated from Eq. 3 as a function of the initial cadmium concentration (C_i). Although *S. lapazeanum* had a higher q_{max} than *S. sinicola*, *S. sinicola* outperforms *S. lapazeanum* because it has a higher b value (Fig. 3). *S. sinicola* has lower biosorption capacity than *S. lapazeanum*, but its affinity for cadmium makes *S. sinicola* more suitable. This is not apparent if both algae are compared only on the basis of the q_{max} parameter. Also, in the Gulf of California, *S. sinicola* is a potential biosorbent because it has a high q_{max} and large biomass. On the east coast of the Baja California Peninsula, *Sargassum* biomass is estimated at 180,000 t (wet), of which *S. sinicola* contributes >70%. The technology to harvest, dry, and mill this seaweed is available (Casas-Valdez 2009). Paul-Chávez (2005) suggests harvesting during late May and early June, when most of the thalli have released gametes and are still healthy. This ensures acceptable quality. After this period, the biomass begins to deteriorate and fragment.

Table 1 Maximum capacity of biosorption (q_{max}) reported for several macroalgae

	Species	q_{max} (mg g^{-1})	Reference
Green algae	*Codium vermilara*	21.8	Romera et al. (2007)
	Chaetomorpha linum	53.9	Hashim and Chu (2004)
	Spirogyra insignis	22.9	Romera et al. (2007)
	Ulva sp.	65.1	Sheng et al. (2004)
Brown algae	*Fucus spiralis*	114.9	Romera et al. (2007)
	Padina sp.	84.3	Sheng et al. (2004)
	Sargassum baccularia	83.1	Hashim and Chu (2004)
	Sargassum filipendula	74.1	Davis et al. (2000)
	Sargassum fluitans	106.7	Davis et al. (2004)
	Sargassum lapazeanum	71.2	This work
	Sargassum sinicola	62.4	This work
	Sargassum vulgare	88.7	Davis et al. (2000)
	Sargassum sp.	85.4	Sheng et al. (2004)
Red algae	*Asparagopsis armata*	32.3	Romera et al. (2007)
	Chondrus crispus	75.2	Romera et al. (2007)
	Gracilaria edulis	26.9	Hashim and Chu (2004)
	Gracilaria sp.	33.7	Sheng et al. (2004)

Capacity of cadmium sequestration by nonliving algal biomass is largely dependent on availability of metals in solution and composition of the algae, mostly the concentration and composition of alginic acid in brown algae (Davis et al. 2003b; Mata et al. 2009). The concentration of alginate in *S. sinicola* was 19.2± 1.52%; in *S. lapazeanum*, it was 12.7±1.31%. The yield of alginate from *S. sinicola* was higher than that reported by Pérez-Reyes (1997) and Yabur et al. (2007), 16.8% and 15%, respectively, but it was lower than the 26% reported by Hernández-Carmona (1985) and similar to the 20.5% for *Sargassum oligocystum* reported by Davis et al. (2004). Differences in concen-
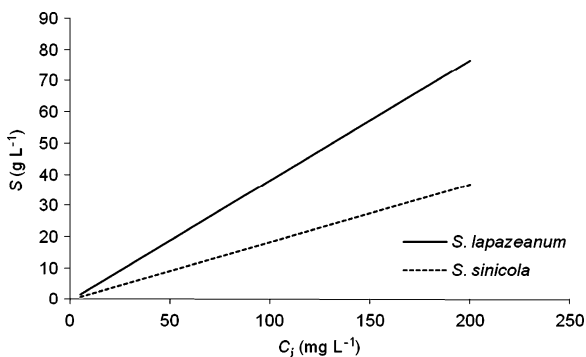
Fig. 3 Algal biomass required to reduce the final concentration to 1 mg L^{-1} as a function of initial concentration of cadmium

trations of alginate among species may be explained by seasonal and yearly fluctuations, local conditions, or characteristics of the species (Hernández-Carmona 1985; Pérez-Reyes 1997).

Alginate is the salt of alginic acid, which is present as a gel inside the cell walls and mucilage or intracellular material (Chapman and Chapman 1980). It is a linear polysaccharide composed of two monomer β-D-mannuronic acid (M) and α-L-guluronic acid (G). These monomers are grouped into sequences MM and MG with glycosidic bonds β (1–4) and blocks GG and GM by glycosidic bonds α (1–4) (Haug et al. 1966). In *S. vulgaris*, Sheng et al. (2004) found that carboxyl groups of alginates are the dominant functional groups for heavy metal biosorption. According to their observations, the lower concentration of alginate in *S. lapazeanum* should mean a lower capacity to remove cadmium than *S. sinicola*; however, the opposite condition was observed in our study. This may relate to the presence of other compounds, particularly fucoidan, which contribute to metal sequestration or to different chemical composition of alginates (Figueira et al. 1999; Davis et al. 2003b; Sheng et al. 2004). Smidsrod and Haug (1968) report that affinity of alginate for divalent cations increased with increasing content of guluronic acid residues. No reports related to alginate composition of *S.*

lapazeanum has been found, but studies of *S. sinicola* show that this alga contains a greater proportion of guluronic acid residues than other brown algae species and similar to quantities found in *S. fluitans* (Davis et al. 2004; Murillo-Álvarez and Hernández-Carmona 2007). However, *S. fluitans* has higher biosorption capacity than *S. sinicola* (Table 1), but Davis et al. (2003a) did not find a direct relationship between high guluronic acid content in alginate and cadmium biosorption. Therefore, identification of other functional groups related to biosorption capacity of brown algae is required to explain the mechanisms involved in sorption of metals.

