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BATCH AND CONTINUOUS HEAVY METALS BIOSORPTION BY A BROWN SEAWEED

12

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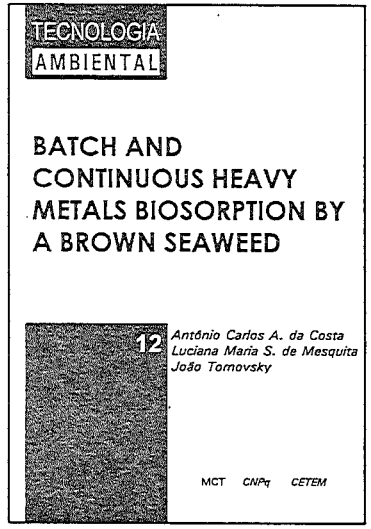

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PRESENTATION

Heavy metals in the environment is being a subject to which scientists and researchers all over the world are devoting their most deep attention.

The reason?

We, at the present, still know very little of their fate into the environment, their speciation and their mobility.

Nevertheless, their danger and toxicity are being put forward here and there, and some of the most proeminent heavy metals indeed had shown their deleterious effects to the biota and living organisms.

Therefore, ways of immobilizing or recovering such heavy metals from industrial effluents are gainning more and more space in the technical litterature.

This present work is part of such attempts, focused on the removal of several cations, i.e, Zn (II), Cd (II), Cu (II), Al (III), Ca (II), Mg (II) and Na (I), contained in simulated effluents from zinc producing plants, through biomass.

The interested reader will certainly enjoy the text and the discussions here in presented.

Rio de Janeiro, April, 1996.

Roberto C. Villas Bôas
Director

CONTENTS

ABSTRACT

The removal of heavy metals by a dry biomass of a brown seaweed was evaluated. It was used a continuous system, with an effluent from a Brazilian zinc-producing industry, containing several metals. Preliminary results, in batch conditions, indicated a fast uptake kinetics. The continuous run was conducted in a laboratory acrylic column, containing several samplers, filled with the dry biomass. The system operated in upflow condition with a high operational stability. The results showed a high efficiency in the biosorption of heavy metals. Sodium, calcium and magnesium were not incorporated by the biomass, probably because they are present in the structural polysaccharides of the biomass. The analysis of the obtained results did not indicate a selective uptake of the metals, probably as a function of their marked concentrations differences in solution.

Key words: *Sargassum, biosorption, complex metals solution.*

RESUMO

A biosorção de metais pesados por uma biomassa seca de uma alga parda foi estudada. Foi empregado um sistema contínuo para o tratamento de um efluente complexo de uma indústria brasileira produtora de zinco. Resultados preliminares indicaram uma cinética rápida para o processo. Um experimento contínuo, empregando uma coluna de laboratório contendo vários amostradores, foi estudado com a biomassa como material adsorvente. O sistema operou em fluxo ascendente, com elevada estabilidade operacional. Os resultados indicaram elevada eficiência de captação dos metais, exceção feita para o sódio, cálcio e magnésio, provavelmente por serem constituintes da biomassa.

Palavras chave: *Sargassum, biosorção, solução complexa de metais.*

1. INTRODUCTION

The intensification of industrial activities during the last few years, has been greatly contributing to an increasing dispersion of toxic compounds in natural environments, mainly in aquatic systems. In most cases it is possible to reduce dramatically the level of toxic substances through the use of conventional technologies, although the cost associated to these processes is very high and the efficiency of the treatment not fully satisfied. When these compounds are associated to metallic ions, those technologies are not completely efficient and the non-degradable nature of these elements dictates that they must have suffered with additional treatments to fit environmental discharge patterns and legislations.

Although these elements are not metabolized by biological organisms, they can be incorporated by passive or active difusion processes, as well as by simple adsorption phenomena onto cellular structural components [2,5,10,12]. Difusion processes (active or not) are a function of the incorporated ionic species, and it occurs due to the lack of specificity of cellular transport systems. Adsorption occurs through several types of chemical reactions with constituents of the cells, usually negativelly charged groups present in the structural polysaccharides and surface proteins of the different biological organisms.

The remarkable ability of biomass to concentrate heavy metals, acting as a biological resin, is becoming an useful tool for treating industrial solutions contaminated with heavy metals [1,8]. This phenomenon, generally called biosorption, is easily handled conventional fixed-bed reactors design. This reactor has a very simple operational mode, with a reduced cost, in comparison to sophisticated treatment techniques. So biosorption could be used as a complementary technology to treat effluents contaminated with heavy metals.

The main aim was to study the behaviour of a specific biomass as a biological resin for the accumulation of heavy metals. The main results obtained in preliminary investigations using a Brazilian brown seaweed, in batch systems, for the treatment of an effluent from a Brazilian mining-metallurgical company are presented. The study was carried out in a laboratory fixed-bed continuous reactor, using the algae as the bed of the reactor.

2. MATERIAL AND METHODS

2.1 Biomass

The biomass used in all the experiments was a seaweed from the genus *Sargassum* (*Phaeophyta, Sargassaceae*), collected at the coast of Pernambuco State, in the Northeastern Region of Brazil. The biomass was oven-dried at 70° C before using it in the biosorption tests. The biomass was pulverized (mortar and pistill) and classified for particles size, from 0.841 to 0.595 mm (+20-28 mesh Tyler), for the batch tests. The biomass was used without grinding for the continuous experiments.

