AN EMERGING BIOTECHNOLOGY FOR METAL CONTAINING WASTE WATER TREATMENT

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A **Série Tecnologia Ambiental** divulga trabalhos relacionados ao setor mínero-metalúrgico, nas áreas de tratamento e recuperação ambiental, que tenham sido desenvolvidos, ao menos em parte, no CETEM.

Celso de O. Santos COORDENAÇÃO EDITORIAL
Vera Lúcia Ribeiro DIAGRAMAÇÃO

PRESENTATION

This monography presents the results obtained by M.Sc. Antonio Carlos da Costa while participating in the bilateral programme between Brazil and Germany on heavy metals in the environment.

The idea that originated this report is based upon a comparison between two technologies: solvent-extraction and biosorption, which is the best suited for a given legislation framework?

Thus, we at CETEM pursued the biosorption route for cleaning heavy metals from solutions and KFA, the German counterpart, followed the S-X route, for a more stringed final heavy metals content.

Throughout the development work, however, it was found out that the two technologies are not alternatives per se, but rather, they complement each other, biosorption being used as a pre-cleaning stage and solvent-extraction for the ultimate stage, if thus required by the particular country legislation.

This article will be enjoyed by the "clean technologist"!

Rio de Janeiro, May, 1997.

Roberto C. Villas Bôas
Director

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ABSTRACT

The main purpose of this publication is to describe some technical goals obtained during the conduction of a part of the project ENV 36. This project is included in the Science an Technology Cooperation Germany/Brazil, and started in March were KFA/IPC (Forschungszentrum Jülich GmbH, Institute für Angewandte Physikalische Chemie), and CETEM (Centro de Tecnologia Mineral). Regarding the biosorption process, here described, well defined steps including the selection of a suitable biomass to be used as metals biosorbent, conduction of continuous scale experiments with synthetic and real effluents, studies about the most suitable conditions for metals desorption and also the scale-up and economic evaluation of a continuous unit for the treatment of heavy metals contaminated solutions were done.

Key-words: *heavy metals, biomasses, technology*

RESUMO

O principal objetivo da presente publicação é descrever os principais resultados obtidos durante a condução do projeto ENV 36. Este projeto está inserico no Programa de Cooperação em Ciência e Tecnologia Brasil/Alemanha, com início em março de 1994. As instituições envolvidas na condução do projeto foram o KFA/IPC (Forschungszentrum Jülich GmbH, Institute für Angewandte Physikalische Chemie) e o CETEM (Centro de Tecnologia Mineral). Com relação à biosorção, aqui descrita, etapas bem definidas foram conduzidas, incluindo-se a seleção da biomassa mais adequada ao processo para emprego como material acumulador de metais, condução de experimentos em regime contínuo com efluentes sintéticos e efluentes reais, estudos sobre as condições ideais de dessorção dos metais, bem como escalonamento e avaliação econômica de uma unidade contínua de tratamento.

Palavras-Chave: *metais pesados, biomassa, tecnologia*

1. INTRODUCTION

Restrictive environmental legislations, ecological problems due to the dispersion of heavy metals in natural environments, and the high cost of technologies for treatment of effluents containing heavy metals have stimulated the development of technologies to compete with or complement conventional techniques. Among the technologies under development, much is being written about techniques involving the use of microorganisms (bacteria, fungi and microalgae), and, above all, inactivated seaweeds (Volesky, 1994; Ting *et al.*, 1995; da Costa & de França, 1996). Several examples have proved the potential employment of microorganisms to accumulate heavy metals; the results, however, are still a bit far from a technological reality that could render the use of microorganisms technically and economically viable as biological metal sorbents. Nevertheless, employing other materials of biological origin such as plants and seaweeds allows us to apply the knowledge available from conventional processes to the development of a technology for the treatment of solutions contaminated by heavy metals.

The competitiveness of a new technology for heavy metals recovery depends upon a series of factors related to the characteristics of the biomass as well as those of the operational system. One such viable system would employ fixed-bed reactors such as conventional processes that use ion-exchange resins or activated carbon. This type of system permits treating great volumes of solution, although limited by the loading of the biomass by heavy metals. At this stage, desorption of the metals is necessary to be able to reuse the biomass in order to employ it in the largest number of sorption/desorption cycles. Other parameters, such as operational stability of the system, adequate flow-rate, and residence time compatible with the process, must be considered as well. As regards the biomass, bed of the reactor, it should have high mechanical strength and metal uptake capacity and be available in large quantities at low cost.

Research in this field of biohydrometallurgy has been seeking to develop technologies employing biomasses with those characteristics to make viable the large-scale use of heavy metal biosorption.

Marine algae have been used as biological indicators of heavy metal pollution in contaminated areas, and such property is the basis of biotechnologies developed for residual metal ion recovery (Haug *et al.*, 1974; Melhuus *et al.*, 1978). Some studies describe the use of these organisms as passive heavy metal adsorbers, substituting for conventional resins (Kuyucak & Volesky, 1988, 1989, 1990). However, the mechanism associated with this biosorptive uptake is not completely understood. If one considers that dead algae are not biologically active, their metal uptake can be regarded as a passive adsorption process and, thus, be correlated with mathematical sorption models, such as the Langmuir and Freundlich equations.

Toxic metals are usually present at high concentrations in several kinds of effluents, especially those from metallurgical activities. In view of their high toxicity, it is of interest to develop a recovery process which may prevent their discharge into water streams.

The intensification of industrial activities during the last few years, is 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 diffusion processes, as well as by simple adsorption

phenomena onto cellular structural components (da Costa *et al.*, 1994; Crist *et al.*, 1988; Macaskie *et al.*, 1987; Volesky *et al.*, 1993). Diffusion 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 negatively charged groups present in the structural polysaccharides and surface proteins of the different biological organisms.

The remarkable ability of biomasses to concentrate heavy metals, acting as a biological resins, is becoming an useful tool for treating industrial solutions contaminated with heavy metals (Awadalla & Pesic, 1992; Jeffers *et al.*, 1991). 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 uptake of metals by biomasses (inactivated or not) is already used for the treatment of heavy metal containing effluents. Gale (1986) reports the use of microalgae as an example of environmental protection, mentioning the *Missouri's New Lead Belt*, where, in closed reservoirs for the cultivation of microbial species, the heavy metal lead is recovered from contaminated solutions.

The *Bureau of Mines - United States Department of the Interior,* developed a kind of bead, constituted of a certain type of biomass dispersed in polysulfone matrix, with a high mechanical strength and also a high uptake capacity, named BIOFIX (Biomass Foam Immobilized Extractant). The relevant parameters for the use of these beads in industrial processes were already investigated, and BIOFIX is used in the secondary treatment of heavy metals loaded effluents (Jeffers *et al.*, 1991).

The *Advanced Minerals Technologies* developed the AMT-BIOCLAIM™, for the recovery of cadmium and other heavy

metal elements. This is a granulated product with a high adsorption capacity, ranging from 86 mg metal/g granules for silver, to 601 mg/g for lead.

It is not known what kind of agent is responsible for the uptake, being described as *biomasses discharged during fermentation processes* (Awadalla & Pesic, 1992).

Analogously, Environmental Protection Agency developed AlgaSORB®, a natural algal-based product with a high uptake capacity.

It must be emphasized that the described experimental results should not be faced as definite and absolute values, being obtained for a specific effluent, and for specific working conditions. The interaction between anionic surfaces and metallic ions is also driven by physico-chemical parameters, highly variable for different solutions and highly dependent on the nature of the effluent.

For the effective implementation of a biosorption technology for the accumulation of heavy metals, a series of conditions should be considered:

(i) the biomass should accumulate around 100 mg metal/g biomass; *(ii)* biosorption and desorption should be rapid and efficient; *(iii)* the biological material must be cheap and reusable; and, *(iv)* the biological material should be adaptable to different reactors.

Fundamentally two main groups of metals are studied: metals of economical interest and metals of a toxic nature (Kuyucak & Volesky, 1989b; da Costa *et al.*, 1994; Tsezos & Volesky, 1981).

The wide diversity of biological materials, with distinct structural compositions, stimulates the search for new materials to be used as metals biosorbers, and, in this context, algal biomasses are being widely employed for such a kind of process.

Green, red and brown seaweeds are the most widely investigated; due to their variability and complexity of structural polysaccharides they possess carboxilated, sulphated and phosphate-rich compounds, that means, all possess potential binding sites for the accumulation of heavy metals.

One of the purposes of this cooperative research was to study the behavior of specific biomasses as biological resins for the accumulation of heavy metals. The main results obtained in preliminary investigations using Brazilian seaweeds, 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. Several other experiments are also described in this report by using synthetic metals solutions both in batch and continuous systems.

1.1 A Brief Overview about Langmuir and Freundlich Adsorption Models

Solid-liquid equilibrium can be easily described by adsorption isotherms. The Langmuir and Freundlich Equations are the mathematical functions most commonly used to describe this process. The Langmuir isotherm can be expressed as:

$$q = kdc/(1+kc)$$

By plotting **q** *versus* **c**, a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering. The Langmuir equation can also be described by taking the reciprocal value of its terms. Thus:

$$1/q = (1/kd)(1/c) + (1/d)$$

From this form, by plotting **1/q** *versus* **1/c**, a straight line is obtained. Parameters **k** and **d** can be calculated from the angular and linear coefficients, respectively. The Langmuir

isotherm assumes that the adsorption free energy is independent of both the surface coverage and the formation of a monolayer when the solid surface reaches saturation.

By analogy, a similar treatment can be applied to the Freundlich equation. Its general form can be expressed as:

$$q = Kc^{1/n}$$

Constants **K** and **n** are characteristic of this model and are dependent on different assumptions. This equation can also be linearized by plotting the logarithm of its terms, as follows:

$$\log q = (1/n)\log c + \log K$$

By plotting **log q** *versus* **log c**, a straight line is obtained. Therefore, parameters **n** and **K** can be predicted from the angular and linear coefficients. The Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, the surface covering being mathematically unlimited.

In this work, some experimental results obtained in laboratory were expressed by adsorption isotherms, which were linearized by simple linear regression to predict the respective constants for each model. The fitting of the models to the data was evaluated taking into account the range of cadmium concentrations tested.

Notation:

c Equilibrium concentration of solute (mg/L)

d Constant that represents monolayer covering per unit weight of adsorbent (mg adsorbate/g adsorbent)

k Equilibrium constant (L adsorbent/mg of adsorbate)

K Constant related to the strength of the adsorptive bond

n Constant related to bond distribution

q Weight of adsorbate/weight of adsorbent (mg/g)

1.2 Immobilization Techniques and Cross-linking Reactions

Several studies are being conducted to improve the stability and mechanical properties of biopolimeric materials from algae, bacteria and several other kinds of biomasses. According to Karel *et al* (1985), immobilization can be defined as the physical confinement of the intact biomass in a certain region of the space, being preserved the important characteristics and activity of the biomass.

There are several immobilization techniques and the specific use of one or another will depend on the purpose of the immobilization and the purpose of the process to be conducted. An interesting approach of these immobilization methods has been mentioned by Karel *et al.* (1985), including several immobilization mechanisms, mainly divided in four groups based on the type of physical action that promotes the immobilization of the material.

In the case of seaweeds, a widely used method for immobilization is self-aggregation. This consists of a modification in the constitutive molecules of the biopolymers, with the main purpose of changing their physical-chemical characteristics. The idea is to promote cross-linking reactions in the structure of the biomass through the action of a proper chemical agent. The formation of cell aggregates, artificially induced through cross-linking treatment, are based, mainly on the surface constituents of the biomass.

According to Tager (1978), cross-linkings can be defined as chemical reactions forming links between macromolecules, resulting in the formation of polymers with reticulate tridimensional structure. Thus, the resulting molecules are of a stronger mechanical resistance making it insoluble some polymers.

Several cross-linking agents were reported by Volesky (1995), and the classification of these agents is mainly based on the products formed. Studies were conducted by Leusch (1995) using brown seaweeds *Ascophyllum nodosum* and *Sargassum*

fluitans previously treated with glutaraldehyde and formaldehyde. In that study the purpose was to treat different metal solutions, containing lead, copper, cadmium, nickel and zinc. The results proved to be effective in the treatment of the metal solutions, using different chemical cross-linking reagents, and the best ones used were glutaraldehyde, formaldehyde and imine polyethylene. These reagents can improve the hardness of the biomass, but they can also inhibit the metal uptake capacity if binding sites are involved in the cross-linking reactions.

