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Cadmium and zinc biosorption by *Macrocystis pyrifera*: changes in the biomass

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Abstract. *Macrocystis pyrifera* was used for the recovery of Zn^{2+} and Cd^{2+} from slightly acidic solutions (i.e., pH 4). Sorption isotherms were obtained from mono- and bi-component solutions. For the study of metal desorption, EDTA, HNO_3 and $Ca(NO_3)_2$ were used as eluents. Metal release (Ca^{2+}, Mg^{2+}, K^+ and Na^+) was monitored in order to evaluate ion exchange mechanisms. After metal sorption/desorption steps the sorbent was characterized using SEM-EDAX analysis. SEM-EDAX analysis also allowed identifying the presence of elements such as Si, Al, Co, Ag, S, P, and Fe in the cell wall. Zinc desorption was almost complete when using 0.1 M nitric acid solution and the sorbent was not significantly damaged by the acidic treatment. Cadmium was completely removed from loaded sorbent when using EDTA, but at the expense of a partial degradation of the biomass as evidenced by the decrease in the intensity of the C and O peaks (SEM-EDAX).

Introduction

Biosorption is a technique that can be used for removal pollutants from waters, especially those that not easily degradable such as metals and dye. This technique employed no living biomass, like bacteria, algae, fungi and yeast. The algae specially brown algae show an extraordinary capacity to bind heavy metals on their cell wall. The binding of the metals depends on the components present on the cell surface and the special structure of the cell wall. The cell wall of algae is constituted of at least two different layers. The innermost layer consists of a microfibrillar skeleton and the outer layer is an amorphous embedding matrix; the two layers do not interpenetrate but they are bound to each other through hydrogen bonds. The inner layer is mainly composed of uncharged cellulose polymer (β -1.4- linked unbranched glucan) [1], while the outer layer is alginate-rich. The cell walls of brown algae generally contain three components: cellulose, the structural support; acidic alginic (a heteropolymer constituted of mannuronic (M) and guluronic acids (G) (and their corresponding salts of Na^+, K^+, Mg^{2+} and Ca^{2+}); and sulfate polysaccharides (fucoidan matrix). The most important groups involved are, carbonyl, carboxyl, sulfhydryl, sulfonate, thioether, amine, secondary amine, amide, imine, phosphonate, phosphodiester. The active sites can be determined using several techniques such as titration, FT-IR analysis, electron dispersive spectroscopy (EDS), nuclear magnetic resonance (NMR), X-ray diffraction analysis (XRD), etc [2]. Modifying the cell wall can greatly alter the binding of heavy metals. The main objective of this work was the evaluation of the modifications of the *Macrocystis pyrifera* cell wall, a brown macroalgae (part of the *Phaeophyta* family) is characterized by a high alginate content (i.e., 40 %, dry weight) [3] occurring during metal sorption.

Materials and Methods

Biomass Treatment. The sun dried samples of *Macrocystis pyrifera* biomass were cut and sieved to collect the fraction 1000-1700 µm. Biomass was washed with demineralized water before being dried in an oven at 50 °C overnight.

Biosorption: Monometallic and bimetallic systems. For single-metal isotherms, a given amount of sorbent (i.e., 0.2 g) was in contact for 30 min with 100 mL of a metal solution at selected pH (i.e., pH 4 for Zn^{2+} and pH 3 for Cd^{2+}) with metal concentration varying between 30 and 400 mg L^{-1}. In the case of bi-component solutions, zinc and cadmium concentrations were simultaneously varied. All the experiments were conducted at room temperature and the suspensions were agitated in a rotary shaker at 160 rpm for 30 minutes. The samples were filtrated with a syringe and filters of 0.45 µm. Metal analyses were performed using an atomic absorption spectrophotometer (AA-CC66-50). Additionally to Zn^{2+} and Cd^{2+} analysis, the concentrations of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} were also monitored in order to evaluate the ion exchange. For the studies of desorption EDTA, HNO_3 and $Ca(NO_3)_2$ were used as eluents; two different concentrations (i.e., 0.1 M y 0.01 M) were tested in bath experiment during 24 hs.

SEM-EDAX. The loaded biomass (from single and bi-component solutions) and the samples that were submitted to desorption were recovered by filtration, washed with demineralized water and dried in an oven at 50°C for 24 h. The same procedure was followed with the control samples. All these samples were analyzed with SEM – EDAX for the characterization and qualitative determination of the changes in the cell wall during the biosorption process.