2.2 Synthetic and Natural Effluents

Due to the high variability of metals concentration all over the year for the effluent selected, two different solutions were used in the experiments: a synthetic one, based on the average concentration of the effluent during summer time; and a true solution, collected during winter time, and with a different quantitative profile. Batch experiments were conducted using a multi-metals solution, prepared from sulphate salts of the following elements: Zn(II), Cd(II), Cu(II), Al(III), Ca(II), Mg(II) and Na(I), simulating the average composition of the effluent collected during summer time. The composition of the synthetic effluent is described in Table 1 (summer time). The other experiments were conducted with a natural effluent collected during winter time (Table 2).

Table 1- Average composition of the synthetic effluent - summer time

Metals	Concentration (mg/L)
Zinc	385 ± 34
Cadmium	18 ± 4
Copper	10.1 ± 0.6
Aluminium	1.2 ± 0.3
Calcium	467 ± 27
Magnesium	90 ± 11
Sodium	26 ± 1

Table 2 - Average composition of the natural effluent*

Metals	Concentration (mg/L)
Zinc	88.0
Cadmium	1.4
Manganese	11.7
Copper	0.35
Calcium	444.0
Magnesium	100.0
Sodium	37.0

* Samples collected and preserved for analysis according to APHA, *Standard Methods for the Examination of Water and Wastewater*, L.S. Clesceri, A. E. Greenberg and R.R. Trussel (eds.), 17th edition, 1989.

2.3 Batch Experiments with Synthetic Effluent - Summer Time

In this series of tests, the biosorption of every single metals (zinc, cadmium, copper, aluminium, calcium, magnesium and sodium) was evaluated individually in the concentrations described in Table 1. The tests were conducted in 250 mL Erlenmeyer flasks, containing 50 mL of each metal solution and 0.1 g of the dry and pulverized biomass (2.0 g/L). The flasks were incubated in a rotary shaker with internal temperature

adjusted to 30° C, and left overnight, to ensure equilibrium between solid and liquid phases. After that, the content of the flasks was filtered, in a vacuum filtration device using a Millipore membrane with 0.45 μm pore diameter. The filtrate was then acidified for analyzing residual metals concentration by atomic absorption spectrometry (Espectrometer Varian-Techtron, Model AA6).

In a second set of experiments, biosorption was studied in solutions presenting higher ionic complexity, i.e., solutions containing all the heavy metals and solutions containing heavy metals plus alkaline and alkaline-earth elements. The concentrations of these elements are listed in Table 1.

Considering zinc as the main contaminating agent in solution, some tests were conducted in order to check the effect of alkaline and alkaline-earth elements on zinc uptake by the biomass. For this purpose, a solution containing ionic zinc, sodium, magnesium and calcium, individually added, was investigated, as well as in combination.

In order to compare the performance of the biomass, an experiment was conducted with commercial activated carbon, added to the metals solution in the same concentration and experimental conditions used for *Sargassum sp.*. The average metals concentrations used were those described in Table 1. All these experiments were carried out in triplicate.

2.4 Kinetic Batch Studies with Natural Effluent - Winter Time

The metals uptake kinetics was evaluated in experiments performed in Erlenmeyer flasks. The biomass was added in the concentration of 2.0 g/L, in a 100 mL of the effluent. The flasks were incubated in a rotary shaker, at 30° C, for 5 hours. Samples were taken for the determination of residual metal concentration. The experiments were carried out in triplicate.

2.5 Continuous Metals Biosorption from the Natural Effluent - Winter Time

The continuous run was conducted in a laboratory acrylic column, 1 meter high, containing samplers, located at three different points of the system (10.0, 40.0 and 70.0 cm from the bottom, samplers 1, 2 and 3, respectively) and filled with the dry biomass. The system was operated with the help of a peristaltic Masterflex® pump, being the effluent pumped at a flow rate of 25 mL/min. The continuous system operated for more than 70 hours with periodical sampling to evaluate the efficiency of the treatment. The outlet samples were vacuum filtered through a Millipore® membrane with 0.45 μm of pore diameter. The filtrate was acidified to check the outlet concentrations of the different metals through atomic absorption spectrometry (Espectrometer Varian-Techtron, Model AA6).

3. RESULTS AND DISCUSSION

3.1 Batch Experiments with Synthetic Effluent - Summer Time

The uptake of zinc, cadmium, copper and aluminium by the biomass of *Sargassum sp.* was initially evaluated, in batch condition, for three distinct situations: (i) from solutions containing individually the heavy metals; (ii) from a solution containing simultaneously the four heavy metals and, (iii) from a solution simulating the effluent described in Table 1. Figure 1 displays the results obtained for the three sets of experiments.

