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The Performance of a Continuous System for Biosorption and Desorption of Zinc, Cadmium, Manganese and Copper by the Seaweed *Sargassum* sp.

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ABSTRACT

The biosorption of cadmium, zinc, manganese and copper was carried out using brown seaweed *Sargassum* sp. *in natura* and regenerated with EDTA. The study was done in a continuous system consisting of four serial fixed-bed reactors filled up with a dry biomass of *Sargassum* sp. as adsorbing bed. The synthetic effluent consisted of a mixed solution containing the four metal ions, at 150mg/l concentration, each one. It could be observed that the system was able to treat the mixed solution, in the preference order of Cu>Cd>Zn>Mn, both when *in natura* and regenerated biomass were used. Results also indicated that the amount of metals biosorbed by each column decreased, as a function of the pre-treatment performed by the previous reactor. The regenerated *Sargassum* sp. biomass presented a decreased biosorption capacity, due to partial desorption or destruction of adsorption sites on the surface of the seaweed. The system, as a whole, was able to treat a high amount of concentrated metals solution, generating outlet solutions able to be discharged according to Brazilian federal environmental legislation.

Keywords: Heavy metals; Biosorption; *Sargassum*; Desorption; Continuous System

1. INTRODUCTION

Industrialization and urban growth are increasingly accelerating the deposition of toxic compounds in aqueous streams, contributing for a marked decrease in the quality of the environment (Senthilkumaar *et al.*, 2000). Specifically, the increasing discharge of heavy metals in the environment contributes for this degradation, mainly due to their non biodegradable nature (Esposito *et al.*, 2001; Kaewsarn and Yu, 2001).

Conventional technologies have several disadvantages, being not effective for metal concentrations smaller than 100mg/l, beyond being expensive, requiring wide spaces for installation associated to a high production of sewage to be discharged (Kaewsarn and Yu, 2001; Valdman and Leite, 2000; Senthilkumaar *et al.*, 2000).

The use of biological materials for the removal and recovery of heavy metals from industrial wastes seems to be an interesting alternative to conventional techniques, both with living or inactivated biomasses (Valdman *et al.*, 2001, Singh *et al.*, 2000; Figueira *et al.*, 2000).

Some important factors about the use of biomasses include their low cost, their high metal uptake capacity, their availability and their possible application in several sorption/desorption cycles after regeneration (Vegliò *et al.*, 1997).

Hamdy (2000a) studied Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} biosorption by *Sargassum asperifolium, Cystoseira trinode, Turbinarina decurrens* (brown seaweeds) and *Laurencia obtusa*

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(red seaweed), observing different uptake capacities due to differences in their polysaccharide contents. In fixed-bed reactors, Hamdy (2000b) studied the uptake of lead by a green (*Ulva lactuca*), a red (*Jania rubens*) and a brown seaweed (*Sargassum asperifolium*). Using both seaweeds as the bed of the reactor, lead uptake was around 282mg lead/g biomass, not being affected by increasing flow rates.

Little is known about the use of seaweeds for the uptake of more than one heavy metal present in the same solution in fixed-bed bioreactors (Sag *et al.*, 2000; Singh *et al.*, 2000; Costa and França, 1997; Valdman *et al.*, 2001).

Fixed-bed biosorption columns continuously work through sorption, regeneration and washing cycles. Their operation initiates by loading the biosorbent material, responsible for treating the feeding metal solution. When the metal uptake capacity of the biosorption column reaches its maximum value, regeneration starts. After regeneration of the biomass, washing of the biomass is conducted to remove particulate materials from the surface of the bed. For a continuous operation of the system, paired columns are used; while one column is gradually saturating with adsorbing metals, the other one is subjected to regeneration and washing (Kratochvil and Volesky, 1998; Vegliò *et al.*, 1997; Volesky, 2001).

The purpose of this work was to develop a technology for the treatment of multimetal solutions with the use of the brown seaweed *Sargassum* sp., using several serial fixed-bed bioreactors, also investigating the possibility of reusing the biomass after desorption and regeneration of the adsorbing biomass.

2. MATERIALS AND METHODS

2.1. Biomass

The biomass used in the present work was *Sargassum* sp., a brown seaweed obtained in the Northeastern coast of Brazil. For use in the experiments, the biomass was extensively washed with water to remove salts, sand and particulate materials from its surface, and dried at 60±1°C for 24 hours.