Good results were obtained during lead biosorption (370 mg lead/g dry biomass) with the seaweeds *A. nodosum* and *F. vesiculosus* treated by different cross-linking agents (Holan *et al.*, 1993). In this study improved chemical and mechanical stabilities were obtained, not followed, however, by an increase in the uptake capacity.

2. PURPOSE OF THE REPORT

The main purpose of the present report is to present the technical results obtained during the conduction of the project ENV 36. This project is included in the Science and Technology Cooperation Germany/Brazil, and started in March 1994. The partners involved in the development of the research were KFA/IPC (Forschungszentrum Jülich GmbH, Institute für Angewandte Physikalische Chemie), and CETEM (Centro de Tecnologia Mineral).

The target objective of this applied research was the separation of heavy metals from aqueous phases by liquid/liquid extraction (from the German partner) and/or biosorption (from the Brazilian partner). The time-course of the project included the comparison of both methods as regards the efficiency and environmental impact, for the decontamination of industrial wastewaters and aqueous effluents from landfills and sites.

As regards these objectives the obtained results will be presented and discussed in this final project report.

3. MATERIALS AND METHODS

3.1 Cadmium Solutions

A set of experiments has been done solely with the use of ionic cadmium solutions. Cadmium solutions were made with analytical grade $3CdSO_4.8H_2O$. Concentrations of the metal in solution were determined by atomic absorption spectrometry (Varian Techtron Spectrometer, Model AA6).

3.2 Seaweeds

Six different genera of seaweeds collected from the Brazilian Coast and making up a total of 15 algal samples were tested for their cadmium uptake capacities. Samples code, classification and site of collection are listed in Table 1.

3.3 Processing of Seaweeds Samples

The algal samples, listed in Table 1, were extensively washed with distilled water, to remove particulate material from their surface, and oven-dried at 70 °C. Dried biomasses were ground in a mortar with a pestle and then sorted by particle size through a series of Tyler sieves. Fraction [0.503-0.711mm] was selected for use in the experiments.

Table 1 - Marine Algal Samples - Genera, Sites of Collection and Classification (Joly, 1970)

Genus	Site of collection	Sample code	Classification [2]
Sargassum [1]	Sepetiba Bay	BS$_1$	D = Phaeophyta
	Sepetiba Bay	BS$_2$	C = Cyclosporeae
	Sepetiba Bay	BS$_3$	O = Fucales
	Grande Island	IGr	F = Sargassaceae
Padina [1]	Sepetiba Bay	BS$_1$	D = Phaeophyta
	Sepetiba Bay	BS$_2$	C = Isogeneratae
	Gato Island	IG	O = Dictyotales
			F = Dictyotaceae
Ulva	Sepetiba Bay	BS	D = Chlorophyta
	Guanabara Bay	BG	O = Ulvales
	Vermelha Beach	PV	F = Ulvaceae
Gelidium	Itaipu Beach	IP	D = Rhodophyta
	Itacoatiara Beach	IT	C = Rhodophyceae
			O = Gelidiales
			F = Gelidiaceae
Codium	Vermelha Beach	PV	D = Chlorophyta
	Itacoatiara	IT	O = Siphonales
			F = Codiaceae
Colpomenia	Itaipu Beach	IP	D = Phaeophyta
			C = Heterogeneratae
			O = Chordariales
			F = Punctariaceae

(1) Samples from the same genus and site were collected during different seasons of the year

(2) D = Division, C = Class, O = Order, F = Family.

3.4 Cadmium Biosorption Experiments

The 15 samples collected were tested for their capacity to sequester cadmium by evaluation of their adsorption isotherms. A series of cadmium solutions was prepared by dissolving cadmium salts in deionized distilled water, with concentrations ranging from 10.0 to 350.0 mg Cd^{+2}/L. The contact experiments were performed in 250-ml Erlenmeyer flasks (2.0 g L of biomass, 50 mL of cadmium-bearing solution of known initial

concentration, 30 ± 0.5 °C, 8 hours) on a rotary shaker (Ética, Model 500). After incubation, the eluent solution was separated from the biomass by filtration through an in-line Millipore membrane filter (0.47 μm pore diameter). Final cadmium concentrations were determined by atomic absorption spectrometry. The results presented correspond to the average values obtained.

3.5 Release of Elements during Cadmium Biosorption

Release of alkaline-earth elements during cadmium biosorption may indicate the involvement of an ion-exchange mechanism in the recovery of this metal from contaminated solutions. Using adsorption isotherms, the *mg cadmium adsorbed/g dry biomass* ratio can be estimated for each solid-liquid equilibrium, and this ratio can then be associated with the release of alkaline-earth elements from the polysaccharide structure of some algal genera. These elements can act as linkers within the polysaccharide structure, connecting monomeric units or cross-linking adjacent complex molecules. One sample from each algal genus was used in this set of experiments. The alkaline-earth elements were also quantified by atomic absorption spectrometry. Due to the great number of experimental determinations, the data obtained were computer adjusted by power regression.

3.6 Cadmium Adsorption and Acid Desorption Cycles

In this set of experiments, 1.0 g of algal sample was added to 250 mL Erlenmeyer flasks containing 50.0 mL of a 10.0 mg/L cadmium solution and incubated for 1 hour in a rotary shaker (30 ± 0.5 °C). The content of each flask was then filtered and the filtrate analyzed for its cadmium residual content. Cadmium-laden biomasses were treated with 50 mL of 0.5 N HCl to strip the adsorbed metal. The stripped solutions were analyzed for their cadmium content to check the efficiency of the elution. Next, samples were oven-dried (70 °C; 24 hours) and re-used in successive sorption/desorption cycles, as previously

described. It is important to mention that the incubation time for this set of experiments was established as 1 hour on the basis of previous determinations of adsorption equilibrium kinetics carried out for all the algal samples.

3.7 Effect of pH on Cadmium Biosorption

Only *Sargassum sp.* (sample BS_1) was used in this set of experiments, due to its outstanding performance as a cadmium biosorbent. 50 mL aliquots of a 11.0 mg/L cadmium solution were placed into 250 mL Erlenmeyer flasks and the pH of individual aliquots then adjusted to the desired value with HCl or NaOH (pH range: 2.0 to 12.0). Next, the dried and pulverized biomass of *Sargassum sp.* (sample BS_1) was added to the flasks at a concentration of 2.0 g/L. The flasks were placed on a rotary shaker at 30 ± 0.5 °C and incubated for 24 hours to ensure equilibrium. Biosorbent-free blanks were used as controls, to evaluate chemical precipitation (Hahne & Kroontje, 1973). The genus *Sargassum* was also selected for its high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it, at least in theory, very liable to the influence of the medium's pH. The experimental determinations reported here correspond to average values.

3.8 Continuous Biosorption of Cadmium, Copper and Zinc with the Selected *Sargassum sp.* Biomass

The seaweed used in this study is *Sargassum sp.* (*Phaeophyta, Cyclosporeae, Fucales, Sargassaceae*), collected in the Atlantic Ocean, in the Northeast region of Brazil. For its use in the experiment, the biomass was dried in an oven at 60 °C for twenty-four hours.

The solution used was prepared from $ZnSO_4.7H_2O$, $3CdSO_4.8H_2O$, and $CuSO_4.5H_2O$ dissolved in distilled water, obtaining a solution with zinc, cadmium, and copper concentrations of 10.0 mg/L for each metal. The metal

concentrations were determined by means of an atomic absorption spectrometer Varian Techtron, Model AA6.

The continuous system used was made up of three columns in series, each filled with 15.0 g of the dry biomass. Each column was 25.0 cm high, with a 3.5 cm internal diameter. The system operated with a Masterflex peristaltic pump, the metal solution being fed to the first column in an upward flow, at a flow-rate of 10.0 mL/min. The working volume of each column was 150 mL, which corresponds to a residence time of 15 minutes. The outlet solution from the first column was fed to the second column, the later's outlet solution in turn becoming the inlet solution of the third column. The final solution, coming from the third column, was then discharged. The outlet solutions of all three columns were periodically evaluated as to concentration levels of residual zinc, cadmium, and copper, by atomic absorption spectrometry. Data presented constitute average values from four replicates. Some hydraulic conditions such as pressure drop in the columns, channeling in the packing material, will also be briefly discussed. Even though hydraulic conditions constitute a key factor in the operation of this sort of reactor, in the present work, metals concentration and flow rate were not changed. For future studies these parameters will be studied and optimized.

3.9 Mathematical Treatment of the Data Obtained from the Continuous System

The mathematical treatment of the data consisted initially in determining the polynomial equation which would best represent the experimental data of the system's saturation curve regarding the three columns. This procedure was realized for the three metals, with the saturation profile related to the columns filled with the biomass, adjusted and determined through a simple computer program. The polynomial fit was carried out for the different curves, taking into account experimental results until the outlet concentration indicated saturation of the biomass by each metal (10.0 mg/L, initial metals concentration). Immediately thereafter, the different polynomials obtained were mathematically integrated for calculation of the metal uptake by

the different columns. This integration proved to be a simple and useful tool for a suitable estimation of the amount of metals recovered by the biomass.

In this work, the variable y (residual metal concentration) was integrated as a function of x (volume of inlet effluent processed by the continuous system), in the limits of the function from $x = 0$ to $x =$ volume of solution at the moment of biomass saturation by the metal. In this way it is possible to evaluate the quantity of metal not accumulated by the biomass, and based upon the difference from the total fed to the columns, the amount of metal adsorbed by the seaweed could be calculated. Mathematically:

$$\int_{y_0}^{y} dy = \int_{x_0}^{x} f(x,y)dx$$

After integration of the results:

$$y = y_0 + \int_{x_0}^{x} f(x,y)dx$$

This kind of equation can be solved through a series of successive approximations, a very useful system used for differential equations. Analogously:

$$y_1 = y_0 + \int_{x_0}^{x} f(x,y_0)dx$$

and,

$$y_n = y_0 + \int_{x_0}^{x} f(x,y_{(n-1)})dx$$

3.10 Synthetic and Natural Effluents

The effluent selected for future studies was the one from a zinc-producing plant, located in the city of Juiz de Fora, Minas Gerais State, in Brazil. 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 2 (summer time). The other experiments were conducted with a natural effluent collected during winter time (Table 3).

Table 2 - 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 3 - 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 (1989).

3.11 Batch Experiments with Synthetic Effluent - Summer Time

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 pistil) 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.

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 2. 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 (Spectrometer 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 also listed in Table 2.

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 a 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 2. All these experiments were carried out in triplicate.

3.12 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.

3.13 Continuous Biosorption (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 (Spectrometer Varian-Techtron, Model AA6).

3.14 General Remarks about Continuous Operation

Figure 1 shows an schematic flow-sheet of the continuous biosorption process, as proposed in the present report.
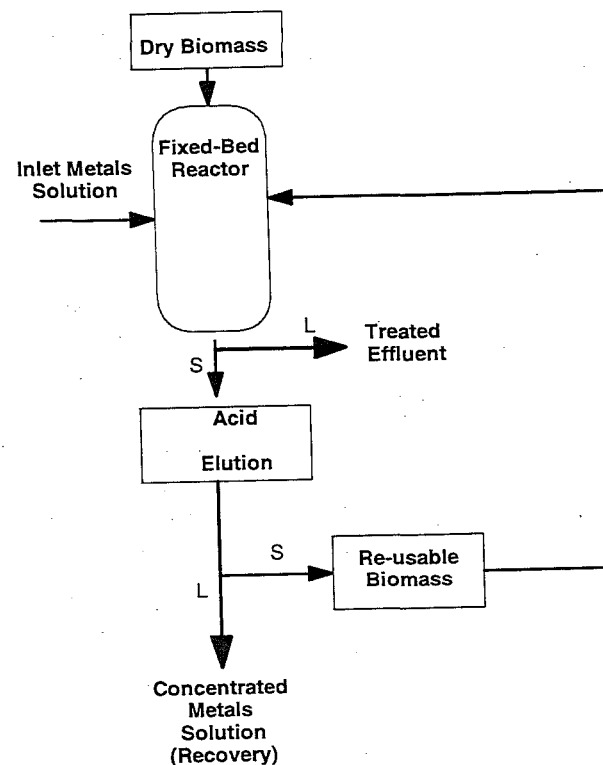

Figure 1 - Schematic flow-sheet of the continuous biosorption of heavy metals

The biomass, previously dry, is extensively washed to remove particulate materials, usually done with distilled water.

After this step, the biomass is oven-dried at 50-60 $^{\circ}$C, for approximately 24 hours to be used in the process. At this stage

the process itself occurs. The biomass, through its structural chemical binding sites accumulate the heavy metals. The outlet solution from this stage dictates the efficiency of the process.