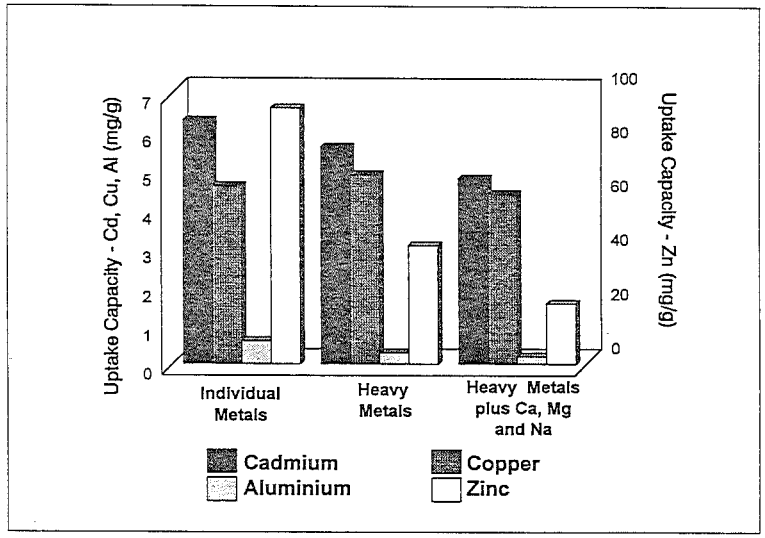

Figure 1 - Metals biosorption by *Sargassum sp.* - Individual metals uptake and multi-ion situation

It can be observed that the individual heavy metals uptake was markedly influenced by the presence of other elements in solution, a fact that can be characterized by the decrease in the uptake capacities observed as the complexity of the solutions increase.

For the solutions containing only heavy metals, this decrease is probably associated to the competition of different heavy metals for the binding sites in the biomass, and, for the solution containing all the elements (including alkaline and alkaline-earth elements) this decrease is even more pronounced due to the greater complexity of the solution rather than to competition, as the alkaline and alkaline-earth elements were not recovered by the biomass, as observed for the heavy metals (Figure 2).

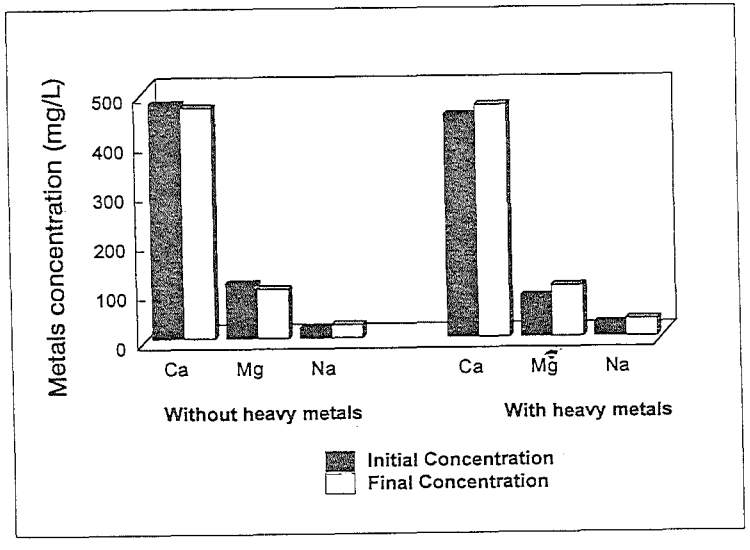

Figure 2 - Alkaline and alkaline-earth elements biosorption by *Sargassum sp.*

Specifically for copper biosorption the same behaviour was not observed, as for the three different sorts of solutions. The recovery levels were equivalent, indicating that the presence of other elements in solution does not stimulate the competition of the metals for the adsorption binding sites. This fact can be attributed to the presence of a selective binding site for copper or to a distinct mechanism for the recovery of this metal.

Seaweeds from the genus *Sargassum* (and brown seaweeds, in general) have a very complex chemical structure. Alginic acid is the main structural polysaccharide of the brown seaweeds, being usually present as alginate salts, mainly sodium, magnesium, potassium and calcium alginates.

As shown in Figure 2, calcium, magnesium and sodium presented a negligible uptake by the biomass, in comparison to heavy metal elements. Probably, these elements were not adsorbed by the biomass due to their presence in the constitutive structural polysaccharides of the *Sargassum* seaweed, as alginate salts. This way, these elements are already stabilized in the surface structure of these algae, not favouring ion-exchange with these elements present in solution [11]. However, in presence of heavy metals, it could be observed that the final concentration of these elements in solution is slightly higher, due to ion-exchange reactions between structural elements and the heavy metals in solution, recovered by the biomass, responsible for the displacement of calcium, magnesium and sodium from the algae to the solution. Attempts to reinforce this hypothesis could be based in the ion-exchange properties of alginic acid, previously described by other authors [4,6,7].

The results obtained in the present work give an indication that calcium, magnesium and sodium do not compete with the heavy metals for the binding sites from the biomass however, they affect the biological heavy metals uptake capacity, by altering the ionic equilibria of the different solutions.

To evaluate the extent to which calcium, magnesium and sodium influence the uptake of heavy metals, different solutions containing alkaline and alkaline-earth elements were evaluated against the biosorption of zinc, the main contaminating metal in the effluent (Figure 3).