2.2. Synthetic effluent

Solutions used were prepared by simultaneous dissolution of $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$ $3CdSO_4.8H_2O$ and $MnSO_4.H_2O$ in distilled water. Final metal ion concentrations were 150mg/l, simulating a complex effluent from zinc producing plants, containing the four elements zinc, copper, cadmium and manganese.

2.3. Biosorption of cadmium, zinc, manganese and copper by virgin (*in natura*) biomass of *Sargassum* sp.

Experiments were conducted in a continuous system with four tubular fixed-bed column reactors, all of them filled with *Sargassum* sp., containing 120g biomass per column (Figure 1) and working in series. Each cylinder column was 50.0cm high and 7.0cm internal diameter. The system worked feeding the first column with the synthetic effluent (upwards); outlet solution from the first column was fed to the second one, and successively until outlet of the fourth column. pH of the influent was adjusted to 4.5. Flow rate used was 25ml/min. Outlet solutions from the four columns were periodically collected (3 hour interval, during 24 hours) to determine the residual metals concentrations. All the experiments were conducted in triplicate, at 30±1°C, being here reported average values observed.

Figure 1. Continuous bioreactors used for the biosorption of Cd^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}

2.4. Biosorption of cadmium, zinc, manganese and copper by regenerated biomass of *Sargassum* sp.

The virgin biomass of *Sargassum* sp., loaded with heavy metals from the biosorption cycle, was regenerated with 15g/l EDTA solution, in order to be reused in another biosorption cycle, in the same conditions as described above. The desorption of metals was conducted by contacting 1.3L of EDTA solution with the loaded biomass, for 30 minutes. This procedure was conducted five times to ensure an efficient metals recovery. Samples from every washing were collected to determine the efficiency of the desorption. Analogously, experiments were conducted in triplicate, at 30±1°C.

2.5. Cadmium, zinc, manganese and copper determinations

Standard metals solutions and all the process solutions (biosorption and desorption) were determined by atomic absorption spectrometry (Perkin-Elmer Aanalyst, Model 300), at Universidade do Estado do Rio de Janeiro.

3. RESULTS AND DISCUSSION

3.1. Biosorption of cadmium, zinc, manganese and copper by virgin biomass of *Sargassum* sp.

3.1.1. Cadmium biosorption

The biosorption of cadmium from the mixture of four metals, by *Sargassum* sp. *in natura* is presented in Figure 2.

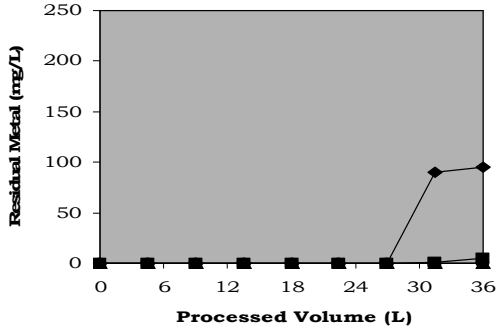

Figure 2. Cadmium biosorption by *Sargassum* sp. *in natura*, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Results presented indicate a gradual saturation of the first column, due to the high metals concentration in the inlet effluent. This way, it could purify 27 liters of effluent, according to Brazilian CONAMA regulations. The second reactor presented an equivalent treatment capacity and third and fourth columns were able to treat 36 liters of effluent, according to Brazilian regulations (below 0.2g/l). This was possible, because third and fourth reactors received a less concentrated effluent, due to the pre treatment performed by the first and second columns. The curves that represent biosorption of the metals by regenerated biomass (after desorption with EDTA) are shown in Figure 3. The results revealed a decrease in cadmium uptake capacity, after the fourth regeneration of the biomass.

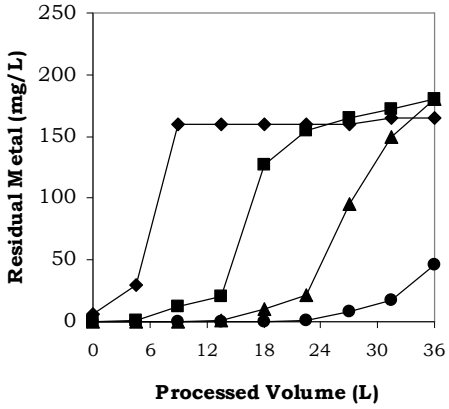

Figure 3. Cadmium biosorption by *Sargassum* sp. after the 4th regeneration, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Table 1 presents cadmium uptake capacity by virgin and regenerated *Sargassum* sp. biomass. The amount of cadmium accumulated by *Sargassum* sp. *in natura* was 24.5±14.2mg Cd^{2+}/g dry biomass. This value was higher than the average value from four sorption/regeneration cycles performed (12.6±0.6mg Cd^{2+}/g dry biomass). Even though a marked decrease has been observed after regeneration of the biomass, it was still capable of treating, efficiently, the inlet solution.