Results and Discussion

Sorption isotherms. Table 1 shows that *M. pyrifera* has a higher affinity for Zn^{2+} than Cd^{2+}. *M. pyrifera* is one of the biosorbents that have the highest affinity (b=12.71 $L.mmol^{-1}$) for Zn^{2+} in monometallic systems. This is of the same order of magnitude than the value cited by Romera et al. [4] using *Fucus spiralis* (b=14.38 $L.mmol^{-1}$). The values of q_m (obtained from the Langmuir model) were 0.56 $mmol.g^{-1}$ for Zn^{2+}, and 0.66 $mmol.g^{-1}$ for Cd^{2+}, these values are lower than the values cited by Romera et al. [4] (i.e., 0.67 $mmol.g^{-1}$ for Zn^{2+} and 0.93 $mmol.g^{-1}$ for Cd^{2+}).

Table 1. Langmuir constants in monometallic system for Zn^{2+} and Cd^{2+} using *M. pyrifera* biomass.

Metals	q_m [$mmol.g^{-1}$]	b [$L.mmol^{-1}$]	R^2
Zn^{2+}	0.56	12.71	0.99
Cd^{2+}	0.66	1.9	0.92

In bi-component solutions, both the biosorption affinity and the capacity of *M. pyrifera* for Zn^{2+}decreased (q_m= 0.45 $mmol.g^{-1}$; b= 2.27 $L.mmol^{-1}$) in the presence of a high concentration of Cd^{2+} (i.e., 240 mg L^{-1}). Figure 1 shows the behavior of biosorption process when Zn^{2+} and Cd^{2+} varied simultaneously in the solution. The results indicate that *M. pyrifera* has a higher affinity of Zn^{2+} in presence of Cd^{2+}. The total q_m (Zn+Cd) reached 1.2 $mmol.g^{-1}$; this value is consistent with the value obtained adding the maximum sorption capacities for Zn^{2+} and Cd^{2+} in monometallic solutions. This could indicate that the two metals are not competing for the same sorption sites. Though the mass balance (on light metal cations) in the ion exchange process was not reached, it was possible to show that K^{+} ions were exchanged in a major proportion than Ca^{2+} ions for both mono- and bi-metallic systems.

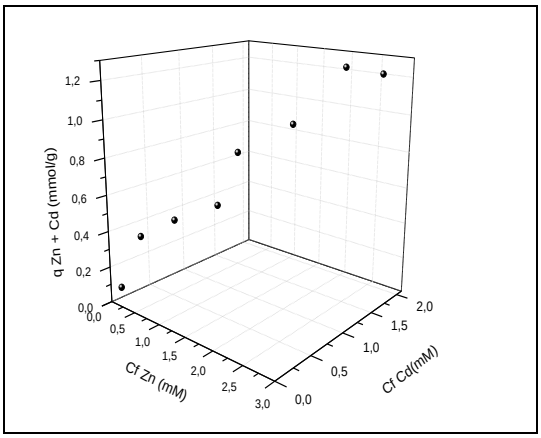

Figure 1. Metal uptake capacity of *M. pyrifera* in bimetallic system (pH 4).

The SEM-EDAX analysis showed the existence of other metals adsorbed in the superficial and inner cell wall. Elements such as Si, Al, Co, S, P, Fe were identified (Fig. 2a and b). The desorption efficiency exceeded 90 % for Zn^{2+} using 0.1 M HNO_3 solutions. SEM-EDAX analysis showed that the structure of *M. pyrifera* biomass was not altered (Fig. 2c). In the case of Cd^{2+} desorption using 0.1 M EDTA solution, the desorption efficiency was also higher than 90 %, but the *M. pyrifera* biomass was modified. The spectrum shows that the pecks of C disappeared (Fig. 2d). In Figure 2, it is possible to see the heterogeneity of the biomaterial; in addition, it can be seen that not only the superficial area is involved in the biosorption process but also the inner cell wall participates. The sample from the bimetallic system does not differ to the control sample after the biosorption process in terms of morphologic aspect (Fig. 2a and b). The spectrum indicates that carboxylic groups play an important role in biosorption process.

Conclusion

This work confirmed the high adsorption capacity and affinity of Zn^{2+} for *M. pyrifera.* The presence of others elements such as Co, Al, Si, Fe etc. adsorbed on the superficial and inner cell walls did not inhibited metal binding. For Zn^{2+} the best desorption was obtained with HNO_3 solutions (0.1 M), allowing high desorption efficiency and great stability of the biomass. Cadmium desorption with 0.1 M EDTA solutions though very efficient revealed inappropriate due to a partial degradation of the biomass. The development of the process is conditioned by the selection of an appropriate biomass treatment in order to reinforce its stability (both mechanical and chemical) for using this material in column systems.