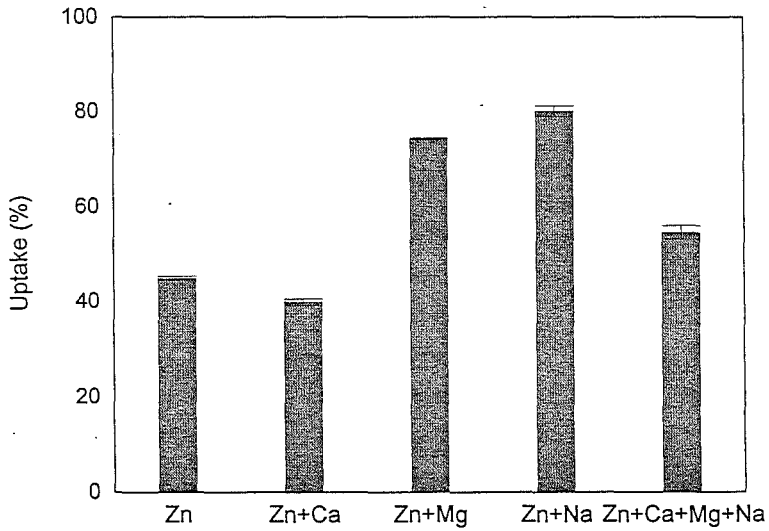

Figure 3 - Effect of alkaline and alkaline-earth elements on zinc biosorption by *Sargassum sp.*

From Figure 3 it can be extracted that calcium imposes a negative effect on zinc uptake, while magnesium and sodium impose a positive effect on it. This different behaviour is probably related to the ionic equilibria of the different solutions, because, as previously observed, these elements do not compete effectively with the heavy metals for the binding sites in the biomass. The combined effect of alkaline and alkaline-earth elements on zinc uptake, reinforces the previous observations, showing, once more, the positive effect of magnesium and sodium and the antagonic effect of calcium on zinc uptake.

The presence of divalent ions may alter the biosorption of heavy metals by algal biomass, specially if these ions are alkaline or alkaline-earth elements. According to Kuyucak & Volesky [9] the presence of potassium ion improved cobalt biosorption by *A. nodosum*. Analogously, in the present work, the presence of sodium and magnesium contributed to the increase in the uptake capacity for zinc by *Sargassum sp.* Thus, the presence of some alkaline or alkaline-earth elements may influence the biosorption of specific heavy metals.

From Figure 4 it could be observed that the biomass, compared to a commercial activated carbon, presented a superior performance, in the same experimental conditions, and based on the metals concentrations listed in Table 1.

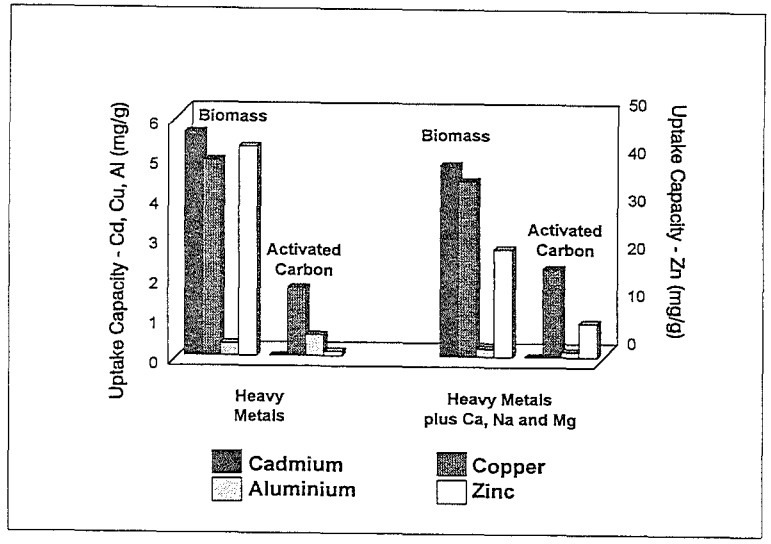

Figure 4 - Comparison between the biomass of *Sargassum sp.* and commercial activated carbon for the biosorption of heavy metals.

These results emphasize the potential use of *Sargassum sp.* biomass as a biological resin for the biosorption of heavy metals, although a series of other parameters should be still evaluated to compare with conventional adsorbers regarding technical and economic levels.

3.2 Kinetic Batch Studies with Natural Effluent - Winter Time

Figure 5 shows the kinetics of copper, cadmium and zinc biosorption. In general, it can be observed that equilibrium between the solid phase (biomass) and liquid phase (effluent) was rapidly established for the three metals simultaneously.

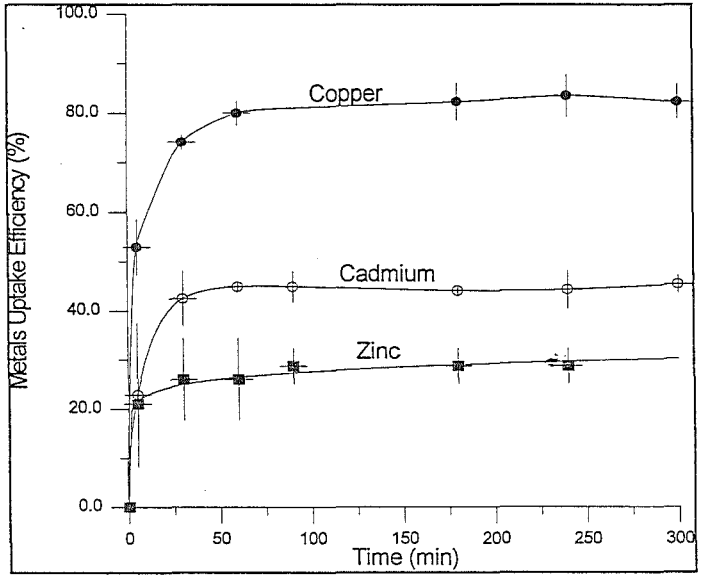

Figure 5 - Kinetic behaviour of copper, cadmium and zinc during biosorption by *Sargassum sp.*

