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RESEARCH ARTICLE

The release of light metals from a brown seaweed (*Sargassum* sp.) during zinc biosorption in a continuous system

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The biosorption of zinc and calcium was investigated with a biomass of *Sargassum* sp., a brown seaweed, in a continuous system consisting of three serial tubular fixed-bed laboratory reactors. Results indicated that zinc was efficiently recovered by the biomass. After treatment of 9.0 liters of a mixed solution containing 130.0 mg/l zinc and 260.0 mg/l calcium, the first column of the system saturated with zinc; the remaining columns did not saturate with zinc as a result of the pre treatment performed by the first reactor. Calcium was also efficiently biosorbed by the biomass, saturating the system much faster than zinc. X-ray fluorescence spectrum indicated the presence of various elements in the structure of the *Sargassum* sp. biomass, especially alkaline and alkaline-earth elements. Alkaline and alkaline earth elements played a key role in the biosorption of zinc, being responsible for ion-exchange reactions performed during zinc biosorption.

Nonliving seaweed biomass can be used in the development of biosorbent materials to accumulate heavy metals. The biomass, in this case, must be selective, reusable and cheap, thus constituting an alternative technology for residual metal ions recovery. Non living biomass of seaweeds can be used for this purpose, being an efficient treatment for heavy metals contaminated effluents.

For the uptake of heavy metals two different reactor configurations can be used: continuous stirred tank reactor and fixed bed columns.

Even though the literature presents papers using bacteria (da Costa and Duta, 2001), algal cells (Schmitt et al. 2001), fungi (McAfee et al. 2001) and other biomaterials (Lister and Line, 2001; Schneider et al. 2001), little is known about the behavior of a continuous system, for this kind of treatment. The purpose of the present work was to investigate the behavior of continuous serial reactors for the uptake of zinc. As well, little is known about ion-exchange properties of the biomass. Most papers describe this process as a typical adsorption process, not investigating the

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possible involvement of ion-exchange reactions (Esposito et al. 2001; Hatzikioseyian et al. 2001).

The brown seaweed *Sargassum* sp. is mainly constituted by the polysaccharide alginate, usually calcium and sodium alginates, thus with a high potential for the accumulation of heavy metals, as compared to other algal genera (da Costa and de França, 1996). Those polysaccharides are produced due to the interaction between alginic acid and alkaline and alkaline-earth elements from seawater. Those elements constitute efficient ion-exchangers for heavy metals present in solution. On the other hand, calcium, when in solution, is usually present due to precipitation with calcium salts, performed during primary effluent treatment.

The objective of the present work was to evaluate zinc and calcium biosorption by *Sargassum* sp., and also to evaluate the release of light metals from the structure of the biomass, due to ion-exchange reactions, in a continuous laboratory system.

Materials and Methods

Biomass

The biomass used in the present study was the brown seaweed *Sargassum* sp., collected in the northeastern coast of Brazil. To be used in the experiments, the samples were extensively washed with distilled water to remove particulate material and salts from the surface, being further, oven-dried at 60ºC for 24 hours (da Costa and de França, 1997).

Synthetic effluent and metal ions analysis

Analytical grade $ZnSO_4.7H_2O$ and $CaSO_4.2H_2O$ were dissolved in distilled water in order to obtain a solution containing zinc and calcium at the concentrations of 130.0 mg/L and 260.0 mg/l, respectively. This solution was used for metal biosorption experiments. Concentrations of standard and process solutions were evaluated by atomic absorption spectrometry (Perkin-Elmer, Model Aanalyst 300).

