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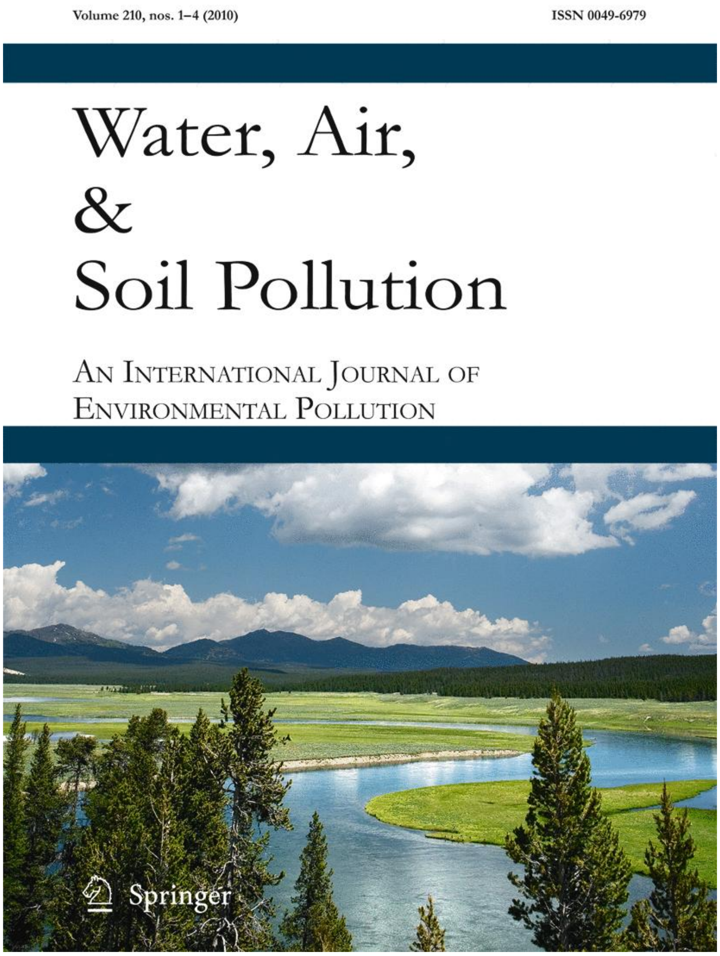

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Copper and Cadmium Biosorption by Dried Seaweed *Sargassum sinicola* in Saline Wastewater

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Abstract Rates of biosorption of cadmium and copper ions by nonliving biomass of the brown macroalga *Sargassum sinicola* under saline conditions were studied. Batch experiments show that the ability to remove cadmium is significantly diminished (from 81.8% to 5.8%), while the ability to remove copper remains high (from 89% to 80%) at a range of salinity from 0 to 40 psu. Maximum capacity of biosorption at 35 psu was 3.44 mg g^{-1} for cadmium and 116 mg g^{-1} for copper. The presence of salt did not significantly affect the rate of biosorption, which was about 90% of saturation in 60 min for both metals. There is an antagonistic effect on biosorption when both metals are present in the solution.

Keywords Cooper · Cadmium · Biosorption · *Sargassum* · Gulf of California

1 Introduction

On the borders of the Gulf of California, human activities have resulted in greatly increased pollutants discharged into coastal waters. Among the sources of pollution are copper mining at Santa Rosalia and phosphorite mining near La Paz on the eastern shore of the Baja California Peninsula, adding copper and cadmium to sediments and organisms in these areas (Shumilin et al. 2000; Rodríguez-Figueroa et al. 2008; Méndez et al. 2006).

The effects of heavy metals on functions of ecosystems vary considerably and are of concern to the economy and public health (Cañizares-Villanueva 2000). In cases, governments may consider it necessary to remove some pollutants from the ecosystem; however, the economic cost of treatment may be very high, based on volume, concentration of metals, and salinity of wastewaters, making it impossible to use conventional technologies, such as precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, electrochemical treatment, and evaporation. In the last two decades, biosorption has drawn attention because of its low cost, sometimes high efficiency, and minimization of chemical or biological sludge. According to Gadd (2008), biosorption may be simply defined as the removal of substances (including heavy metals) from solution by biological material (biosorbent): It is a property of both living and dead organisms (and their components). Biosorbents exhibit this property, acting just as a chemical substance, as ion exchanger of biological origin. Besides, biosorbents may be reused and the metals may be recovered (Kratochivil and Volesky 1998; Lodeiro et al. 2004). Among the biosorbents are some species of the brown algae *Sargassum* that have proved to be a highly effective biosorbent because of their capacity to remove

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high metals at a relatively rapid rate (Schiewer and Volesky 1999; Davis et al. 2000; Lodeiro et al. 2004).