For cadmium and zinc the equilibrium was established around 25 minutes of contact between the biomass and the effluent, while for copper it was around 50 minutes. It also can be extracted from Figure 5 that zinc, cadmium and copper uptake efficiencies were around 30, 42 and 80%, respectively, in the solid/liquid ratio used. It must be emphasized that the above results were obtained for a natural effluent, containing high levels of alkaline and alkaline-earth ions, that previously showed their competitive effect on the uptake of heavy metals by *Sargassum sp.*.

Figure 6 indicates a similar behaviour during biosorption of manganese, being this equilibrium reached in a very short period of time; one can consider manganese uptake as an instantaneous process, at least in the considered process conditions.However, its uptake efficiency was considerably lower, much lower than the ones previously described for the other heavy metals. Although different uptake efficiencies were observed, the uptake process could not be considered as a selective uptake process, because the metals concentrations in solution are considerably different; an approach to evaluate any kind of selectivity could only be envisaged if the elements were present at equimolecular ratio [3].

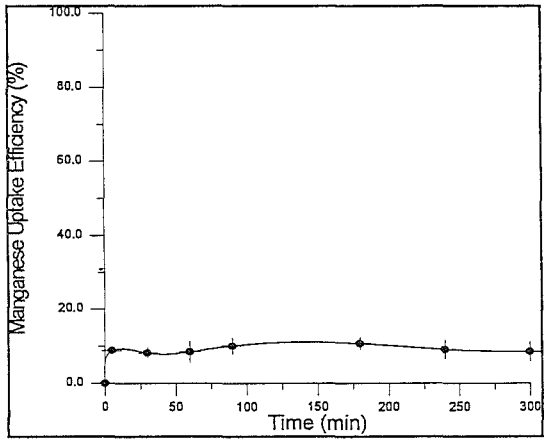

Figure 6 - Kinetic behaviour of manganese during biosorption by *Sargassum sp.*

A similar kinetic behaviour was also observed for calcium, magnesium and sodium, if one only considers the aspect concerning the solid/liquid equilibrium (Figures 7, 8 and 9).

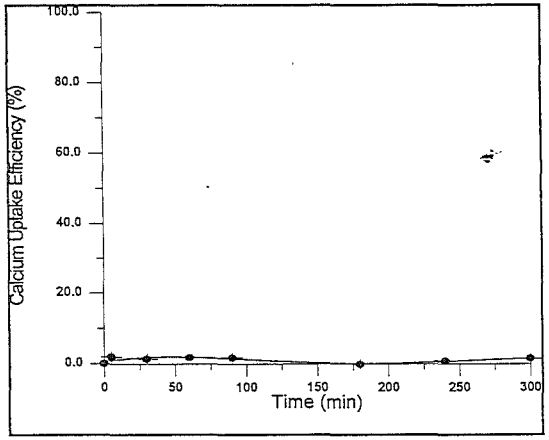

Figure 7 - Kinetic behaviour of calcium during biosorption by *Sargassum sp.*

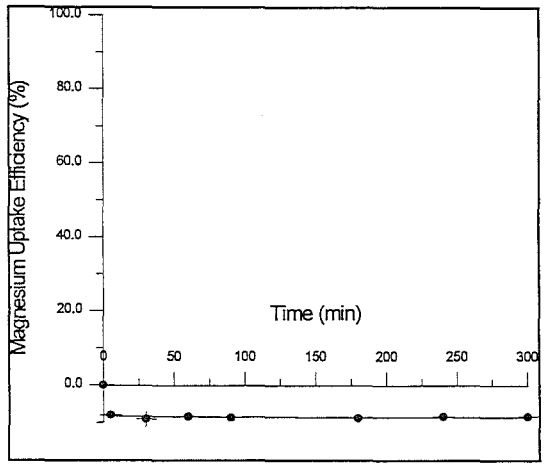

Figure 8 - Kinetic behaviour of magnesium during biosorption by *Sargassum sp.*

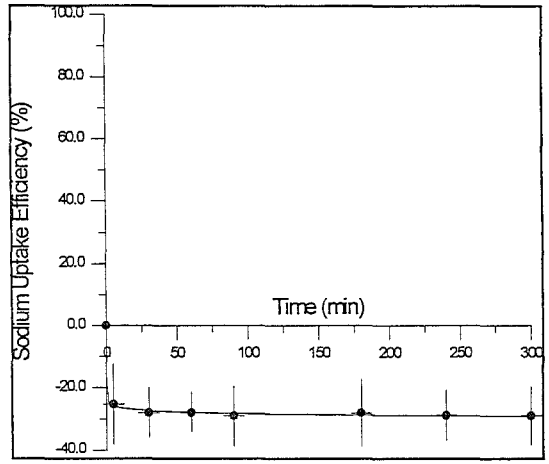

Figure 9 - Kinetic behaviour of sodium during biosorption by *Sargassum sp.*

Nevertheless, calcium was not recovered by the biomass, being constant its outlet concentration against time, in the presence of the biomass. Magnesium and sodium ions were released from the biomass, thus indicating a **negative uptake efficiency**. That means, the results presented indicated that their final concentrations in solution were higher than their initial ones, showing that some sodium and magnesium ions were displaced from the biomass into solution, probably by ion-exchange mechanisms associated to the presence of heavy metals.