3.2 Concentration of Cadmium

The highest concentration of cadmium in *S. sinicola* was recorded at San Juan de la Costa adjacent to the discharge site of waste from the phosphorite mine. Specimens collected north and south of San Juan had lower concentrations and were not significantly different from each other. In contrast, *S. lapazeanum* did not show significant differences in concentrations between San Juan and Califin. Also, this species was no found at Tarabillas (Table 2). Differences in concentration of cadmium between the two species could result from differences in metabolic rates or, more likely, to the affinity of each species for cadmium. Our results (Table 2) were above the average values reported for macroalgae (0.92 ± 1.32 mg kg^{-1}) from five regions throughout the world (Baoli and Congquiang 2004). However, these values, with the exception of results for *S. sinicola* from San Juan, are within the range reported in macroalgae in upwelling areas, such as Bahía Magdalena (24.5°N, 112°W) on the Pacific side of the peninsula (Riosmena-Rodríguez et al. 2010) where the range was from not detectable to 4.8 mg kg^{-1} and Playa El Monteón in the State of Nayarit (21°0′18″N, 105°19′10″W) on the eastern side

of the gulf (Páez-Osuna et al. 2000), where the concentration averaged 5.6 mg kg^{-1}. Concentrations of this metal in *S. sinicola* from San Juan de La Costa are similar to the brown alga *Padina durvillaei* from Santa Rosalía, ranging from 1.45 to 9.1 mg kg^{-1} (Rodríguez-Figueroa et al. 2009), which is contaminated by waste from copper mining. However, this value is lower than in brown and red macroalgae along the coast of Chile that is also contaminated by waste from copper mining, where Andrade et al. (2006) reports 17.8 mg kg^{-1} in *Ahnfeltiopsis* sp.

Differences in the ability to absorb or adsorb cadmium by living and nonliving algae are affected by a variety of factors, such as temperature, salinity, light, pH, availability of nitrogen, seasonal differences, age, metabolic processes, and affinity of the organism for each element (Sánchez-Rodríguez et al. 2001; Davis et al. 2003b). Uptake of heavy metals in living algae occurs in two phases: (1) Ions bind to the inert ligands occurring on the cell surface, which is a fast, reversible process and does not require energy; and (2) Ions are bound, often irreversibly, to the cell wall or are actively taken up and bound within the cells (Wilde and Benemann 1993; Knauer et al. 1997). In nonliving algal biomass, only the first phase is involved, and environmental factors do not appear to participate (Stirk and Van Staden 2000). This ability also depends on two other main factors, the bioavailability of the metals in the water and the uptake capacity of live algae (Malea and Haritonidis 1999).

Capacity to accumulate metals in living and nonliving algae is strongly influenced by the ionic form of the metal in the solution. In marine environments, accumulation of cadmium is influenced by the presence of other divalent metals, which compete with cadmium ions at the active sites in the algae. Previous work showed that the capacity of biosorption in *S. sinicola* is remarkably reduced by increasing salinity, apparently from complexing of cadmium ions with chloride ions in seawater (Patrón-Prado et al. 2010). Such interferences are avoided in laboratory tests, where cadmium biosorption by nonliving algae can be greater than the accumulation by living algae.

4 Conclusions

The capacity for biosorption of cadmium by nonliving *S. sinicola* and *S. lapazeanum* was determined as

Table 2 Concentrations of cadmium (milligram per kilogram) in *Sargassum* species in the vicinity of San Juan de la Costa, BCS, Mexico

	Tarabillas	San Juan	Califin
S. lapazeanum	–[a]	2.75±0.20	2.75±0.22
S. sinicola	4.67±0.21	10.96±0.15	4.15±0.19

[a] Species not found

62.42±0.44 mg g^{-1} and 71.20±0.80 mg g^{-1}, respectively; their corresponding alginate concentration was 19.2±1.52% and 12.7±1.31% w/w. Although *S. sinicola* had lower biosorption capacity than *S. lapazeanum*, the affinity of *S. sinicola* for cadmium makes this alga more suitable as a biosorbent. Concentration of cadmium in *S. sinicola* varied at three coastal sites that reflected variations in cadmium bioavailability in seawater. Biosorption capacity of *S. sinicola*, coupled with the large algal biomass available, may be economically effective in bioremediation efforts at cadmium-impacted localities.

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