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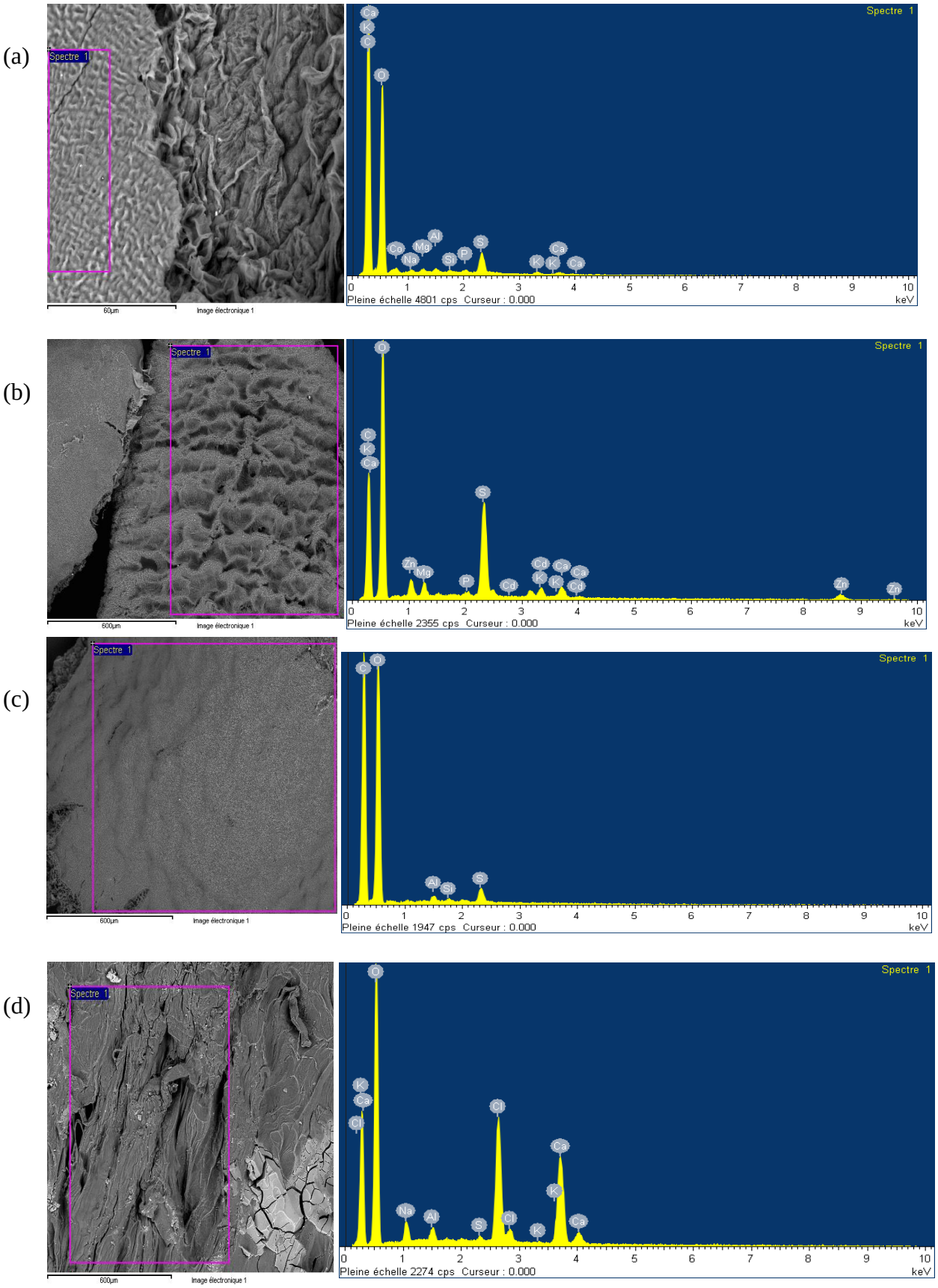

Figure 2. SEM- EDAX micrographs of *M. pyrifera* particles (a) control sample (b) sample of bimetallic system, zinc and cadmium (c) sample after zinc desorption with HNO_3 0.1 M (d) sample after cadmium desorption with EDTA 0.1M.

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