After saturation of the biomass with the heavy metals, an elution should be made, in order to regenerate the biomass for future use, with the production of highly concentrated solution, feasible to recover the heavy metals. The regenerated biomass returns to the process.

3.15 Desorption Experiments - Multi-ion Situation

The biomass of *Sargassum* sp was previously exposed to an aqueous solution containing cadmium, copper and zinc, according to the previously mentioned methodology for the biosorption of heavy metals. For the selection of a suitable eluting agent, a 30.0 mg/L metal solution was used (for each metal); for the additional experiments a 200 mg/L concentrated metals solutions was used.

The metal loaded biomass was batchwise conducted in Erlenmeyer flasks in a rotary shaker at 27 C. The loaded biomass (mg) per volume of eluting agent (mL) ratio was fixed as the solid/liquid ratio, fixed as 5 for the whole experiments. The separation of the eluting solution was conducted through filtration using a Millipore filtration system using 0.45 µm pore diameter for the membranes.

For the selection of the most suitable eluting agent, the following solutions were used: HCl (0.1 M), H_2SO_4 (0.1 M), $CaCl_2$ (0.1 M/pH<3), $MgSO_4$ (0.5 M/pH<3), K_2SO_4 (0.5 M/pH< 3) and Na_2SO_4 (0.5 M/pH<3). After selection, the kinetics of the desorption was done in order to define the minimum contact time between the biomass and the metal solution. After that several biosorption/desorption cycles were conducted. All these experiments were conducted in duplicate.

3.16 Adsorption Studies with the Treated *Sargassum sp.* Biomass

The biomass used was the seaweed *Sargassum sp.*, washed with distilled water and dried at 50ºC, during 24 hours. A particle size between -28# + 20# Tyler was selected for use in the experiments.

The chemical treatment with formaldehyde was conducted by using a dry biomass of *Sargassum sp.*, adding formaldehyde (37% v/v) as to produce a partial wetting of the biomass, in order to produce a partially dry reaction. The treated biomass was maintained at 50ºC, for 1 hour to improve the rate of the reaction. Later, the biomaterial was washed with deionized water, HCl 0.1 N, NaOH 0.1 N and again with deionized water. This procedure was conducted until the final washing water reached a neutral pH. Later on the dry material was kept at 50ºC for 24 hours.

The chemical treatment with glutaraldehyde included the addition of half of the molar concentration needed to treat the biomass (considering the biomass as composed of 100% glucose), in a 0.1 N HCl solution. The treated biomass remained in contact with this solution for three days, followed by filtration and washing with water, later with a 0.5 % w/v Na_2CO_3 solution and again with deionized water, until neutral pH. The treated material was kept drying overnight at 80ºC.

The synthetic cadmium copper and zinc solutions were prepared in a wide range of concentrations (from 10.0 to 250.0 mg/L), all the solutions being prepared from sulphate salts in deionized water. The flasks contained 0.1 g of biomass added to 100 mL of the synthetic metal solution. The results presented correspond to average values from duplicate experiments and the evaluation of the results was as previously described. The adsorption isotherms were achieved for the virgin biomass of *Sargassum sp.*, as well as for formaldehyde and glutaraldehyde treated biomasses. The concentration of heavy metals were determined by atomic absorption spectrometry.

4. RESULTS AND DISCUSSION

4.1 Cadmium Biosorption Experiments (Fitness to Langmuir and Freundlich Equations)

The results on cadmium biosorption for each algal sample assayed are presented in Figures 2 to 7. Together with the experimental data, the corresponding theoretical adjustments of experimental determinations by the Langmuir and Freundlich equations were also plotted.
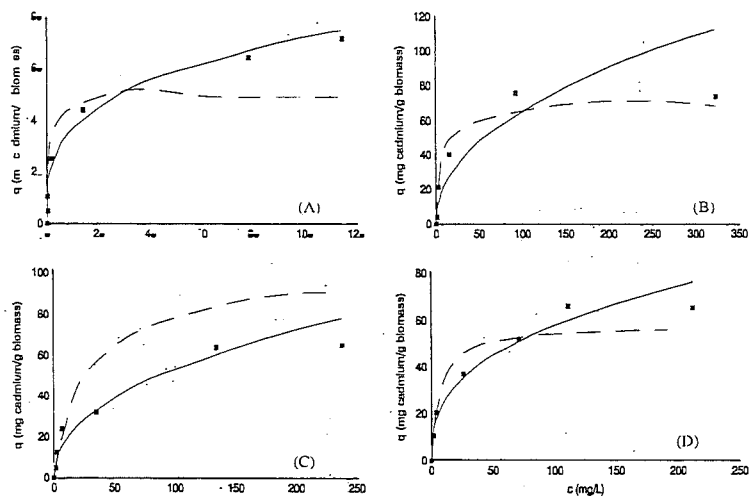

Figure 2 - Cd adsorption isotherms of *Sargassum sp.* [BS1-(A)], [BS2-(B)], [BS3-(C)] and [IGr-(D)] at 30 oC. Legend: Full square-Experimental; full line - Freundlich isotherm; dotted line - Langmuir isotherm.
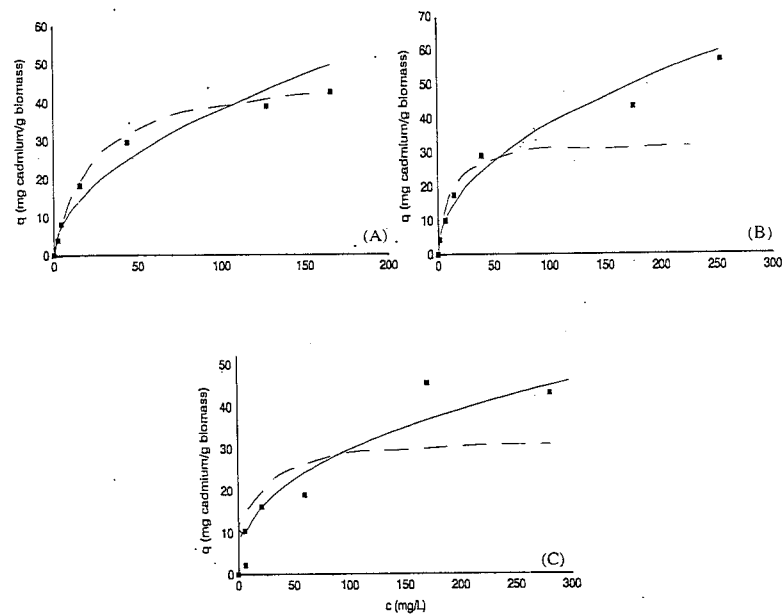

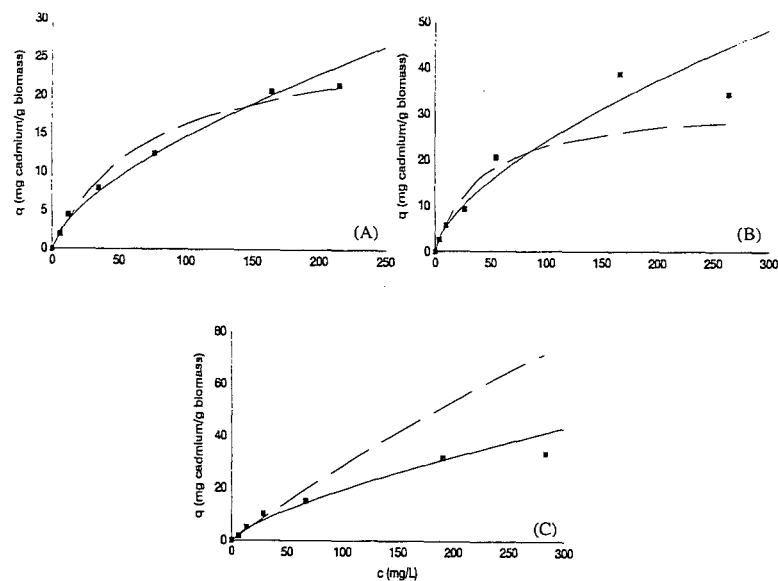Figure 3 - Cd adsorption isotherms of Padina sp. [BS1-(A)], [BS2-(B)] and [IG-(C)] at 30 °C. Same key as in Figure 2.

Figure 4 - Cd adsorption isotherms of Ulva sp. [BS-(A)], [BG-(B)] and [PV-(C)] at 30 °C. Same key as in Figure 2.
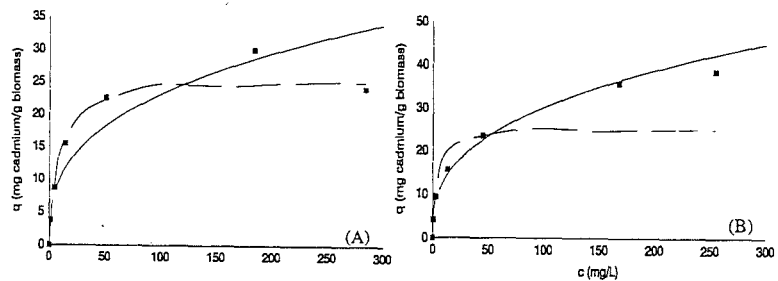
Figure 5 - Cd adsorption isotherms of Gelidium sp. [IT-(A) and [IP-(B)] at 30 °C. Same key as in Figure 2.
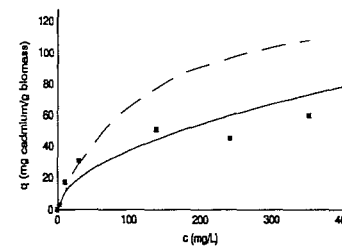
Figure 6 - Cd adsorption isotherms of Colpomenia sp. [IP] at 30 °C. Same key as in Figure 2.
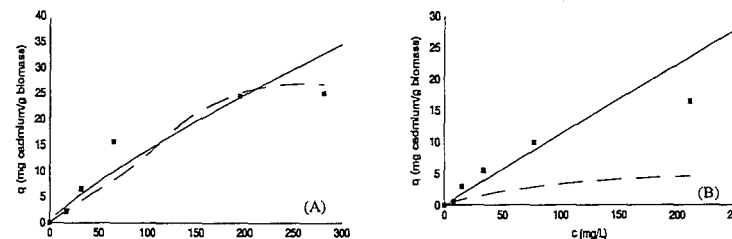
Figure 7 - Cd adsorption isotherms of Codium sp. [IT-(A)] and [PV-(B)] at 30 °C. Same key as in Figure 2.

From the data for *Sargassum sp.* (Figure 2: B, C and D) it can be inferred that, according to experimental **q** values, the adsorption process reached saturation in samples BS_2, BS_3 and IGr. For *Sargassum sp*, sample BS_1 (Figure 2A), the experimental determinations indicate a pattern of increasing **q** values within the range of concentrations tested.

Such behavior shows that this particular sample is a better cadmium adsorber than the other *Sargassum* isolates tested. The constant **q** values observed for samples BS_2, BS_3 and IGr of this genus at equilibrium concentrations greater than 100.0 mg/L suggest that, above this level of solute, solid-liquid equilibrium is probably limited by the diffusion of the cadmium ions towards the negatively charged metal-sequestering sites on the surface of the seaweed: that is, the algal surface does not display free sites for metal uptake, being saturated.

There was a good fit between the experimental data for *Sargassum sp.* seaweeds and the Freundlich model, exception made for sample BS_2 (Figure 2B), although multilayers of adsorbed cadmium ions are anyway expected to exist at equilibrium metal concentrations of around 100.0 mg/L. One possible explanation for this could be a variation in the chemical structure of surface polysaccharides, as their synthesis may differ between species and may also change as a function of environmental conditions. The Langmuir model, on the other hand, fitted well the experimental data in the case of sample BS_2 (Figure 2B). With the other *Sargassum sp.* isolates, a good fitting of this model was restricted to low equilibrium concentrations, as expected. Alginates, the main structural polysaccharide of the *Sargassum* seaweeds, can sometimes make up extremely large polymeric chains that might have supplied enough carboxyl sites for cadmium sorption within the metal concentration range studied, thus allowing the formation of a solute monolayer. It must be emphasized that both models consider the solid adsorbing surface as a homogeneous structure with only one type of binding site. However, in complex structures like algal polysaccharides, distinct chemical groups of a diverse nature can make up a heterogeneous matrix and contribute differently to the adsorption process.

For all *Padina* samples, the Freundlich equation fitted the data less well than the Langmuir one (Figure 3).