Zinc and calcium biosorption

The biosorption process was conducted in a continuous system operating with three serial fixed bed columns working at a flow-rate of 25.0 ml/min. Each column was 25.0 cm high and 3.5 cm internal diameter, each one filled with 15.0 g of dry biomass of the seaweed. The mixed zinc and calcium solution was pumped upwards through the first column. Outlet solution from the first column was fed to the bottom of the second column. As well, outlet solution from the second column was fed to the third column. A total period of 12 h has been established to run the process. Samples were periodically collected to determine zinc and calcium concentrations in the outlet of each column. Conditions selected for the experiments were based on previous tests performed to obtain suitable flow-rate and residence time. Calcium, magnesium, sodium and potassium were also determined in the process solutions, in order to investigate the release of light metals during the uptake of zinc, associated to ion-exchange mechanisms. Experiments were conducted in triplicate and results represent average values.

Characterization of the biomass by X-ray fluorescence

To identify the metal ions presents in the *Sargassum* sp. structure X-ray fluorescence technique was used (RIGAKV DENKIN Co., Model 3063, P. GEIGERFLEX). In order to determine quantitatively the metals present in the biomass, an acid digestion of the biomass, using concentrated hydrochloric acid, was carried out on a hot plate, following evaporation to a few milliliters. This was performed in the stipes and blades of the seaweed, separately. In the digested material metal ions concentrations were determined by atomic absorption spectrometry (Perkin-Elmer, Model Aanalyst 300).

Results and Discussion

Zinc biosorption by *Sargassum* sp. in the continuous system is presented in Figure 1.

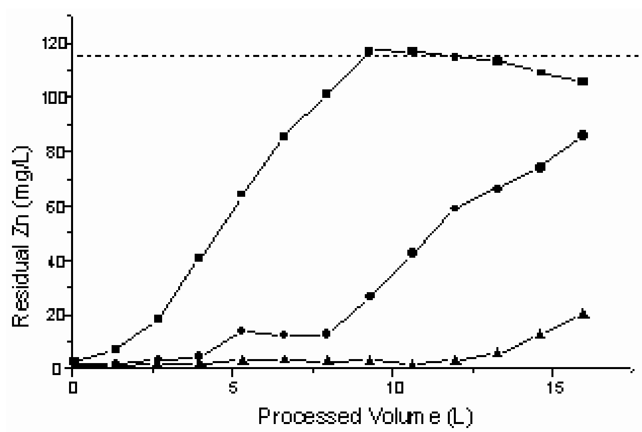

Figure 1. Zinc biosorption by *Sargassum* sp. in continuous system.
-■- First column; -●- Second column; -▲- Third column.

According to the results, it can be observed that the first column of the system gradually lost its zinc uptake capacity, saturating after receiving 10 liters of the metals solution. Analogously, the second column of the system was gradually saturated; however, even after receiving 15 liters of the synthetic effluent saturation levels were not achieved. This was expected to happen because the second column received a much more diluted solution, due to the pre-treatment performed by the first column. The third column, as well, was far beyond saturation, also due to the fact that it received practically metal-free solutions up to 5.0 liters of effluent. If it is considered the overall results obtained by the system, that means, from the inlet of the first column to the outlet of the third column reactor, we can observe that the system completely treated 10.0 liters of zinc solution, whose discharge level is 1.0 mg/l, according to the Brazilian legislation (CONAMA, 1986). Valdman et al. (2001) also working with *Sargassum* sp. for the biosorption of copper, also observed a high efficiency of the process, although working with small volume column bioreactors.

Figure 2 presents the results observed for the simultaneous calcium biosorption. The breakthrough curves obtained for calcium biosorption were analogous to those obtained during zinc biosorption. Initially, the first column saturated, followed by the second and third columns. However, saturation levels were achieved much faster than those observed for zinc.