In the Gulf of California, the genus *Sargassum* is an untapped resource that could be used for treating effluents from mining activity. This brown macroalga showed a tendency to incorporate higher concentrations of elements from marine environments than red and green algae present in the region (Sánchez-Rodríguez et al. 2001; Huerta-Diaz et al. 2007). Moreover, on the eastern coast of the Baja California Peninsula, the biomass of *Sargassum* was estimated around 180,000 t; besides, at present, there is technology to harvest, dry, and mill this seaweed (Casas-Valdez 2009). Determining the removal efficiency of metals under common conditions of production of these effluents, including high salinity, could have a positive economic and ecological value. Currently, very few studies focused on biosorption performance under saline conditions. The objective of this study was to determine whether dried seaweed *Sargassum sinicola* could remove copper and cadmium in seawater and parameters that influence the rate of biosorption.

2 Materials and Methods

2.1 Biomass and Treatment

Fresh samples of the brown marine macroalga *S. sinicola* were collected from rocky seashores near San Carlos, Nuevo Guaymas, Sonora, Mexico (27°57′ N, 111°01′ W). The material was rinsed with freshwater to remove external salt and sand. Pretreatment of the biomass involved: A sample of 100 g of the macroalga was treated with 0.2 M H_2SO_4 and NaOH 0.2 M solutions (1 L) for 1 h with slow stirring, with the purpose of removing divalent ions present in the native alga and replacing them with sodium ions (which can be easily displaced by metal ions); the biomass was then washed several times with deionized water to remove excess of solutions. The samples were then dried to a constant weight and roughly chopped (particle size 0.2–0.5 mm) and stored in polyethylene bottles until they need to be used.

2.2 General Procedure

A 50-mL volume of metallic solution was placed in a propylene tube containing 0.5 g of treated macroalga. The mixtures were stirred in an orbital shaker at 100 rpm for 24 h. The algal biomass was then filtered through a 400-μm pore size nylon mesh filter. The filtrates were analyzed for concentrations of cadmium and copper ions with an atomic absorption spectrophotometer (Avanta, GBC Scientific Equipment, Melbourne, Australia). All experiments were performed in triplicate.

2.3 Effect of Salinity

To predict biosorption performance in marine environments, chloride salts (analytical grade) of the two metals were used to prepare standard solutions of copper (Cu^{2+}) and cadmium (Cd^{2+}) by molecular weight calculation. This provided single metal ion solutions at concentrations of 30 mg L^{-1} in water at several salinities (0, 5, 10, 15, 20, 25, 30, 35, and 40 psu). We proceeded with the assay as described in Section 2.2.

2.4 Equilibrium Time

To determine equilibrium time for each ion species, solutions of Cd^{2+} 2 mg L^{-1} and Cu^{2+} 30 mg L^{-1} were prepared in seawater at 35 psu. We proceeded with the assay as described in Section 2.2. Samples of solutions were taken at fixed time intervals (15, 30, 45, 60, 75, and 90 min) for cadmium and copper concentration analyses.

2.5 Equilibrium Studies

To compare biosorption rates between the ion species, the results from Langmuir adsorption equations were plotted. For this, single metal ion solutions of each metal were prepared at concentrations of 2, 4, 8, 16, 32, 64, 128, and 256 mg L^{-1} by dissolving chloride salts (analytical grade) in seawater at 35 psu. We proceeded with the assay as described in Section 2.2.

For confirmation of metals present in the algal biomass following the biosorption process, the metal mass balance was also assayed by analyzing the biomass for metal content. For extraction, the biomass was collected from filters, dried at 50°C for 16 h, and then digested in HNO_3. Water was added to the resulting solutions until reaching 50 mL. The same digestion procedure was performed for native biomass to determine the basal value of the procedures; the results showed negligible contamination.

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2.6 Competition in Metal Ion Uptake

To study the effect of competing ions on the sorption of Cu^{2+} and Cd^{2+}, a solution of eight Cd^{2+} and Cu^{2+} simultaneous metals at several concentrations (2, 4, 8, 16, 32, 64, 128, and 256 mg L^{-1}) was prepared by dissolving chloride salts (analytical grade) in seawater at 35 psu. We proceeded with the assay as described in Section 2.2.

2.7 Data Analysis

Metal uptake (q) was determined as follows:

$$q = \left[V\left(C_\mathrm{i} - C_f\right)\right]S^{-1}, \tag{1}$$

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

The Langmuir adsorption model was used for estimating maximum metal adsorption by the biosorbent. The Langmuir adsorption isotherm can be expressed as:

$$q = (q_{\max} \times b \times C_\mathrm{f})(1 + [b \times C_\mathrm{f}])^{-1}, \tag{2}$$

where b is a constant related to the adsorption/desorption energy, $q_{\max}$ is the maximum biosorption upon complete saturation of the surface, and C_f is the equilibrium concentration, as defined in the previous paragraph.