Table 1
Cadmium biosorption by *Sargassum* sp.

	Column 1	Column 2	Column 3	Column 4
% biosorbed [a]	89.5±2.0	99.7±0.2	99.9±0.1	100
% biosorbed [b]	27.0±4.0	62.8±8.5	81.3±8.9	97.9±1.4
mg Cd/g biomass [a]	44.3±0.5	24.7±1.0	16.5±0.8	12.4±0.6
mg Cd/g biomass [b]	12.7±2.0	12.5±0.9	13.4±1.9	12.1±0.2

a: *in natura* biomass, b: regenerated biomass (average value from 4 sorption/regeneration cycles – Values up to saturation point of the breakthrough curves).

Costa and França (1997) also studied the simultaneous biosorption of zinc, cadmium and copper by *Sargassum* sp. in a continuous system with three serial fixed-bed reactors. They observed that the amount of cadmium biosorbed was 19.72mg Cd^{2+}/g, 18.24mg Cd^{2+}/g and 21.99mg Cd^{2+}/g, in the first, second and third bioreactors, respectively. Those values are smaller than the ones observed in the present work; here, operational conditions used were quite distinct (smaller column reactors, different flow-rate and metal concentrations) markedly influencing the biosorption of cadmium.

The decrease in the efficiency observed in sorption/desorption cycles was also evaluated by Chu *et al.* (1997), however, under batch conditions. Chu *et al.* (1997), working with *Sargassum baccularia*, performed five consecutive sorption/desorption cycles, using HCl and EDTA as desorbing agents, observing a decrease in the metal uptake capacity by the biomass and a marked loss in biomass content, after treatment with HCl. This was due to the dissolution of polysaccharides from the biomass, compromising surface uptake.

Esteves *et al.* (2000), working with a waste biomass of *Sargassum* sp. performed sorption/desorption studies, after zinc biosorption, observing distinct desorption efficiencies as a function of the type of desorbing agent and concentration.

3.1.2. Zinc biosorption

Figure 4 shows zinc breakthrough curves, as previously presented for cadmium. Results indicate a gradual saturation of the first column of the system, being this saturation more abrupt than that observed for cadmium. After 24 hours of operation of the system, the first column was able to treat 9.5 liters of effluent, against 27 liters for cadmium. Second, third and fourth columns treated 22.5, 31.5 and 36.0 liters of effluent, respectively, during 24 hours.

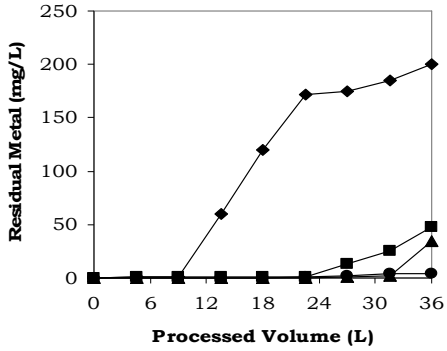

Figure 4. Zinc biosorption by *Sargassum* sp. *in natura*, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Zinc breakthrough curves, when regenerated *Sargassum* sp. biomass was used, are presented in Figure 5. It can be observed a marked decrease in the biosorption of zinc as compared to virgin *Sargassum* sp. biomass.

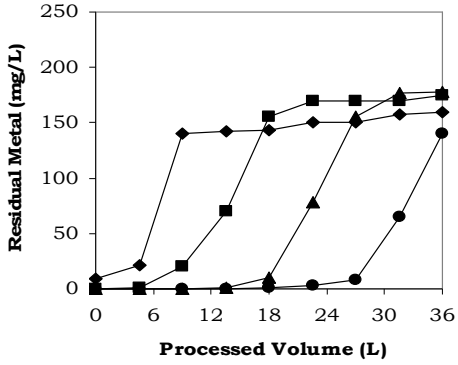

Figure 5. Zinc biosorption by *Sargassum* sp. after the 4th regeneration, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Desorption equilibrium was here observed for zinc, represented by higher outlet zinc concentrations, in comparison to inlet zinc concentrations. Tavares (2000) also observed this fact, working with a biomass containing this element in its structure, as indicated by X-Ray diffraction.