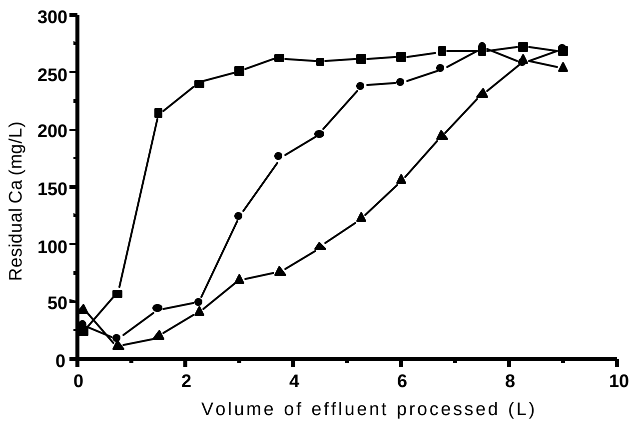

Figure 2. Calcium biosorption by *Sargassum sp*. in continuous system.
-■- First column; -●-Second column; -▲- Third column.

Column 1 and 2 reached saturation after processing 3.0 liters and 6.0 liters of solution respectively, and column 3, after receiving 8.0 liters of solution. Calcium rapidly saturated the biomass, probably because this is a constitutive element in the structure of the brown seaweeds. This way, calcium should have restored some uptake sites on the biomass, especially those damaged due to ion-exchange reactions during zinc biosorption. In order to investigate possible ion-exchange properties of the biomass X-ray analysis of the biomass revealed the presence of several elements: Mn, Fe, Cu, As, Br, Sr, Na, K, Mg, P, S, Al, Ca, Cl and Si (Figure 3). Some of these elements could be involved in ion- exchange properties of the biomass during the uptake of heavy metals.

This previous identification of the presence of light metals was quantitatively confirmed by acid digestion of the biomass, since the main constituents of the biomass are probably involved in ion-exchange reactions (Table 1).

From the results it can be observed that in both parts of the seaweed the concentration of the light metals followed the same order: Ca>Mg>K>Na. Another conclusion can be taken from the results – stipes of the seaweed present all the elements in a higher concentration than the blades, and calcium is present in a much higher concentration than the remaining elements. Thus, it can be concluded that both parts of the biomass can probably take part in the biosorption process, contributing through ion- exchange reactions.

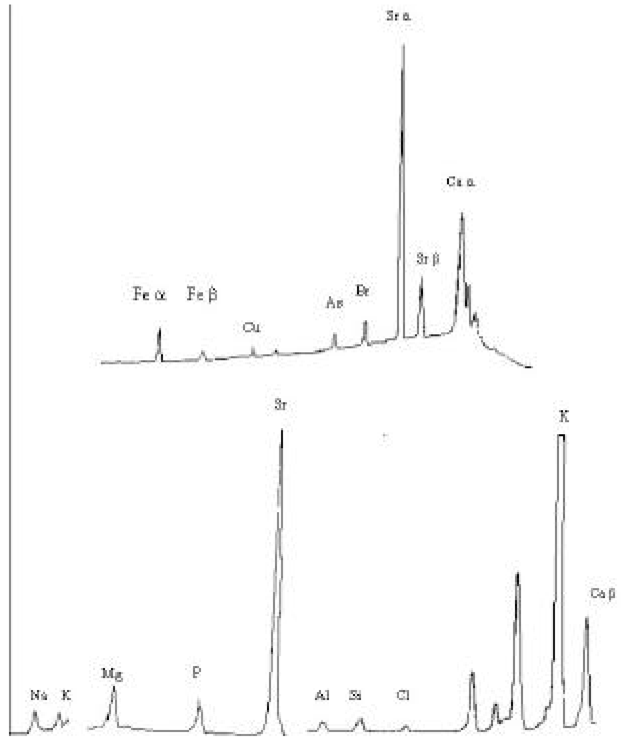

Figure 3. Identification of the main elements presents in the structure of *Sargassum* sp. biomass by X-ray fluorescence.

Table 1. Quantitative determination of light metals in the stipes and blades of *Sargassum* sp. biomass.

Light metal ion	Quantity in the biomass (mg/g biomass)	
	Stipe	Blade
Na^+	3.94	2.77
K^+	4.75	3.93
Mg^{2+}	5.96	5.51
Ca^{2+}	25.71	20.79

Light metals release during zinc uptake by biomass

The release of the light metals Ca, Mg, Na and K is presented in Figure 4. From the results it can be observed that all light metals were released from the biomass during zinc uptake.