These results can be explained based on the chemical composition of the brown algae. The main structural polysaccharides from these algae, as previously mentioned, are the alginates, a dimer of mannuronic and guluronic acids, usually found in these biological materials as calcium, magnesium and sodium alginates, depending on the environmental conditions that stimulate their biosynthesis. These polysaccharides are arranged as parallel chains, stabilized through cross-linked elements, such as alkaline and alkaline-earth metals, through reaction with carboxyl groups. The result of such reactions is a strong polysaccharide network that supplies mechanical strength to the algal surface.

Based on these assumptions, these elements were not recovered by the biomass, as previously demonstrated from the batch experiments, being ion-exchange reactions made possible only with other divalent ions, such as the heavy metals present in solution. This way, an effective ion-exchange between structural ions and metals in solution promoted the negative efficiency values observed, due to a partial displacement of calcium, sodium and magnesium, for the location of heavy metals in the algal structure.

3.3 Continuous Metals Biosorption from the Natural Effluent - Winter Time

Figure 10 shows the results of cadmium biosorption obtained during the continuous operation of the laboratory system.

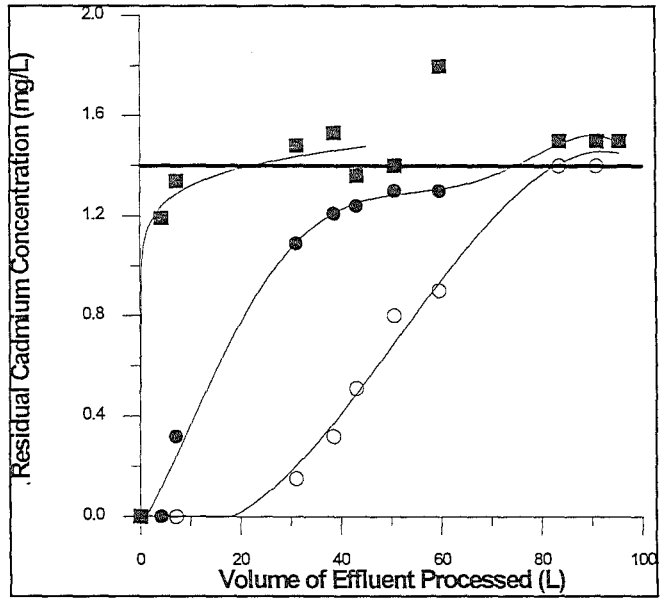

Figure 10 - Cadmium biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

By considering the different samplers of the column, it is observed that after pumping 20 L of solution, the outlet cadmium concentration measured from sampler 1 indicated that, up to this point, the column is no longer able to treat the effluent (saturation). The outlet cadmium concentration measured from sampler 2, indicated that, after pumping 75 L of solution, the column was saturated. The system, as a whole, saturated after treatment of 82 L of effluent. That means the reactional sites from the biomass were no longer able to accumulate cadmium,

indicating saturation of the system by this metal. From the breakthrough curve observed for sampler 3 it is possible to estimate, mathematically, the expression that dictates the behaviour of the experimental points up to the saturation of the system. The mathematical integration of this equation, in the limits from zero to the saturation point can give an estimation of the amount of metals **not recovered** by the biomass (*y* axis indicates residual concentration, that means, outlet solution); by subtracting from the total mass of metal fed to the column it is possible, by difference, to determine the amount of cadmium recovered by *Sargassum sp.* This equation was computer obtained (Grapher, Golden Software Inc., Version 1.09) and adjusted to fit the experimental points being as follows for cadmium (Equation 1):

$$y = \int_0^{82} (-5.33e-6x^3 + 8.19e-4x^2 - 1.47e-2x + 0.03)dx \quad [1]$$

An analogous behaviour was observed during zinc biosorption (Figure 11).

The saturation levels were earlier obtained in comparison to cadmium, indicating that the mechanism involved can be different for distinct metals, or, more reasonably, these differences can be associated to the ionic equilibrium of multi-metals solution, where different ionic species are present at considerably distinct concentrations.