The Langmuir equation fitted almost perfectly the data for sample BS_1 of *Padina sp.* (Figure 3A), indicating a clear tendency to loading stabilization (q) at around 42 mg cadmium/g biomass. This equation also fitted perfectly the data for sample BS_2 of this genus (Figure 3B) at cadmium concentrations of up to 50.0 mg/L yet failed to do so at higher concentrations of the metal. Sample IG of *Padina sp.* (Figure 3C) could be described by the Langmuir model less well than the previous isolates, though still with a reasonable precision at equilibrium concentrations of up to 100.0 mg/L.

The sorption behavior of *Ulva sp.*, sample BS (Figure 4A), differently from the previously discussed patterns, was in good agreement with both equations in the range of cadmium concentrations tested.

However, samples BG and PV of this genus (Figures 4B and 4C, respectively) followed the expected behavior for this seaweed; that is, their experimental data fitted the Langmuir equation at low residual metal concentrations and the Freundlich model for the whole cadmium concentration range tested.

Concerning the genus *Gelidium*, sample IT suited well the Langmuir equation (Figure 5A) and sample IP (Figure 5B) the Freundlich equation. Structural factors may be responsible for this difference, also observed between other algal genera.

Figures 6 and 7 (*Colpomenia sp.*, sample IP and *Codium sp.*, samples IT and PV, respectively) show some discrepancies between experimental points and theoretical predictions, despite the obtention of linear regression coefficients within the confidence limits and correlation coefficients at acceptable values (Table 4).

Variations in cadmium biosorption behavior among the various algae tested can be attributed to polysaccharide variability between the genera, between the species or still between strains of a given species. In other words, the degree of heterogeneity among structural polysaccharides may be one of the underlying factors that determine differences in adsorption capacity between the algal isolates.

Table 4 - Langmuir and Freundlich Parameters for the Algal Samples Assayed

Alga assayed	Parameters from the Langmuir Equation			Parameters from the Freundlich Equation		
Sample	$k^{(1)}$	$d^{(1)}$	$R^{(3)}$	$K^{(2)}$	$n^{(2)}$	$R^{(3)}$
Sargassum (BS$_1$)	131.8	49.3	0.978	18.4	0.29	0.992
Sargassum (BS$_2$)	15.4	69.4	0.962	7.6	0.46	0.897
Sargassum (BS$_3$)	3.6	101.0	0.934	6.6	0.45	0.940
Sargassum (IGr)	14.8	57.8	1.003	10.7	0.36	0.984
Padina (BS$_1$)	4.3	48.3	0.997	3.4	0.52	0.977
Padina (BS$_2$)	10.4	32.8	0.984	4.1	0.48	0.990
Padina (IG)	7.2	32.4	0.929	4.7	0.39	0.965
Ulva (BS)	1.3	28.6	0.996	0.7	0.64	0.991
Ulva (BG)	2.3	32.4	0.995	1.3	0.64	0.984
Ulva (PV)	0.01	400$^{(4)}$	0.988	0.6	0.73	0.979
Gelidium (IP)	29.0	25.4	0.987	5.6	0.36	0.991
Gelidium (IT)	12.3	25.7	0.998	4.6	0.35	0.941
Colpomenia (IP)	0.8	144.9	0.991	3.2	0.53	0.927
Codium (IT)	0.2	81.9	0.976	0.3	0.82	0.945
Codium (PV)	0.9	6.8	0.927	0.1	0.97	0.932

(1) Parameters **k** and **d** were obtained by simple linear regression with an equation of the type $y = a + a_1 x$, where the coefficients **a** and **a$_1$** were calculated at statistically significant confidence intervals .

(2) The same as in (1), for parameters **K** and **n**.

(3) Correlation coefficients, calculated with a 95% confidence limit and corresponding to average values from the experiments.

(4) Theoretical value, mathematically predicted by the Langmuir equation.

The values of the Langmuir and Freundlich constants for the different algal samples and the correlation coefficients of the curves used to calculate them are listed in Table 4. These data must be discussed by groups in order to evaluate the samples with best sorption potential on the basis of the screening conducted and on the information about the parameters of the models tested and their application to the system studied.

As previously mentioned, constant **d** of the Langmuir equation represents the maximum surface density and constant **k** the affinity between the adsorbing surface and the solute. Therefore, increasing values of **k**, obtained from different samples for the same solute and with the same experimental system, indicate increasing affinity for the solute. It can be observed from Table 4 that the affinity of the different algal samples for cadmium was highly variable, as **k** values ranged from 0.01 to 131.8, indicating that the algae studied clearly differ in their cadmium biosorption behavior. To better illustrate this point, the algal samples from Table 4 may be grouped according to **k** values. Thus: **k** values smaller than 1 were obtained for 4 algal samples; **k** values ranging from 1 to 10 were observed for 5 samples; **k** values greater than 10 were observed, in increasing order, for the following samples: *Padina sp.* (sample BS$_2$), *Gelidium sp.* (sample IT), *Sargassum sp.* (sample IGr), *Sargassum sp.* (sample BS$_2$), *Gelidium sp.* (sample IP) and *Sargassum sp.* (sample BS$_1$). The distinct **k** values obtained for samples of the same genus can be attributed to the possible presence of different species or of different strains of the same species. An alternative explanation is that, depending on environmental conditions, different surface structures may have been synthesized. Considering the affinity constants calculated, it can be concluded that samples with **k**>10 should be the most suitable cadmium adsorbers.

Regarding the Freundlich equation, its constants describe the adsorption power of the adsorbent and the distribution of linkages. Constant **n** is related to the distribution of bindings on the solid surface: if **n**<1, then the binding energies increase with surface density; if **n**>1, the opposite behavior is observed; if **n**=1, the surface sites are equivalent. On analyzing the data from Table 4, it is possible to see that **n**<1 for all the samples tested, an observation that seems to be in accordance with the proposed mechanism: as the surface density increases, the value of **n** decreases. That is, the charged sites interact with the metals, increasing surface density - consequently, **n** values smaller than 1 are observed. It is interesting to mention the results obtained for *Codium sp.* samples: their **n** values are smaller than 1 yet they approach 1; this indicates that a marked increase in the binding energies as a function of increasing

surface density is not occurring. Such values are coherent with *Codium sp.* low performance on cadmium biosorption and are also in accordance with its **k** values, that indicate a low affinity of this algal genus for ionic cadmium.

If we consider **n** values of up to 0.5, it can be observed that only 8 algal samples could be selected as biosorbents. These samples belong to the genera *Sargassum* (exception made for sample BS_3, with k=3.6), *Padina* and *Gelidium*, which are exactly the ones with high affinity coefficients predicted by the Langmuir equation. In summary, the experimental data can be mathematically correlated with either the Langmuir or the Freundlich equation. Both models were reasonably suitable for fitting the experimental data, even if their assumptions were not strictly respected. The solid surface affinity for the solute and the change in surface density could be predicted by constants **k** and **n** from the Langmuir and Freundlich equations, respectively. Based on this assumption, algal samples of the genera *Sargassum, Padina* and *Gelidium* were chosen as those with the highest affinity for divalent cadmium. This theoretical prediction was confirmed by the experimental results, that led exactly to the selection of these genera as the most promising adsorbers.

Constants **n** and **k**, although with different meanings, led to the same conclusion about the correlation of the experimental data with the sorption models.

The Langmuir and Freundlich equations impose some basic assumptions for their applicability, and the present experimental data seemed to suit them up to a limit. The Langmuir equation predicts the formation of an adsorbed solute monolayer with no side interactions between the adsorbed molecules/ions. It also assumes that the interaction takes place by adsorption of one molecule/ion per binding site, and that the solid surface is homogeneous and contains only one type of binding site. The Freundlich equation, on the other hand, does not predict surface saturation based on the adsorption process, but mathematically predicts the existence of a multilayered structure. This way, at higher solute concentrations, where multilayers are expected to be formed, the Freundlich model should fit the experimental

data with a greater degree of accuracy than the Langmuir model.

Taking an overall view of the results obtained, it could be said that, in general terms, the Langmuir equation fits better the experimental data than the Freundlich equation, for the range of cadmium concentrations tested. However, it must be pointed out that there was a better fitting to the Langmuir equation at low equilibrium concentrations, as expected, whereas at higher equilibrium concentrations there was an increasing tendency to fit the Freundlich model. The same behavior would probably be predicted at even higher equilibrium concentrations due to the formation of a multilayered network. In the present work, cadmium biosorption was evaluated only within a concentration range representative of the actual cadmium levels found in industrial effluents.

According to the literature, cobalt adsorption has been investigated by uptake evaluation in inactivated algae, fungi, ion-exchange resins and activated carbon. The main goal of that work seemed to be the screening of biological and non-biological materials for the recovery of cobalt (Kuyucak & Volesky, 1989). The authors observed that some samples (Resin IRA-400 and the red alga *Porphyra tenera* and *Chondrus crispus*) suited well the Langmuir model while others (Brown alga *Ascophylum nodosum* and *Macrocystis pyrifera*) the Freundlich one.

Some researchers working with fungal and bacterial strains as well as with ion-exchange resins and activated carbon concluded that the Freundlich model described their experimental results with a higher degree of accuracy than the Langmuir model. However, the authors did not make theoretical considerations about the mechanism involved, only using the equations as mathematical functions that describe experimental results for a specific metal concentration range.

4.2 Release of Elements during Cadmium Biosorption

Figure 8A presents the results for *Sargassum sp.* (sample BS_1), which indicate that ion-exchange is probably associated with cadmium adsorption.

The pattern of calcium and magnesium release as a function of **q** confirms the close relationship between these two parameters. The release of the alkaline-earth elements is probably related to the presence of calcium and magnesium alginates and also with cross-linked atoms between polysaccharide chains in brown algae. As observed, a likely ion-exchange in the alginate, the structural macromolecule of these cells, has occurred; the present data allow the conclusion that cadmium replaced magnesium and calcium. Similar ion-exchange properties have already been reported in the literature for alginic acid (Cozzi *et al.*, 1969).

Padina sp. (BS_1) showed a calcium release pattern similar to that observed for *Sargassum sp.* However, magnesium release was independent of cadmium uptake, probably indicating that the magnesium ions were totally replaced by cadmium ions, even at low equilibrium concentrations (Figure 8B).

As observed for *Padina sp.* (sample BS_1), the substitution of calcium and magnesium for cadmium was also complete, even at low concentrations, in *Ulva* sp (sample PV). An explanation for this is probably found in the chemical structure of this algal genus; alkaline-earth elements might be present at very low concentrations, hence the detection of a complete exchange for cadmium within the whole range of metal concentrations tested (Figure 8C).

The results shown in Figure 8D indicate that red algae of the genus *Gelidium* should have, to a lesser extent than brown algae, an ion-exchange capacity associated with cadmium uptake. Finally, concerning *Colpomenia sp.*, sample IP, a marked release of calcium and magnesium as **q** increases was observed (Figure 8E).
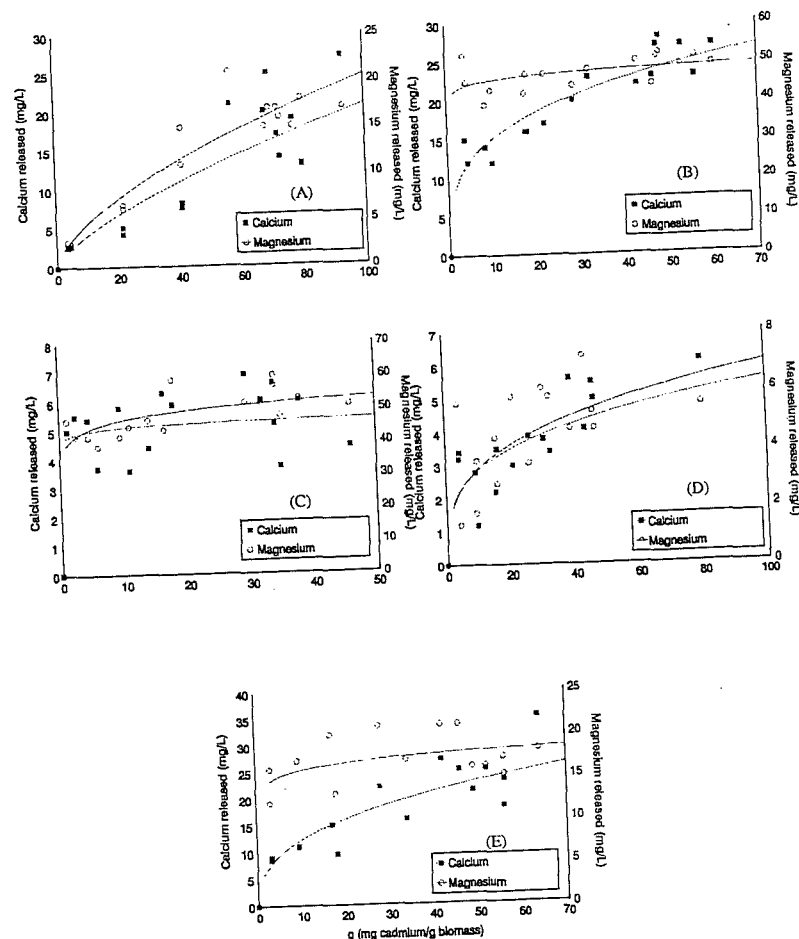

Figure 8 - Release of alkaline-earth elements from *Sargassum sp.* [BS1-(A)], Padina sp. [BS1-(B)], Ulva sp. [PV-(C)], Gelidium sp. [IP-(D)] and Colpomenia sp. [IP-(E)] during Cd biosorption

Of all the algae tested, *Sargassum sp.* and *Gelidium sp.* were those with the lowest release of total alkaline-earth elements. Nevertheless, they presented the highest cadmium uptake capacities if their respective **k** and **n** values are considered. Therefore, it can be concluded that there is more than one mechanism operating during cadmium biosorption in those two genera.