Calcium release

Calcium was released from the biomass as zinc was gradually sorbed by the biomass. Calcium concentration increased from 30.0 to 200.0 mg/l and thus decreased again to 30.0 mg/l, in the first column. In the second column reactor, calcium concentration increased up to 200.0 mg/l, thus decreasing to 125.0 mg/l. The third column reactor presented growing outlet calcium concentrations up to 300.0 mg/l. Maximum calcium release were achieved after receiving 4.0, 10.0 and 15.0 liters of zinc solution in the first, second and third columns, respectively. This is an indication that calcium released from the first reactor was transferred to the second one; calcium released from the second reactor probably was transferred to the third column reactor. This effective calcium release is probably related to ion-exchange properties of the biomass during zinc uptake.

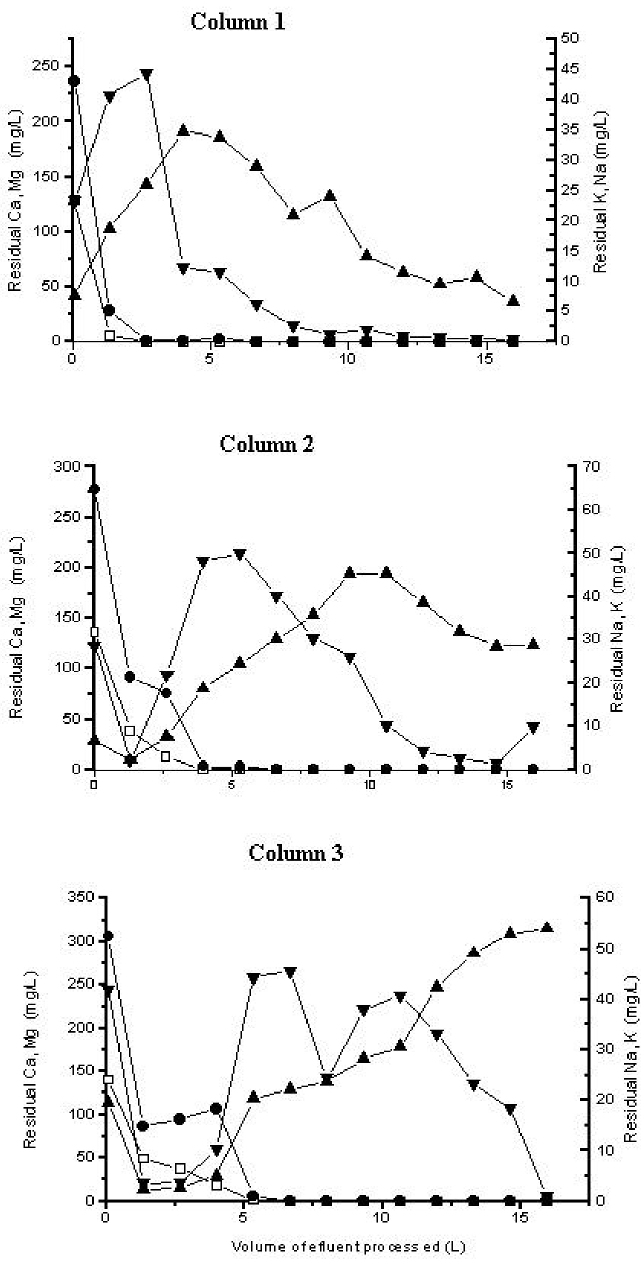

Figure 4. Release of light metals from *Sargassum* sp.
- □ - Na; -● - K; -▲ - Ca; -▼ - Mg.

Magnesium release

Magnesium was released in both columns, reaching a maximum concentration of 250.0 mg/l. After that, magnesium concentration decreased, especially in the final stages of the process, practically not being detected in the outlet solutions.