3 Results and Discussion

3.1 Effect of Salinity

The ability of the *S. sinicola* biomass to remove cadmium is significantly diminished with increasing salinity, ranging from 81.8% at 0 psu to 5.8% at 40 psu (Fig. 1). The results are explained by the chemical speciation of metal ions in the solution; the fraction of uncomplexed Cd^{2+} decreases from 92.2% in river water to 4.4% in seawater by the strong chloride complex (Pivovarov 2003), which is reflected in the rapid decline in the biomass to remove cadmium. The same effect was reported by Dönmez and Aksu (2002); they found that the efficiency of chromium (VI) removal by *Dunaliella* sp. decreases when salt concentration increased from 0% to 20% (*w*/*v*).

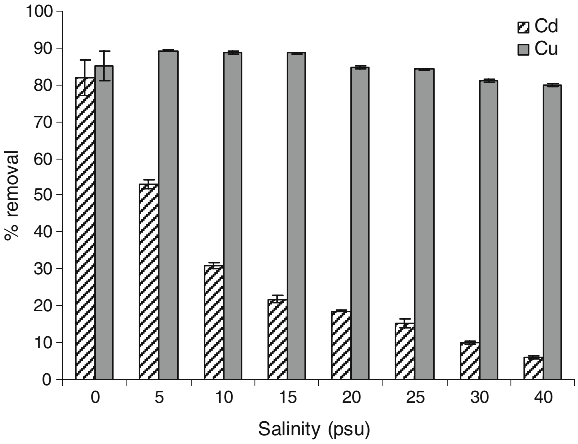

Fig. 1 Effect of increasing salinity on the ability of ion removal by *S. sinicola*

The ability of the *S. sinicola* biomass to remove copper is slightly affected by increased salinity, ranging from 89% to 80%. These results are consistent with the report by Kaewsarn (2002), who found that the efficiency of copper removal on treated *Padina* sp. biomass is not significantly altered by the presence of Ca, Mg, Na, or K ions. Again, chemical speciation of the copper ion is explained because it does not form complexes with chloride ion, allowing a greater fraction of free copper ion to be adsorbed by the macroalga biomass. In this case, the slight decrease in copper removal can be attributed to complexing of copper with sulfates and carbonates in seawater (Pivovarov 2003).

Similar differences in the effect of salinity in biosorption of different metals was observed by Yun et al. (2001) who found that the ability to remove chromium and vanadium by treated crab shell in the presence of salt (NaCl) is diminished and that the effect of the concentration of salt on removing vanadium was far less than on removing chromium. This suggests that the ability of the chloride ion to form complexes with certain metal ions is the main interference in biosorption under saline conditions.

3.2 Equilibrium Time

We found 66% saturation after 15 min of processing with the treated alga (Fig. 2) and 90% saturation in slightly more than 1 h for both metals. Sheng et al.

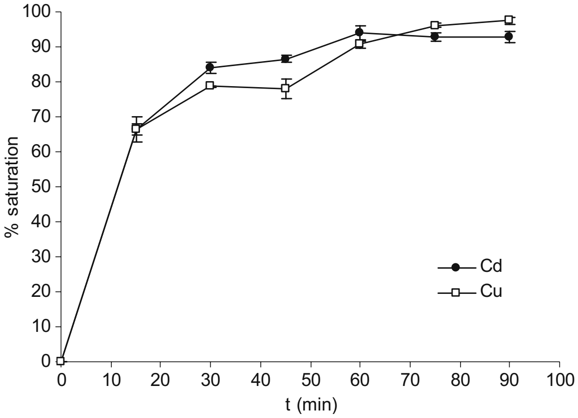

Fig. 2 Kinetics of metal biosorption by *S. sinicola*

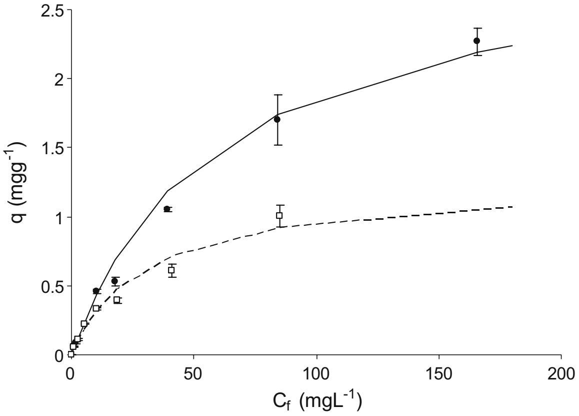

Fig. 3 Sorption isotherms for cadmium (Cd^{2+}) in single metal system (*circle*) and mixed metal system (*square*). *Lines* show results calculated using the Langmuir model (Eq. 2)

(2004) reported that 90% of the total sorption of Pb, Cu, Cd, Zn, and Ni by *Sargassum* sp. is reached in 60 min, and Antunes et al. (2003) reported the rapid removal of copper (Cu^{2+}) during the first 10 min by *Sargassum* sp. in freshwater.