Table 2 presents zinc percent uptake and the amount of zinc biosorbed by *in natura* and regenerated biomass of *Sargassum* sp. *In natura* biomass presented an average uptake 17.0±4.5mg Zn^{2+}/g dry biomass and the regenerated biomass 9.8±0.7mg Zn^{2+}/g dry biomass. Results indicated that cadmium was recovered more efficiently than zinc.

Table 2
Zinc biosorption by *Sargassum* sp.

	Column 1	Column 2	Column 3	Column 4
% biosorbed [a]	71.2±1.0	93.8±0.3	98.2±0.5	99.2±0.1
% biosorbed [b]	32.8±3.5	56.7±5.2	77.9±5.1	91.1±3.4
mg Zn/g biomass [a]	19.3±1.0	21.8±1.1	15.2±0.8	11.5±0.6
mg Zn/g biomass [b]	9.4±0.8	9.1±1.8	10.2±0.9	10.6±0.4

a: *in natura* biomass, b: regenerated biomass (average value from 4 sorption/regeneration cycles – Values up to saturation point of the breakthrough curves).

3.1.3. Manganese biosorption

As expected, manganese biosorption breakthrough curves showed a gradual saturation of the first column, practically in the same stage as did for zinc. During 24 hours of operation the first column was able to treat 7.0 liters of effluent, against 9.5 liters for zinc. Second, third and fourth columns of the system presented smaller efficiencies in the treatment of manganese, as compared to zinc and cadmium. Those columns were able to treat 9.0, 13.5 and 18.0 liters of effluent, respectively (Figure 6). Breakthrough curves obtained with the use of regenerated biomass are presented in Figure 7. After regeneration of the biomass with EDTA, average volume of effluent treated was 18.0±2.0 liters, during 24 hours. This result, equivalent to the result obtained for zinc, indicate that zinc probably do not affect manganese biosorption and vice-versa.

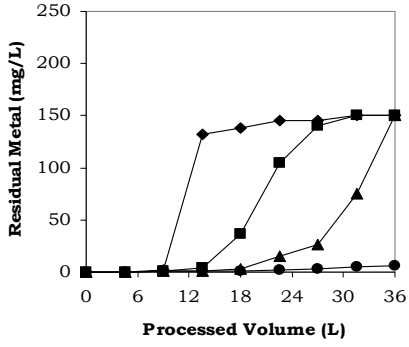

Figure 6. Manganese biosorption by *Sargassum* sp. *in natura*, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

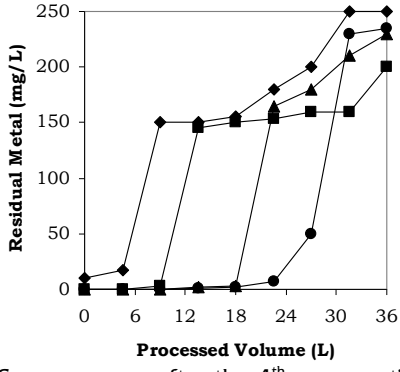

Figure 7. Manganese biosorption by *Sargassum* sp. after the 4th regeneration, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd; -λ- 4th

Table 3 shows percent manganese biosorbed and the uptake capacity of the biomass for this element.

Table 3
Manganese biosorption by *Sargassum* sp.

	Column 1	Column 2	Column 3	Column 4
% biosorbed [a]	66.7±2.0	56.5±1.0	81.8±2.0	98.5±0.5
% biosorbed [b]	44.5±4.7	65.0±9.1	89.5±0.6	91.9±1.7
mg Mn/g biomass [a]	15.5±0.8	12.7±0.6	12.3±0.6	11.1±0.6
mg Mn/g biomass [b]	8.1±0.4	8.2±0.8	8.4±0.1	8.6±0.3

a: *in natura* biomass, b: regenerated biomass (average value from 4 sorption/regeneration cycles – Values up to saturation point of the breakthrough curves).