Sodium release

In the first column, sodium outlet concentrations decreased abruptly, reaching not detectable concentrations at the initial stages of the process. The same behavior was observed for the remaining two columns; however, this decrease was less pronounced than the decrease observed for the first column. This is an indication that sodium is rapidly exchanged with zinc ions.

Potassium release

The same behavior, as observed for sodium, was detected for potassium release during zinc biosorption. Both potassium outlet concentrations decreased, indicating a rapid exchange between the heavy metal and this element.

It can be concluded that both alkaline and alkaline-earth elements contributed for the biosorption of zinc. Monovalent ions rapidly disappeared from solution, probably due to their low content in the biomass. Thus, a rapid and total exchange with zinc was expected to happen. Affinity between light metals and a biomass of marine algae was also described in the literature (Hamdy, 2000). Analogously an affinity order was observed during proton substitution in a biomass of *Sargassum* (Kuyucak and Volesky, 1990). This indicates that, irrespective of the metal solute to be biosorbed divalent alkaline earth ions play a key role in ion-exchange properties.

References

CONAMA. (1986). Resolução Conselho Nacional do Meio Ambiente, No. 20, de 18 de junho de 1986.

da Costa, A.C.A. and Duta, F.P. (2001). Bioaccumulation of ionic copper, zinc, cadmium and lead by *Bacillus* sp., *Bacillus cereus*, *Bacillus sphaericus* and *Bacillus subtilis*. Brazilian Journal of Microbiology 32:1-5.

da Costa, A.C.A. and de França, F.P. (1997). Biosorption of zinc, cadmium, and copper by a brown seaweed (*Sargassum* sp.) in a continuous fixed-bed laboratory reactor. Bioseparation 6:335-341.

da Costa, A.C.A. and de França, F.P. (1996). Cadmium uptake by biosorbent seaweeds: Adsorption isotherms and some process conditions. Separation Science and Technology 31:2373-2393.

Esposito, A.; Pagnanelli, F.; Lodi, A.; Solisio, C. and Veglió, F. (2001). Biosorption of heavy metals by *Sphaerotilus natan*s: an equilibrium study at different pH and biomass concentrations. Hydrometallurgy 60:129-141.

Hamdy, A.A. (2000). Biosorption of heavy metals by marine algae. Current Microbiology 41:232-238.

Hatzikioseyian, A.; Tsezos, M. and Mavituna, F. (2001). Application of simplified rapid equilibrium models in simulating experimental breakthrough curves from fixed bed biosorption reactors. Hydrometallurgy 59:395-406.

Kuyucak, N. and Volesky, B. (1990). Biosorption by algal biomass. In: Volesky, B., ed. Biosorption of heavy metals. CRC Press, Boca Raton, Florida, USA. pp. 175.

Lister, S.K. and Line, M.A. (2001). Potential utilization of sewage sludge and paper mill waste for biosorption of metals from polluted waterways. Bioresource Technology 79:35-39.

McAfee, B.J.; Gould, W.D.; Nadeau, J.C. and da Costa, A.C.A. (2001). Biosorption of metal ions using chitosan, chitin and biomass of *Rhizopus oryzae*. Separation Science and Technology (in press).

Schmitt, D.; Ller, A.M.E.; Cso, Z.; Frimmel, F.H. and Posten C. (2001). The adsorption kinetics of metal ions onto different microalgae and siliceous earth. Water Research 35:779-785.

Schneider, I.A.H.; Rubio, J. and Smith, R.W. (2001). Biosorption of metals onto plant biomass: Exchange adsorption or surface precipitation? International Journal of Mineral Processing 62:111-120.

Valdman, E.; Erijman, L.; Pessoa, F.L.P. and Leite, S.G.F. (2001). Continuous biosorption of copper and zinc by immobilized waste biomass of *Sargassum* sp. Process Biochemistry 36:869-873.