As mentioned before, the structural polysaccharides from the various algal divisions differ in their chemical composition, size and type. They can be sulfated, carboxylated or aminated, show different structural complexities, and are sometimes stabilized by mono and divalent metals, usually calcium and magnesium.

4.3 Cadmium Adsorption and Acid Desorption Cycles

According to Volesky & Holan (1995), one of the key factors for the use of a biomass as a biological resin is the possibility of using it in several sorption/desorption cycles. Thus, the eluted biomass, free of any heavy metal, must be assigned as to its capacity to be re-used, and the effect of its re-use in relation to its uptake efficiency must be evaluated.

This evaluation has been done by conducting ten sorption/desorption cycles, indicating that some of them gradually lost their ability to accumulate cadmium, as a function of the acid treatment performed, that markedly affected the chemical structure of the biomass. The acid washings performed had different effects on the polysaccharide of the different biomasses, and the results of these cycles, with the respective uptake efficiencies are reported in Table 5 below:

Table 5 - Cd uptake efficiency during sorption/desorption cycles

Sample	Cadmium Uptake Efficiency (%)							
	Number of Cycles							
	1	2	4	5	6	8	9	10
Codium (IT)	30	66	37	20	27	14	15	10
Codium (PV)	30	55	62	44	48	52	41	34
Gelidium (IP)	6	70	76	75	77	64	54	60
Ulva (BS)	5	99	68	86	96	57	66	37
Ulva (BG)	7	93	64	83	75	63	60	64
Padina (BS$_1$)	69	100	98	96	100	95	98	92
Padina (IG)	50	100	100	100	99	97	99	98
Sargassum.(BS$_1$)	93	100	100	100	100	94	100	98

It was observed that the PV *Codium sp.* sample was more efficient than IP sample in the uptake of cadmium; however, both of them presented a marked decrease in their uptake capacities from cycle to cycle, probably as a function of the acid attack in their polysaccharide content, thus jeopardizing previously available metal binding sites.

In the case of *Padina sp.* (BS$_1$), the ability of the seaweed in accumulating the metal was kept constant, even after ten cycles; however, *Ulva sp.* (BS e BG) were not so efficient as *Padina sp.* samples, that presented only 37 and 64% uptake efficiencies in the tenth cycle, respectively. The sample IP of *Gelidium sp.* began to present a decrease in its cadmium uptake capacity from the seventh cycle, not so markedly as the decrease observed for *Codium sp.*, however.

Sargassum sp. was the seaweed to keep its structural integrity during the ten cycles, with an uptake capacity around 100%, all over the experiment. This fact, associated to its high uptake capacity and efficiency, gives to this brown seaweed a remarkable potential to be used as a biological resin for the accumulation of heavy metals.

Overall, the results indicate that some algae kept their ability to recover cadmium for a great number of cycles, while others presented a decreased uptake efficiency from cycle to cycle,

probably due to some deleterious effects of acid washings on their chemical structures.

Table 5 also shows that *Sargassum sp.* (sample BS_1) and *Padina sp.* (sample BS_1) were not affected by the acid treatment, as their uptake efficiencies remained constant through all the sorption/desorption cycles. This is a good indication of their potential as biosorbent materials, since they can be reused several times without having to be discarded due to decreased uptake.

The other algae tested, on the other hand, did not behave similarly. Samples of the genera *Ulva*, *Gelidium* and *Codium* were gradually affected by acid washings from cycle to cycle, as shown by a decreasing cadmium uptake efficiency. Such decrease was somehow gradual for *Gelidium sp.* and *Ulva sp.*, and less so for *Codium sp.* Still on these genera, it is interesting to note the increase in uptake efficiency from the first to the second biosorption cycle, with probable release of a greater number of cadmium adsorbing sites. It may be that other metals are present in these algae and that cadmium was not able, by itself, to release them and be adsorbed into the free sites. HCl treatment can strongly affect ion-exchange properties of the polysaccharides as well as the polysaccharide structure. As the number of uptake cycles increased the acid washings affected the algal structure, thus causing a detectable gradual decrease in cadmium biosorption from one cycle to the next. Based on this tendency, it can be estimated, for example, that the use of *Ulva sp.* as a cadmium biosorbent would not last for many consecutive cycles.

During copper biosorption by the fungus *Rhizopus arrhizus*, a reversibility of the process was observed after acid washing (Zhou & Kiff, 1991). However, the biomass maintained its sorption capacity for only two sorption/elution cycles. In another example reported in the literature, where the biosorption of cadmium by a regenerated biofilm of *Enterobacter aerogenes* on activated carbon was studied, a decrease in the efficiency of its sorption capacity from cycle to cycle was also detected (Scott & Karanjkar, 1992).

One of the main requirements for a biological material to be employed as heavy metal adsorption agent is its reuse in successive sorption/desorption cycles with no marked effect on structural characteristics; that is, throughout continuous cycles of metal uptake and acid elution, the biomaterial must be able to maintain its metal recovery capacity.

4.4 Effect of pH on Cadmium Biosorption

Based on preliminary results, sample BS_1 of *Sargassum sp.* was selected for use in this set of experiments. Cadmium biosorption and cadmium precipitation could be predicted, on the basis of a wide pH range.

Figure 9 shows that cadmium biosorption by *Sargassum sp.* is not markedly affected by pH at the tested values.
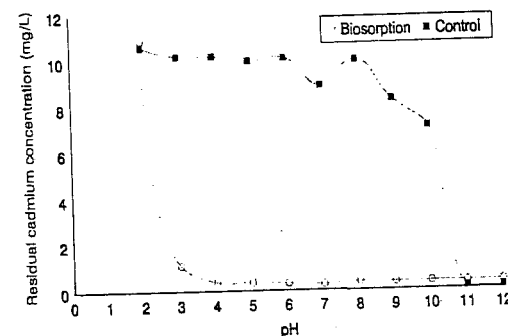

Figure 9 - Effect of pH on Cd biosorption by *Sargassum sp.* (Initial Cd concentration =1.0 mg/L).

For example, between pH 3.0 and 8.0, cadmium biosorption was not significantly different. In the alkaline range between pH 8.0 and pH 10.0, the decreasing residual cadmium concentrations were not exclusively due to biosorption by the seaweed, chemical precipitation having been observed as well. The biosorbent-free control experiments revealed total cadmium

precipitation at pH values 11.0 and 12.0. This affected the *Sargassum sp.* biosorption experiments within this extremely alkaline range (pH 11.0 to pH 12.0), where low residual cadmium concentrations were not just due to metal uptake but also to cadmium precipitation as hydroxyl compounds. At pH 2.0, the equilibrium cadmium concentration was the same as that of the initial solution, indicating the probable non-applicability of the process following treatment with extremely acid solutions. In this situation, metal desorption through the action of the acid medium outweighs the interaction between anionic surface sites and the ionic species.

These results corroborate other findings reported in the literature (Cozzi *et al.*, 1969), which describe that, for pH values up to 8.0, cadmium remains in solution in its ionic divalent state (Cd^{+2}). As pH increases, ionic divalent cadmium is gradually substituted by the insoluble hidroxylated forms ($Cd(OH)^+$ and $Cd(OH)_2$), which precipitate out of solution.

The results presented in this work emphasize the potential use of *Sargassum sp.* as cadmium biosorbent, suggesting its use in continuous units as a treatment system for cadmium contaminated complex metal solutions.

4.5 Continuous Biosorption of Cadmium, Copper and Zinc with the Selected *Sargassum sp.* Biomass

Figure 10 presents the results of the biological uptake of zinc during the process.
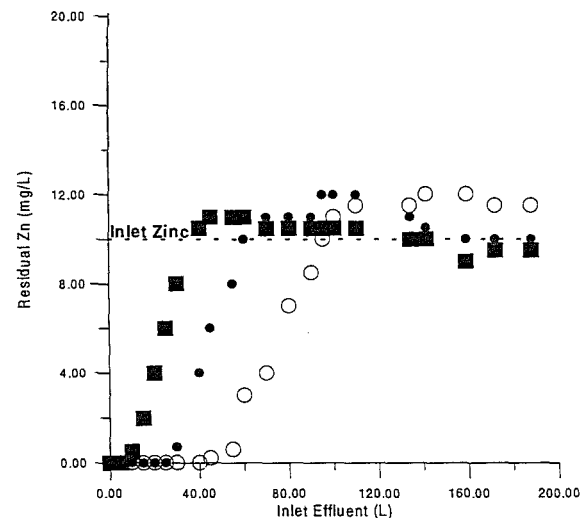
**Figure 10 - Zn biosorption by *Sargassum sp.*
- ■ Column # 1; ● Column # 2; ○ Column # 3**

The results indicate an efficient metal uptake by the biomass, with accumulation taking longer in column 3, followed by column 2, then column 1. It is evident that column 1 no longer accumulated zinc after being fed 40 liters of solution, with zinc concentration in the outlet solution of this column the same as that of the inlet solution, thereby indicating saturation of the biomass by this metal. However, column 2 presented this profile only after being pumped with 60 liters of solution, and column 3 after treatment with 95 liters of solution, these saturation profiles being compatible with the operation of a multi-column fixed-bed continuous system. The first column is fed by a heavy metal-concentrated effluent, whereas the second column is fed by a more diluted solution due to the partial biosorption effected by column 1; column 3 receives a much more diluted solution, consequently being able to support a greater volume of contaminated solution. It is worth mentioning that during the treatment of the initial 40 liters of solution, the column 3 biomass sorbed 100% of the metal fed to it, since it received from column 2 a much more diluted solution in zinc.

In order to evaluate the quantity of zinc accumulated during operation of the system, the different polynomials that govern the curves were determined and mathematically integrated, until the saturation limit of each column, that is, until the columns were no longer capable of accumulating the metal due to saturation of the reaction sites. The adjusted curves related to the different columns are illustrated in Figure 11.
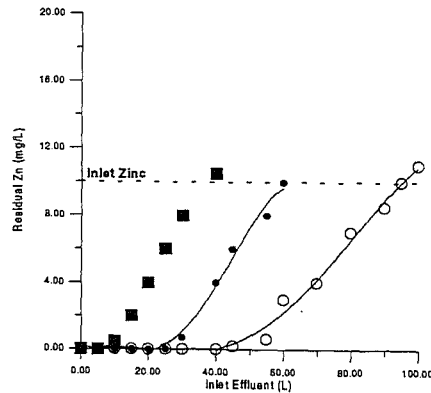

**Figure 11 - Zn biosorption by *Sargassum sp.*, up to saturation.
- ■ Column # 1; ● Column # 2; ○ Column # 3**

After adjustment of the different curves the respective polynomials were mathematically integrated within the limits defined by the saturation of the biomass, obtaining the following equations for zinc biosorption:

Column 1:

$$\int_{0}^{40} (4.66*E-7x^5 - 4.66*E-5x^4 + 0.0013x^3 + 0.0015x^2 - 0.044x + 0.0089)dx$$

Column 2:

$$\int_{0}^{60} (-4.24*E-6x^4 + 0.00046x^3 - 0.011x^2 + 0.062x + 0.0042)dx$$

Column 3:

$$\int_{0}^{95} (-5.63*E-7x^4 + 0.00011x^3 - 0.0052x^2 + 0.066x - 0.1171)dx$$

The mathematical integration of these equations makes it possible to calculate the amount of zinc not adsorbed by the biomass, given that the dependent variable (y) corresponds to the residual concentration of zinc in solution, that is, the amount of metal not accumulated by the biomass during operation of the system. The mathematical integration corresponds to the area under the outlined curve, which, based upon the difference from the quantity of metal fed to the different columns, permits determining the quantity of metal adsorbed by the biomass. Table 6 presents the results of the mathematical integration of the described equations. The quantity of zinc accumulated, until saturation of the system, is around 17.35±4.28 mg Zn/g dry biomass.