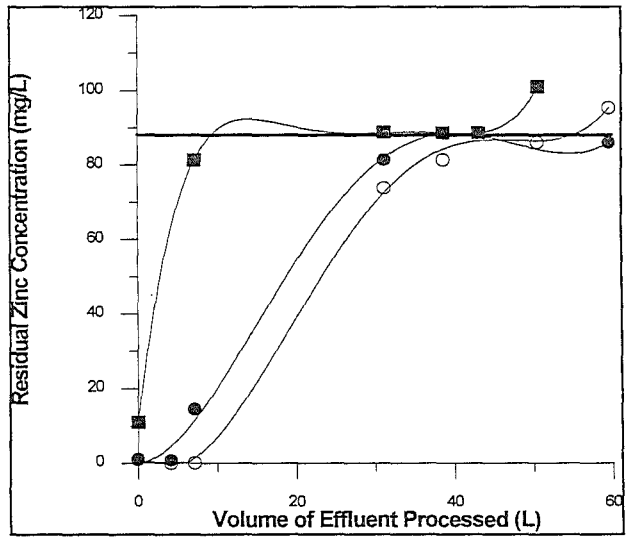

Figure 11 - Zinc biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

The mathematical expression during zinc uptake by the seaweed, similarly as obtained for cadmium, is as follows (Equation 2):

$$y = \int_0^{45} (3.48e-7x^5 + 1.67e-5x^4 - 6.38e-3x^3 + 0.304x^2 - 1.84x + 1.30)dx \quad [2]$$

The less effectively biosorbed metal was manganese (Figure 12).

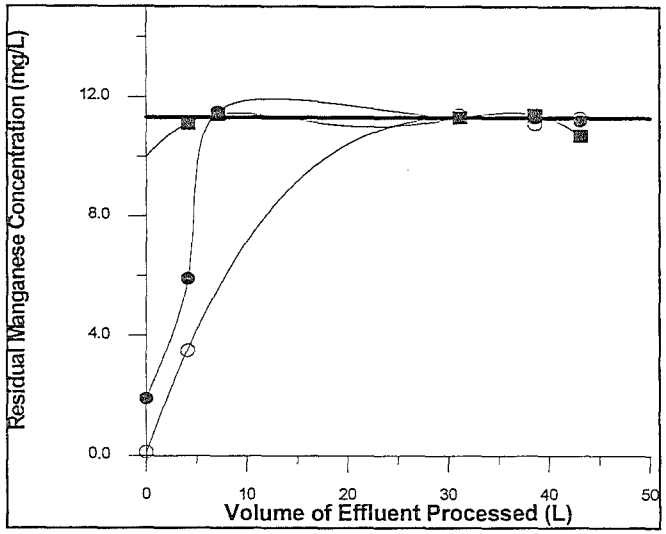

Figure 12 - Manganese biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

Specially if one considers that its concentration in solution is not so high, this fact being an indication that the mechanism involved in the uptake of this metal may be different from the ones involved in the biosorption of cadmium and zinc.

The experimental data, for manganese, are fitted to the following equation, considering the system as a whole (Equation 3):

$$y = \int_0^{32} (2.35e-4x^3 - 2.60e-2x^2 + 0.94x + 0.08)dx \qquad [3]$$

Another point to be mentioned is that it was not detected any copper in the solution collected from the samplers. Previous experiments indicated a very high efficiency in the recovery of this metal by the biomass of *Sargassum sp.*, being its uptake probably mediated by nucleation of the metal, due to the very high efficiency observed [3].

The next results (Figure 13) show the behaviour of alkaline and alkaline-earth elements during the biosorption process.

As previously observed from batch experiments, these elements were not recovered by the biomass, and, at the beginning of the operation some peaks were observed, probably associated to ion-exchange reactions with heavy metal elements, generating outlet solutions at concentrations higher than the initial concentrations (alkaline and alkaline-earth elements present in solution plus elements displaced from the structure of the biomass). These higher values were not constant through the experiment, giving an indication that ion-exchange reactions should be one of the mechanisms involved, serving only as the initial steps of heavy metals uptake. Other mechanisms involving inter-element interactions (not predictable in simple adsorption) should also be an acting process in the uptake.

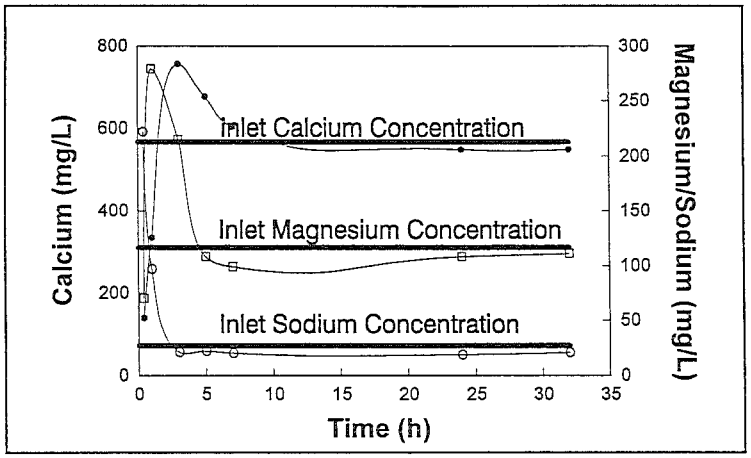

Figure 13 - Calcium, magnesium and sodium biosorption during continuous operation of the laboratory system

Table 3 summarizes the results obtained from the integration of the three mathematical expressions derived from the profiles of heavy metals biosorption, in the limits described.