Table 3 shows that virgin biomass accumulated 12.9±1.9mg Mn^{2+}/g biomass against 8.3±0.2mg Mn^{2+}/g biomass (average value). As observed in the case of cadmium, the amount of manganese accumulated after regeneration was practically the same in both columns.

3.1.4. Copper biosorption

Figure 8 shows the curves obtained during copper biosorption by the virgin biomass of *Sargassum* sp. Copper was recovered by the biomass much more efficiently than the other three metals. The first column was able to treat 27.0 liters of solution with an outlet concentration of 0.1mg/l. Remaining columns treated 36.0 liters of solution.

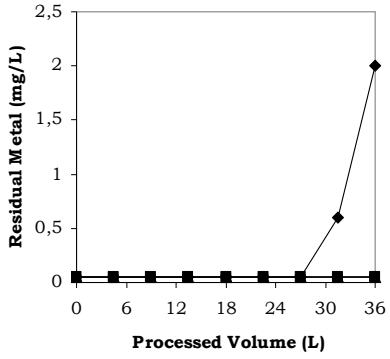

Figure 8. Copper biosorption by *Sargassum* sp. *in natura*, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Breakthrough curves obtained during copper biosorption with regenerated biomass are presented in Figure 9. Although copper biosorption showed to be much more efficient than the other metals, a loss in the uptake capacity of the biomass was also observed after regeneration. It was able to treat 27.0±3.0 liters of effluent, considering average values obtained during all sorption/desorption cycles.

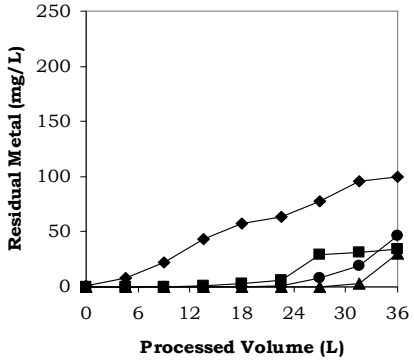

Figure 9. Copper biosorption by *Sargassum* sp. after the 4th regeneration, from the mixed solution, both at 150±5mg/l during 24 hours of process: Column -υ- 1st ; -ν- 2nd ; -σ- 3rd ; -λ- 4th

Results indicate a different uptake pattern, in comparison to cadmium, zinc and manganese biosorption, indicate that copper is probably sorbed through a distinct mechanism. Specifically for copper, this mechanism is probably complexation followed by metallic nucleation, involving interaction between metal ions, thus forming a central nucleus responsible for commencing nucleation (Costa and França, 1997). This fact could be confirmed by the observation of copper precipitates on the surface of the seaweed, indicating a marked biosorption of this metal ion.

Simple adsorption normally predicts that each metal ion can react with only one site on the biomass and also that only one type of site is involved in the process. However, in certain cases, it is observed that after this initial interaction by simple adsorption, the formation of a central nucleus catalyses the deposition of additional metals (Costa and França, 1997). This mechanism explains the higher biosorption of copper by *Sargassum* sp., in comparison to the remaining metal ions.

During 24 hours none of the columns, in all cycles performed, reached saturation, although, in some cases, copper residual concentrations were higher than that standardized for discharge, according to the Brazilian legislation. Table 4 presents percent copper biosorbed and the amount of copper recovered by *Sargassum* sp.

Table 4
Copper biosorption by *Sargassum* sp.

	Column 1	Column 2	Column 3	Column 4
% biosorbed [a]	100	100	100	100
% biosorbed [b]	65.6±5.7	93.8±2.8	98.9±0.6	98.0±1.6
mg Cu/g biomass [a]	45±0.7	22.5±1.1	15.0±0.2	11.3±0.2
mg Cu/g biomass [b]	29.5±2.5	21.1±0.6	14.9±0.1	11.0±0.2

a: *in natura* biomass, b: regenerated biomass (average value from 4 sorption/regeneration cycles – Values up to saturation point of the breakthrough curves).

Maximum average loading capacity of *Sargassum* sp. *in natura* was 23.5±15.1mg Cu^{2+}/g against 19.1±8.1mg Cu^{2+}/g for regenerated *Sargassum* sp., considering average values from those observed for the four column reactors. Zhou *et al.* (1998) also studied adsorption and desorption of copper by *Sargassum kjellmanianum* using EDTA and HCl as desorbing agents. For both reagents copper was efficiently desorbed, being HCl more effective as copper desorbing agent.