Figure 12 presents the results of cadmium uptake with the outlet cadmium concentrations for the three columns.
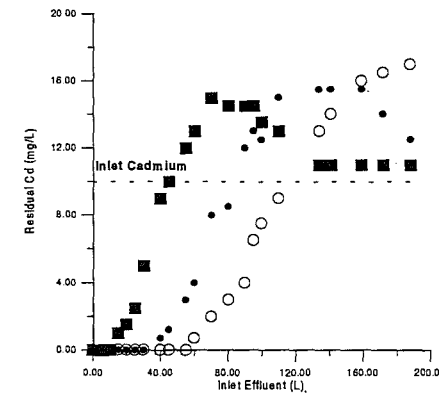
**Figure 12 - Cd biosorption by *Sargassum sp.* - ■ Column # 1; ●
Column # 2; ○ Column # 3**

It is evident that the saturation profile of the three columns followed a pattern similar to that with zinc biosorption. In this instance, however, the columns reached saturation after being treated with 45, 80, and 115 liters of a solution containing cadmium for columns 1, 2, and 3, respectively. These results demonstrate that the biomass is capable of adsorbing cadmium more efficiently than it does zinc, with saturation of the system, on the whole, occurring only after pumping 115 liters of solution. A desorption of the metal after saturation was observed for cadmium, thereby indicating that a desorption equilibrium occurred after saturation of the columns. This seriously jeopardizes the stability of the continuous system, at least under the operational conditions established. Figure 13 follows with the adjustments obtained for cadmium biosorption up to the saturation limits for the three columns utilized.
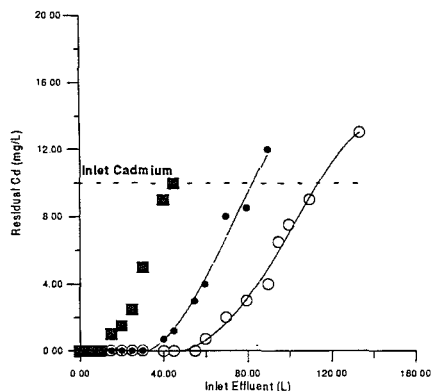
Figure 13 - Cd biosorption by *Sargassum sp.*, up to saturation.
- ■ Column # 1; ● Column # 2; ○ Column # 3

The polynomials that govern these curves, as well as the limits of integration are following described:

Coluna 1:

$$\int_0^{45}(-1.09*E-5x^4+0.00085x^3-0.013x^2+0.082x-0.069)dx$$

Column 2:

$$\int_0^{80}(1.06*E-8x^5-3.08*E-6x^4+0.00031x^3-0.010x^2+0.103x-0.144)dx$$

Column 3:

$$\int_0^{115}(-2.33*E-7x^4+5.94*E-5x^3-0.0035x^2+0.058x-0.162)dx$$

Table 6 lists the results of the mathematical integration of the polynomials derived from adjustment of the cadmium uptake patterns. The outcomes showed that uptake efficiency was equivalent for the three columns (19.98±1.88 mg Cd/g dry biomass), indicating that the fact that the solid/liquid equilibrium for more diluted solutions of ionic cadmium and the biomass can affect metal uptake, although the amount of accumulated metal is approximately the same per column. It is also observed that the quantity of adsorbed cadmium was larger than that of zinc, considering mean values, demonstrating that the first seems to be preferentially accumulated by the *Sargassum sp.* biomass when present in solution in the same concentration and the total amount of cadmium adsorbed by the biomass was approximately 13.19% higher in comparison to zinc uptake, which underscores the fact that cadmium is selectively accumulated when present in solution with ionic zinc.

Analogously, the longest operating time of the system was observed, in columns 2 and 3, and here the uptake capacities varied from 18.24 to 21.99 mg cadmium/g dry biomass, showing that each of the three columns accumulated equivalent amounts of this metal. These results clearly suggest that cadmium uptake is strongly influenced by the presence of other divalent ions, since cadmium loading capacities by brown seaweeds present substantially higher values, in comparison to the obtained results.

Volesky (1994) reports that cadmium loading capacities are approximately 85-100 mg/g biomass for *Ascophylum nodosum*, around 83 mg/g biomass for *Sargassum natans*, and about 50 mg/g biomass for *Fucus vesiculosus*. Da Costa and de França (1996) also observed high loading capacities for *Sargassum sp.* in a batch system, using, however, solutions containing cadmium only. It should be emphasized that these results described in the literature correspond to systems containing one metal only, from operational systems with different solid/liquid equilibrium conditions from those observed in the present study. Nevertheless, it is worthwhile emphasizing that even in the presence of other heavy metals, *Sargassum sp.* performed equally to a cadmium-selected ion exchange resin (Duolite IRA-400), which presented a loading capacity of only 20 mg cadmium/g resin from a cadmium solution (single-ion situation). Volesky and Holan (1995) mention the complexity of working with multi-metal solutions for biosorption of heavy metals, suggesting for the study of continuous systems, two types of reactors: fixed-bed or a CSTR-type reactor. The authors stress that fixed-bed reactors are more efficient; there are, however, very few studies on the former's use as a biotechnology for heavy metal uptake. In the present work, it was not our purpose deeply study the effect of hydraulic conditions on the efficiency of the process. However, it is important to mention that, during operation of the reactor, pressure drop in the reactor did not compromise its normal performance. As the metals solution was pumped upwards, no preferential channeling in the reactors was observed through the packing material. As well, no metal precipitation was detected, indicating that the previously described phenomena could not markedly affect the hydraulic conditions of the process.

Figure 14 shows the copper uptake by the biomass.
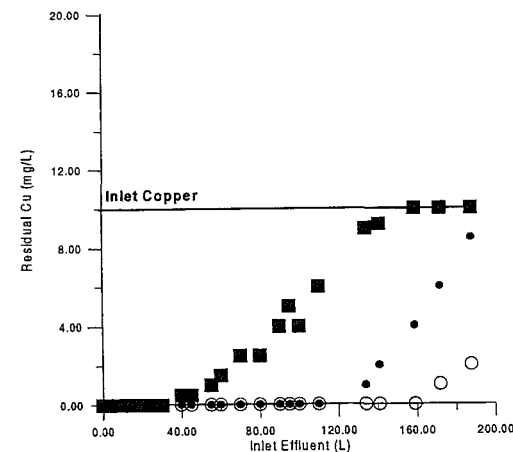
Figure 14 -Cu biosorption by *Sargassum sp.*
- ■ Column # 1; ● Column # 2; ○ Column # 3.

These results reveal a different uptake pattern from those observed for zinc and cadmium, indicating that copper biosorption is not affected by the presence of the other divalent ions. Column 1 became saturated after treatment with only 160 liters of synthetic effluent; column 2 after treatment with 185 liters of solution and column 3 did not reach saturation even after being fed with 195 liters of solution, although the system saturated with zinc and cadmium, but not with copper. Figure 15 presents the experimental data on copper uptake, these adjusted by computer-obtained polynomials.
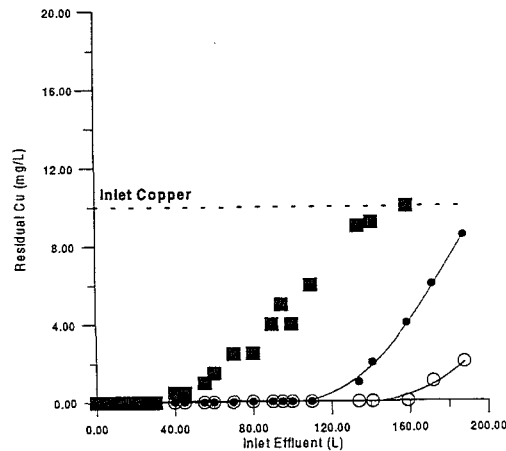
**Figure 15 -Cur biosorption by *Sargassum sp.* , up to saturation
- ■ Column # 1; ● Column # 2; ○ Column # 3**

The different curves followed the mathematical equations are presented:

Column 1:

$$\int_{0}^{160}(-4.93*E-8x^4+1.13*E-5x^3-0.00016x^2+0.0025x-0.0378)dx$$

Column 2:

$$\int_{0}^{185}(-3.87*E-10x^5+1.83*E-7x^4-2.65*E-5x^3+0.0014x^2-0.027x+0.094)dx$$

Column 3:

$$\int_{0}^{195}(1.80*E-8x^4-5.12*E-6x^3+0.00044x^2-0.012x+0.064)dx$$

Table 6 lists the results of the mathematical integration of the polynomials derived from adjustment of the copper uptake profile.

Table 6 - Metals biosorption by *Sargassum sp.*

Column	mass inlet metal up to saturation (mg)	mass outlet metal up to saturation (mg)	mass metal biosorbed (mg)	mg metal/ g dry biomass
		Zinc		
1	400.00	192.91	207.09	13.81
2	600.00	150.85	242.06	16.14
3	950.00	169.19	331.66	22.11
		Cadmium		
1	450.00	154.16	295.84	19.72
2	800.00	230.42	273.74	18.24
3	1150.00	250.52	329.90	21.99
		Copper		
1	1600.00	625.00	975.00	65.00
2	1850.00	95.35	779.65	51.97
3	1950.00	36.12	159.23	10.62

According to Table 6, the copper mass accumulated by column 1 was 470% and 329% higher than the zinc and cadmium masses adsorbed by the same column. Column 2 accumulated 322% and 284% more copper mass than zinc and cadmium. As for the third column the comparison between copper biosorption and the other metals was not evaluated due to the fact that copper saturation was not observed in this third column. Kuyucak and Volesky (1990) affirm that the uptake of heavy metals by the *Laminaria digitata* (brown seaweed), followed a selective order in the biosorption of copper, cadmium, and zinc (Cu>Cd>Zn), similar to the results obtained in the present study for the *Sargassum sp..* The structural polysaccharides, especially calcium, magnesium, and sodium alginates are the primary components responsible for metal uptake, being the mechanism involved in the biosorption mediated by adsorption and reactions of ion-exchange with

elements constituting the biomass (da Costa & de França, 1996).

Copper uptake capacities for columns 1 and 2 were around 56.94 and 58.00 mg copper/g dry biomass, showing that the tendency of the biomass probably would be to accumulate, also in the third column of the system, an equivalent amount of metal, although after treatment with a considerably larger amount of effluent. The larger loading capacities in comparison to zinc and cadmium, associated to the fact that copper was not desorbed from the system after metal saturation, as well as the fact that the presence of zinc and cadmium did not influence copper biosorption, demonstrate that the mechanism associated with the sorption of ionic copper should be different from the mechanism of cadmium and zinc uptake.

It was also observed that until saturation of the whole system, the individual metal uptake efficiency was 82.19%, 78.22%, and 98.14% for zinc, cadmium, and copper, respectively, even though different uptake patterns were observed.

In quantitative terms, the principal structural polysaccharide of the brown algae is alginic acid, made up of blocks of β-1,4 linked D-mannuronic acid and α-1,4 linked L-guluronic acid, with variable quantities, depending upon the algal genera as well as environmental conditions that stimulate its biosynthesis (Percival, 1979). Actually, alginic acid is present in the *Phaeophyceae* as calcium, magnesium, and sodium salts, these elements acting as ion-exchange compounds. The properties presented by these polysaccharides make the external structures of the *Phaeophyceae* potential heavy metal ion-exchange biological resins, this process occurring via alginate salts and divalent elements that stabilize the superficial structures. In this way, these polysaccharides would act as the main agents responsible for the uptake of heavy metals, through mechanisms of adsorption and ion-exchange. da Costa & de França (1996) performed an extensive screening including green, red, and brown seaweeds, showing that with rare exceptions, all algae accumulated heavy metals; the

mechanism at work was well represented by the classical Langmuir and Freundlich isotherms. Similarities between the experimental data and the foreseen metal concentrations obtained using the Langmuir and Freundlich equations confirmed the fact that adsorption is the predominant mechanism, and that some of the algae showed release of alkaline and alkaline-earth elements during loading of the heavy metal, thus including the involvement of ion-exchange reactions with elements constituting the structural polysaccharides of the seaweeds.