Table 3 - Recovery of metals during biosorption in the continuous system

Metal	Total Mass (Inlet)* (mg)	Total Mass Recovered (mg)/ Efficiency (%)
Cadmium*	115	72 / 62
Manganese*	374	113 / 30
Zinc*	3960	1973 / 50
Calcium**	36408	0 / 0
Magnesium**	8200	0 / 0
Sodium**	3034	0 / 0

* Considering the saturation limits from the mathematical expressions.
**Considering extended cadmium saturation (82 L of effluent).

The results show that the efficiency obtained from the biosorption process seems to be compatible with the operation of the continuous system as designed, being the presence of high concentrations of alkaline and alkaline-earth elements the limiting step of the biosorption hovewer. Other tests, conducted in the absence of alkaline and alkaline-earth elements in solution, presented much higher efficiency values [3]. If one considers that the total mass of metals recovered can be eluted with 0.1 L of acid solution, it would be obtained a solution with a concentration of 0.72 g/L cadmium, 19.73 g/L zinc and 1.13 g/L manganese, corresponding to concentration factors of 514, 224 and 96 for cadmium, zinc and manganese, respectively.

4. CONCLUSIONS

Batch experiments indicated no absorption of calcium magnesium and sodium by the biomass of *Sargassum sp.;* these elements, on the other hand, usually influence the uptake of heavy metals, by changing substantially the ionic equilibria of the solution. The process, in the conditions established, presented an uptake efficiency higher than a commercial activated carbon, for the uptake of heavy metals present in the industrial simulated solution. If zinc (the main contaminating agent of the effluent), is to be treated, the addition of calcium, magnesium and sodium, presented distinct behaviour, sometimes improving, sometimes preventing the uptake of the metal, depending on the combination they were present in solution. Regarding solid/liquid equilibrium, in the natural effluent, it was rapidly reached in a period of less than one hour of contact. The continuous system presented a compatible treatment efficiency, with a high operational stability, sometimes rendering viable the recycling of the recovered metals.

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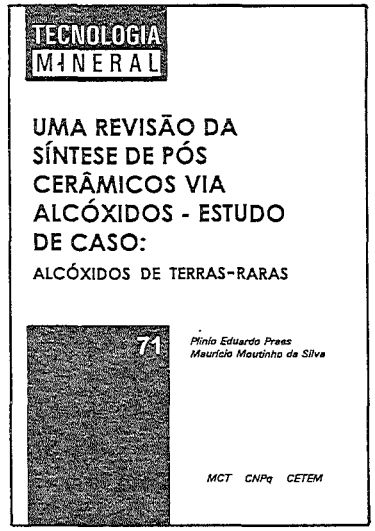

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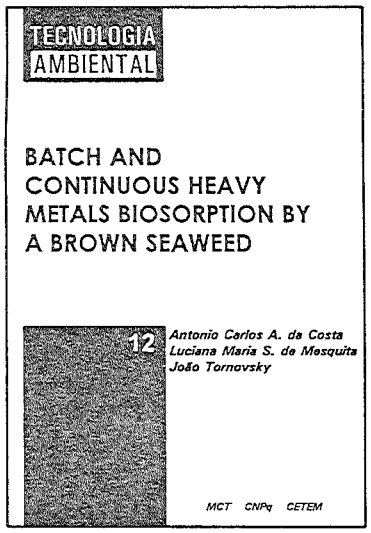

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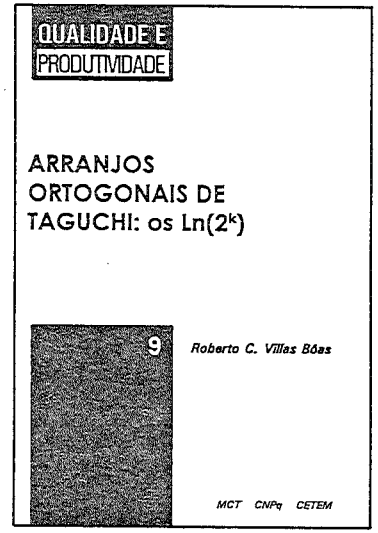

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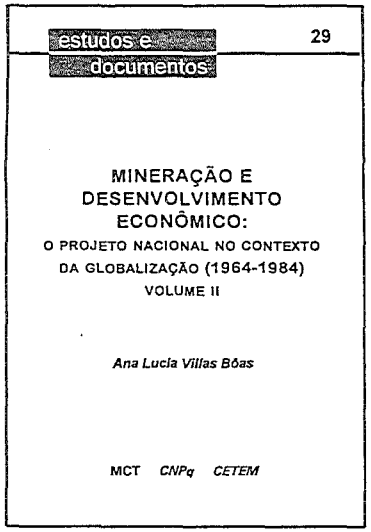

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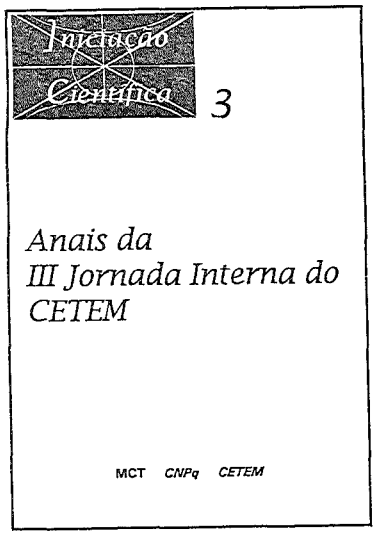

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