An overview of the results obtained in the present work revealed that when *in natura* *Sargassum* sp. biomass was used the uptake preference observed was Cu>Cd>Zn>Mn.
The applicability of "hardness and softness" principle, used for strong acids and bases can be useful to explain the obtained results (Blanco *et al.*, 1998; Pearson, 1968). According to this principle, hard metals are usually non-toxic elements essential for living organisms, interacting mainly with oxygen. On the other hand, soft metals are toxic elements forming strong bonds with nitrogen and sulfur ligands. Borderline elements present chemical properties from both hard and soft metals. This classification is widely used to explain the interaction of metals with biological molecules (Avery and Tobin, 1993; Blanco *et al.*, 1998).

According to this classification, zinc is considered a "borderline" metal, copper and cadmium are "soft" metals and manganese is considered a "hard" metal (Hughes and Poole, 1991).

The most relevant variables for the classification of metals according to "hardness and softness" of acids and bases are the electronegativity of Pauling, charge and ionic radius (Blanco *et al.*, 1998). Table 5 presents some of those properties for the ion metals studied. According to data presented in Table 5, it can be observed that copper is the element with a higher electronegativity, the smaller ionic radius and one of the smaller atomic weights. These properties, as compared to the remaining elements, are quite particular for the element copper, thus explaining its outstanding biosorption. Copper has the higher electronegativity, probably interacting more effectively with the ligand sites in the biomass, difficulting its natural desorption due to saturation on the surface of the seaweed, as observed for the remaining metals. Additionally, its ionic radius is the smaller amongst the elements studied, facilitating its interaction with the sites on the biomass. Also, its small atomic weight may have contributed to an easy interaction.

Table 5
Chemical properties of the ion metals studied

	Metal ions			
Chemical property	Cu^{2+}	Cd^{2+}	Zn^{2+}	Mn^{2+}
Atomic weight (g)	63.5	112.4	65.4	54.9
Ionic radius (A°)	0.72	0.97	0.74	0.80
Electronegativity of Pauling	1.90	1.69	1.65	1.50

Cadmium was the second element preferentially accumulated by the biomass. Although its chemical properties do not contribute for an easy interaction with the biomass its high electronegativity is probably the main responsible for its high uptake. Being a "soft" metal it probably interacts with nitrogen and sulfur groups from polysaccharides present in the surface of *Sargassum* sp. (Esteves *et al.*, 2000).

Esposito *et al.* (2001), comparing copper and cadmium biosorption by *Sphearotilus natans*, also based his conclusions on these chemical properties of these elements. Zinc and manganese present similar chemical properties, acting as "borderline" metals, thus competing with other elements for deposition sites.

Carvalho *et al.* (1995) observed that zinc substantially decreases the uptake of cadmium and copper in binary systems. Chang and Chen (1999) also studied the interference observed when several metals are present in the same solution, using *Pseudomonas aeruginosa* PU 21 (Rip64) as biosorbent material. Adsorption equilibrium showed that lead and copper markedly inhibited the adsorption of cadmium, while cadmium poorly influenced lead biosorption. da Costa *et al.* (1996), working with real and simulated effluents, both containing Zn^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, observed the selectivity order $Cu^{2+}>Cd^{2+}>Zn^{2+}>Mn^{2+}$. Manganese instantly reached equilibrium, however, with a poor uptake by the biomass, as observed in the present work.

4. CONCLUSIONS

- The biomass of *Sargassum* sp. proved to be an efficient alternative for the removal of cadmium, copper, zinc and manganese. *In natura* biomass presented, usually, a higher uptake capacity than the regenerated biomass.
- The preferential uptake capacity was Cu>Cd>Zn>Mn.
- The bioreactors were able to treat 0.75L/h and 0.56L/h, when *in natura* and regenerated *Sargassum* sp. biomass was used, respectively, for a mixed solution containing metals at 150±5mg/l.
- The results demonstrated that a different uptake pattern was observed for the metal copper; copper biosorption probably occur through mechanisms not related to the mechanisms observed during the uptake of cadmium, zinc and manganese. These are probably complexation reactions followed by metallic nucleation, where copper acts as a nucleating center, responsible for starting nucleation and additional copper deposition.
- For a suitable scale-up of the process, there is a need to resize column height and diameter, in order to fit the desirable loads of treatment.

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