Especially in the case of copper, however, there may be other mechanisms at work in the accumulation process, such as complexation reactions followed by metallic nucleation. The latter process, not fully elucidated as yet, involves interactions between the metallic species with the formation of a central accumulating nucleus which is responsible for commencing nucleation. In this case, the mechanism complements adsorption, which by itself does not presuppose lateral interaction between the adsorbed species. Simple adsorption foresees that each metallic ion should react with a binding site of the biomass, and that only one type of binding site is involved in the process. However, in certain cases, it is observed that with the formation of a central nucleus initiated by adsorption, an inter-elementary interaction becomes inevitable, thereby catalyzing in a growing manner the additional deposition of metals, not necessarily at this stage, mediated by components of the adsorbent material.

The fact that *Sargassum sp.* biosorbed copper, despite saturation by zinc and cadmium, suggests that a process of nucleation may have begun in the biomass, thus accounting for the outstanding copper loading capacity of the biomass.

Considering that mean loading capacities were around 17.35, 19.98, and 58.48 mg metal/g dry biomass for zinc, cadmium, and copper, respectively, the total loading capacity of the biomass was about 95.81 mg metal/g dry biomass (taking into consideration average values, up to saturation), which shows that *Sargassum sp.* has great excellent potential as a biological resin for the uptake of heavy metals. Besides this

potential, it was observed that the biomass can be reutilized in various biosorption/desorption cycles. These results associated to the fact that *Sargassum sp.* is easily available off the Brazilian coast, render this seaweed's use on a large scale very promising, although other pertinent parameters must still be determined and optimized.

The total masses of biosorbed zinc, cadmium, and copper were 780.81, 899.48, and 1913.88 mg respectively. Considering 100 mL of a solution of mineral acid as capable of promoting complete desorption of these metals, solutions of 7.81 g/L zinc, 8.99 g/L cadmium, and 19.15 g/L copper would be obtained. These results would correspond to very high concentration factors (concentration of metals in eluent solution/concentration of metals in the initial solution), thus rendering the recycling of metals technically and economically viable.

4.6 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 2. Figure 16 displays the results obtained for the three sets of experiments. 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.
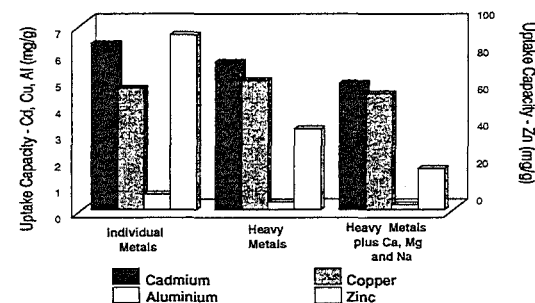
Figure 16 - Metals biosorption by *Sargassum sp.* - Individual metals uptake and multi-ion situation

For 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 still more pronounced, due to the greater complexity of the solution, and not only due to competition, as the alkaline and alkaline-earth elements were not recovered by the biomass, as observed for the heavy metals (Figure 17).

Specifically for copper biosorption the same behavior 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 17, 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 favoring ion-exchange with these elements present in solution (Mautner, 1954). 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 (Cozzi *et al.*, 1969; Gale, 1986; Haug *et al.*, 1974).
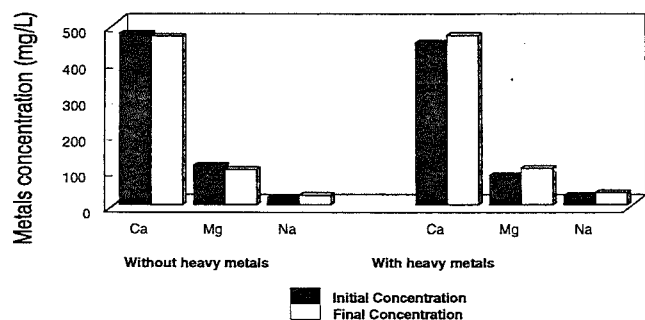
Figure 17 - Alkaline and alkaline-earth elements biosorption by *Sargassum sp.*

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 18).

From Figure 18 it can be extracted that calcium imposes a negative effect on zinc uptake, while magnesium and sodium impose a positive effect on it.

Figure 18 - Effect of alkaline and alkaline-earth elements on Zn biosorption by *Sargassum sp.*

This different behavior 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 (1989) 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 19 it could be observed that the biomass, compared to a commercial activated carbon, presented a superior performance, in the same experimental conditions, and based in the metals concentrations listed in Table 2. 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.
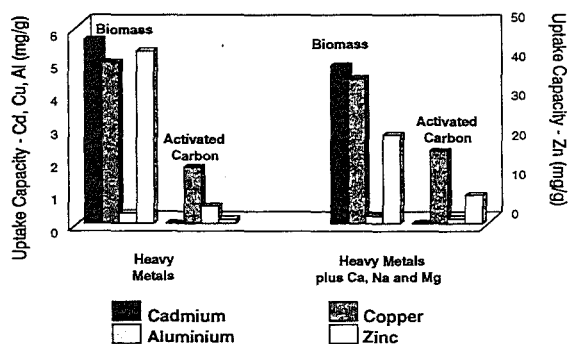
Figure 19 - Comparison between the biomass of *Sargassum sp.* and commercial activated carbon for the biosorption of heavy metals.

4.7 Kinetic Batch Studies with Natural Effluent - Winter Time

Figure 20 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.
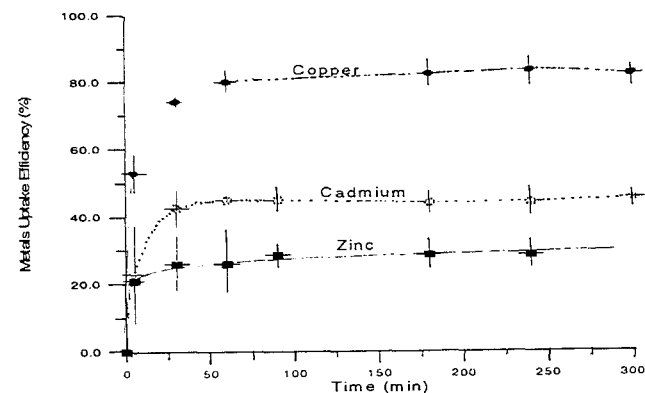
Figure 20 - Kinetic behavior of Cu, Cd and Zn during biosorption by *Sargassum sp.*

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 20 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 21 indicates a similar behavior 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.
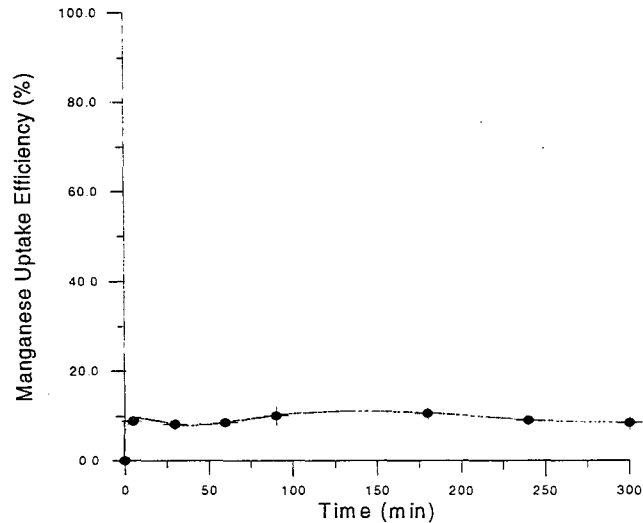
Figure 21 - Kinetic behavior of Mn during biosorption by *Sargassum sp.*

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 (da Costa & de França, 1994).

A similar kinetic behavior was also observed for calcium, magnesium and sodium, if one only considers the aspect concerning the solid/liquid equilibrium (Figures 22, 23 and 24).
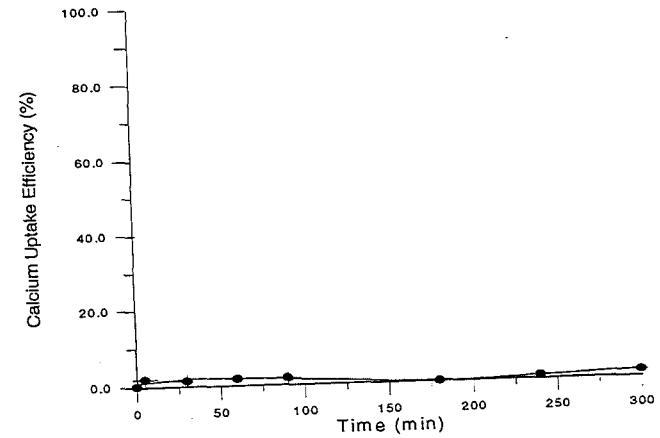
Figure 22 - Kinetic behavior of Ca during biosorption by *Sargassum sp.*
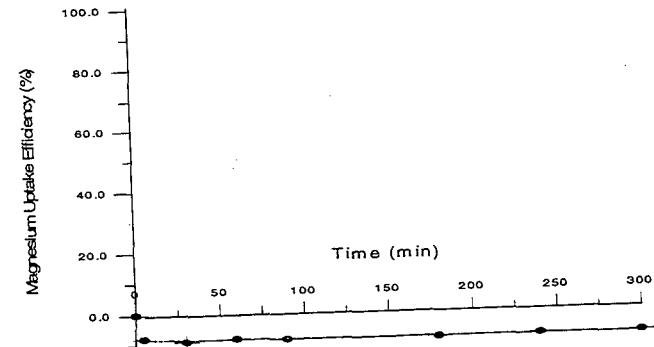
Figure 23 - Kinetic behavior of Mg during biosorption by *Sargassum sp.*
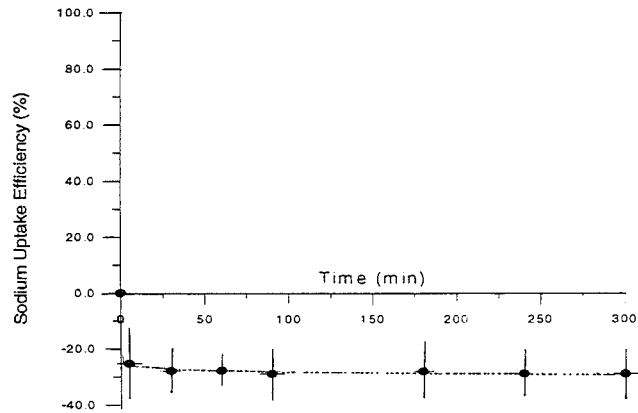
Figure 24 - Kinetic behavior of Na during biosorption by
Sargassum sp.

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 in the chemical composition of the brown algae. The main structural polysaccharides from these algae, as previously mentioned, are the alginates, a dimmer 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.

4.8 Continuous Biosorption (Natural Effluent) - Winter Time

Figure 25 shows the results of cadmium biosorption obtained during the continuous operation of the laboratory system.
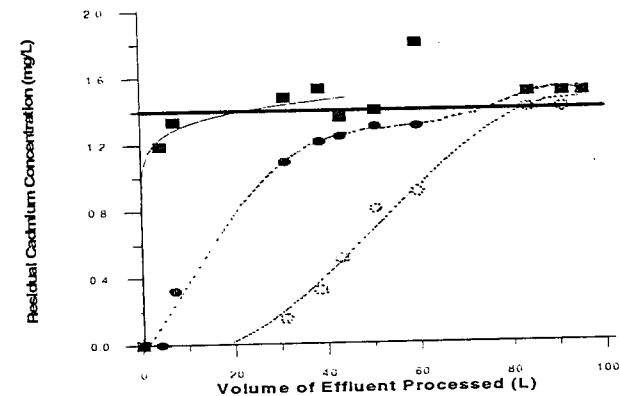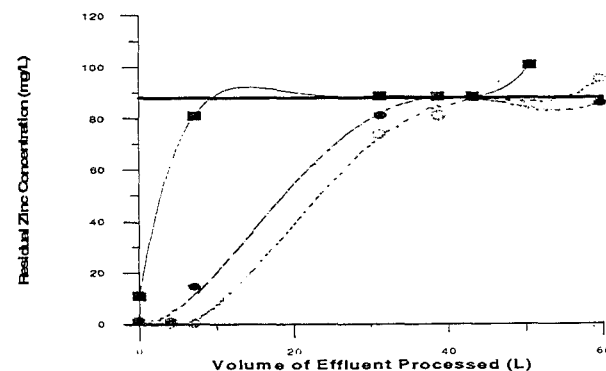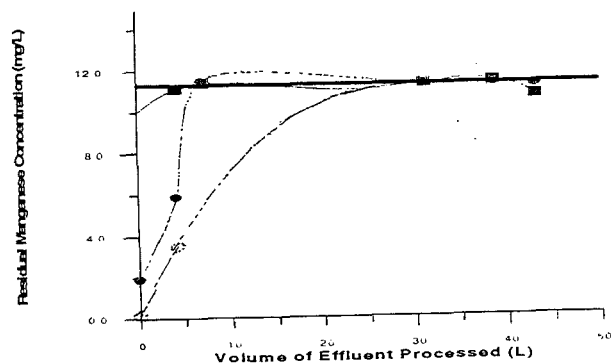

Figure 25 - Cd biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

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 behavior 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):

Equation 1:

$$y = \int_{0}^{82} (-5.33e-6x^3 + 8.19e-4x^2 - 1.47e-2x + 0.03)dx$$

An analogous behavior was observed during zinc biosorption (Figure 26).