Several reports indicate that biosorption during the first 2 h of exposure to metal ions is very fast, attributed to surface anion exchange; this is followed by slow absorption, which is attributed to diffusion of ions into cell structures (Volesky and Holan 1995; Stirk and Van Staden 2000). In our study, the elapsed time for removing the two metals is short; this is especially important because it indicates that the presence of salt does not significantly affect the speed of biosorption.

3.3 Equilibrium Studies

Under saline conditions (35 psu), the maximum capacity of biosorption ($q_{\max}$) for cadmium, according to the Langmuir adsorption isotherm, was 3.44 mg g^{-1} with the *b* constant of 0.01; experimental and estimated data obtained using Langmuir equation are shown in Fig. 3. By contrast, Volesky et al. (1999) reported that $q_{\max}$= 80 mg g^{-1} for *Sargassum fluitans*, and Holan et al. (1993) reported that $q_{\max}$=215 mg g^{-1} for *Ascophyllum nodosum*, values which are much higher than that found in this work; however, these high $q_{\max}$ values were obtained by bioassays without salt interference.

Under the same saline conditions, the maximum capacity of biosorption for copper was $q_{\max}$= 116 mg g^{-1} with the *b* constant of 0.004, which is higher than the $q_{\max}$ value reported for other species of *Sargassum*; Fig. 4 shows copper biosorption isotherms by *S. sinicola*; Volesky et al. (1999) reported that $q_{\max}$= 59, 51, and 56 mg g^{-1} for *Sargassum vulgare*, *S. fluitans*, and *Sargassum filipendula*, respectively, when using freshwater.

Brierley et al. (1986) suggested that competing with existing technologies for the removal of heavy metals in freshwater, the efficiency of removal of a biomass has to be greater than 99% and the ability to biosorption must be greater than 15 mg g^{-1}. Thus, *S. sinicola* would have a low capacity for biosorption of the cadmium ion and would be inappropriate for the removal of this metal under salt water conditions. However, *S. sinicola* has a high capacity to remove copper compared to efficiencies of other biosorbents.

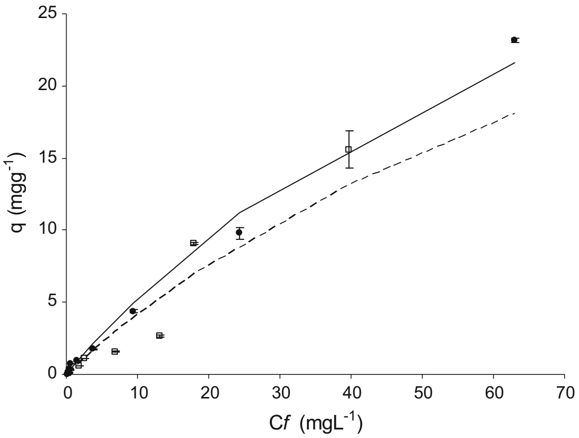

Fig. 4 Sorption isotherms for cadmium (Cu^{2+}) in single metal system (*circle*) and mixed metal system (*square*). *Lines* show results calculated using the Langmuir model (Eq. 2)

3.4 Competition in Metal Ion Uptake

Biosorption of cadmium declined when mixed with copper in solution ($q_{\max}$=1.47 mg g^{-1} with b=0.02); Fig. 3 shows the adsorption isotherms obtained under conditions of single and mixed metal. There was a reduced biosorption of copper when the solution contained cadmium, $q_{\max}$=37.46 mg g^{-1}, and the affinity of algae by copper changed to b=0.11, which was statistically significant. Figure 4 shows the comparison between the biosorption isotherms of copper obtained under single and mixed metal conditions. Zhou et al. (1998) also observed reduction of the biosorption capacity of cadmium and copper by *Laminaria japonica* and *Sargassum kjellmanianum* when both metals are in the same solution. Similarly, Sheng et al. (2007) reported that copper decreased cadmium biosorption by *Sargassum* sp. Therefore, it appears that there is an antagonistic effect when both metals are present in the environment and the presence of salts does not change this behavior.

4 Conclusion

Saline conditions affect adversely the ability *S. sinicola* to remove cadmium while the ability to remove copper is maintained. The speed of biosorption is not affected by the presence of salt, suggesting that *S. sinicola* can be used as a low-cost biosorbent to remove copper from seawater, but not as a biosorbent for removing cadmium.

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