Figure 26 - Zn biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

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.

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

Equation 2:

$$y = \int_{0}^{45} (3.48e-7x^5 + 1.67e-5x^4 - 6.38e-3x^3 + 0.304x^2 - 1.84x + 1.30)dx$$

The less effectively biosorbed metal was manganese (Figure 27), 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.

Figure 27 - Mn biosorption during continuous operation of the laboratory system (Legend - Square: Sampler #1; Dot: Sampler #2; Circle: Sampler #3)

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

Equation 3:

$$y = \int_{0}^{32} (2.35e-4x^3 - 2.60e-2x^2 + 0.94x + 0.08)dx$$

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 (da Costa & de França, 1994).

The next results (Figure 28), show the behavior of alkaline and alkaline-earth elements during the biosorption process.
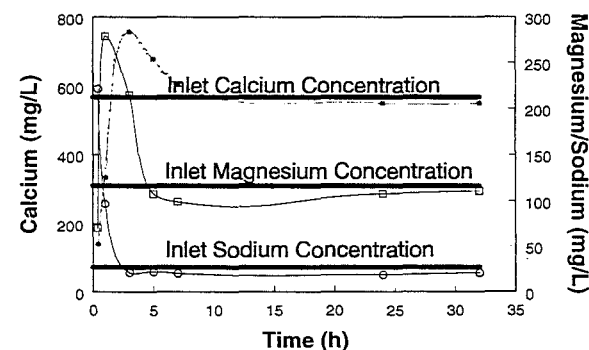
Figure 28 - Ca, Mg and Na biosorption during continuous operation of the laboratory system

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.

Table 7 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 7 - 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, however, the presence of high concentrations of alkaline and alkaline-earth elements the limiting step of the biosorption. Other tests, conducted in the absence of alkaline and alkaline-earth elements in solution, presented much higher efficiency values (da Costa & de França, 1994). 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.

4.9 Desorption Studies - Multi-ion Situation

In a first step it was our purpose to search for suitable eluting agents for cadmium, zinc and copper, biosorbed by the seaweed. This evaluation has been done based on the efficiency of the elution, re-loading capacity and loss of biological mass, after the elution cycle. The results are presented in Figures 29, 30 and 31, respectively. An analysis of Figure 29, efficiency of elution for a single cycle for cadmium, copper and zinc, indicates the remarkable ability of HCl 0.1 M

solution to desorb all the metals, with elution efficiencies around 90 % for all the metals. K_2SO_4 (0.5 M), $MgSO_4$ (0.5M), Na_2SO_4 (0.5M) solutions also proved to be very efficient in the desorption of cadmium and zinc, being the desorption of these elements also around 90 %.
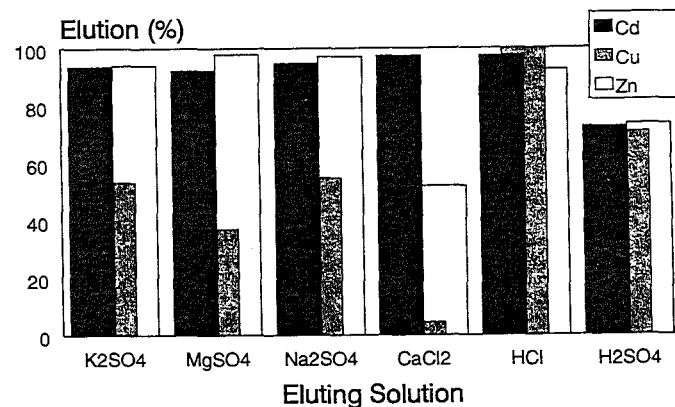
Solutions: K_2SO_4 (0.5 M), $MgSO_4$ (0.5 M), Na_2SO_4 (0.5 M), $CaCl_2$ (0.1 M), HCl (0.1 M), H_2SO_4 (0.1 M). Contact time: 16 hours.

Figure 29 - Cd, Cu and Zn desorption efficiencies.

Even though the desorption efficiency is an important parameter to be considered, an evaluation a little bit more complex must be done, considering the loss of biomass due to the attack promoted by the different solutions, as well as the ability to reuse the biomass in additional biosorption/desorption cycles. Figures 30 and 31 show the results of the re-loading of the biomass and the loss of biomass, respectively.

From the literature, HCl and H_2SO_4 solutions are presented as excellent desorption agents for the recovery of cations sorbed by biomasses (Tsezos, 1984; Farrah & Pickering, 1978). However, these acids can damage the structure of the biomass, thus preventing its re-use in additional biosorption cycles. This attack is responsible, in general, for a partial degradation of the polysaccharides from the biomass, thus destroying some of the

binding sites. This fact is clearly illustrated in Figures 30 and 31. Even though cadmium, copper and zinc were efficiently eluted with HCl solution, the biomass presented a decreasing uptake capacity in a further cycle. This decrease corresponded to 63% and 50%, respectively for cadmium and zinc, in comparison to the first uptake cycle; beyond this a loss of 30% in the mass of adsorbent has been observed.

When the biomass was washed with H_2SO_4 solution it kept its uptake capacity for copper, however, for zinc it was only 20%; here also, a marked loss of adsorbent has been observed.
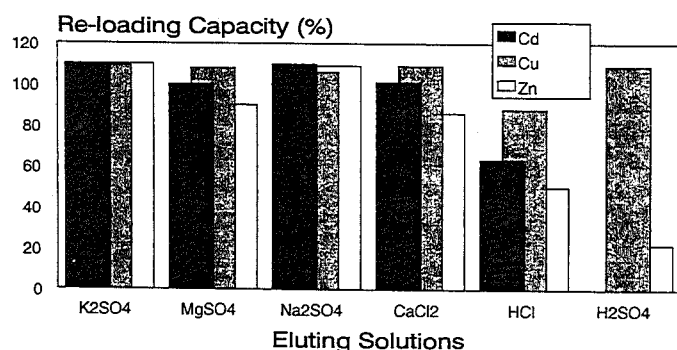
Solutions: K_2SO_4 (0.5 M), $MgSO_4$ (0.5 M), Na_2SO_4 (0.5 M), $CaCl_2$ (0.1 M), HCl (0.1 M), H_2SO_4 (0.1 M). Contact time: 60 minutes.

Figure 30 - Cd, Cu and Zn biosorption by *Sargassum sp.* after the first cycle. Percent values correspond to the uptake from the first cycle.
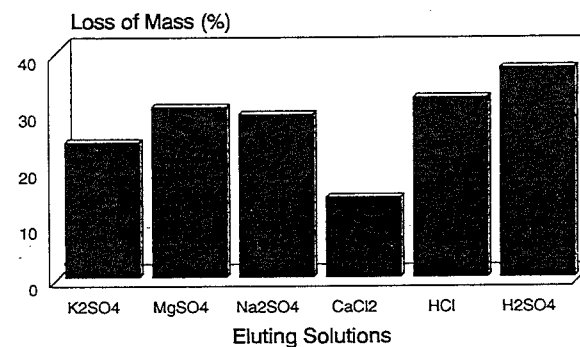
Solutions: K_2SO_4 (0.5 M), $MgSO_4$ (0.5 M), Na_2SO_4 (0.5 M), $CaCl_2$ (0.1 M), HCl (0.1 M), H_2SO_4 (0.1 M).

Figure 31 - Loss of biomass after elution.

The use of alkaline and alkaline-earth elements solution, such as Ca, K, Na and Mg is considered as a good alternative, as, from the literature, these elements can conduct ion-exchange reactions during the biosorption process, thus, regenerating the biomass for future use.

From Figures 30 and 31, the elution conducted with K_2SO_4 (0.5 M) and Na_2SO_4 (0.5 M) solutions presented uptake levels slightly higher (10%) after a first biosorption/desorption cycle. However, they also presented a marked loss of the biomass. In the case of $CaCl_2$ (0.1 M) solution, the biomass kept its uptake capacity for cadmium, a slight increase for copper (10%) and a slight decrease for zinc (15%). Among all the solutions tested, this one presented the least pronounced biomass loss.

The biomass, eluted with a $MgSO_4$ (0.5 M) solution, presented a similar behavior in comparison to $CaCl_2$ (0.1 M) solution, however, with a great loss of biosorbent, 30%.

Based on these results and in the costs of the reagents used, two solutions were selected for desorption of the heavy metals: Na_2SO_4 (0.5 M), with a high desorption efficiency,

around 95% for all three metals, and also keeping the re-loading capacity of the biomass; and, $CaCl_2$ (0.1 M), which kept the uptake capacity and a small loss of biosorbent seaweed.

With the eluting solutions selected, some kinetic studies were done, as well as re-loading capacities tests with the biomass for a number of sorption/desorption cycles. In this step the loading of the biomass was done with a multimetal concentrated solution (200 mg/L for each metal).

The kinetics of the desorption is shown in Figures 32 and 33, revealing that the desorption equilibrium is established in a few minutes for all the metals. After 10 minutes of contact, the maximum desorption was achieved for copper, either by using Na_2SO_4 (0.5 M) solution or $CaCl_2$ (0.1 M) solution. For cadmium and zinc, an extended period of contact was needed for both solutions.
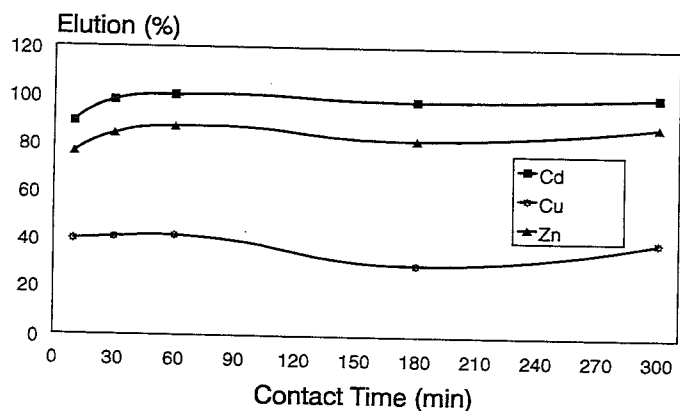
Solution: $CaCl_2$ 0.1 M, pH < 3,0.

Figure 32 - Cd, Cu and Zn desorption kinetics.
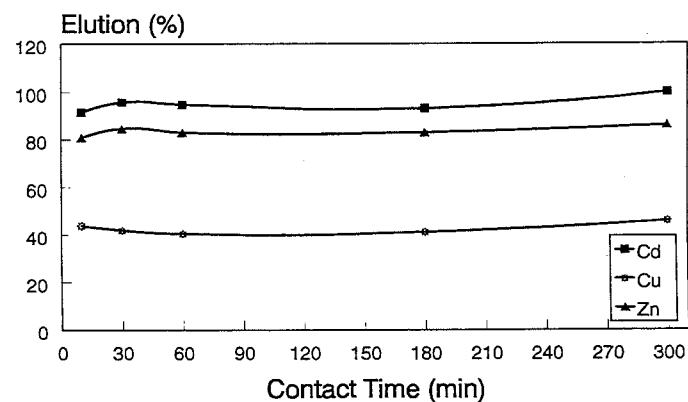
Eluent solution: Na_2SO_4 0.5 M, pH < 3,0

Figure 33 - Cd, Cu and Zn desorption kinetics.

These results indicate that equilibrium is rapidly achieved, showing the possibility of doing the elution directly in a continuous system, without the need to stop the process to do so. An evaluation on the behavior of the biomass, regarding re-loading with metals and desorption in several sorption/desorption cycles is presented in Figures 34 and 35. Figures 34 and 35 show the results of the $CaCl_2$ (0.1 M) eluted biomass, during 20 cycles of biosorption/desorption. The contact time was reduced to 60 minutes, based in previous kinetic investigations.

As can be observed from Figure 34, the desorption efficiency, regarding the three metals, increase after the first cycle, with a slight decrease from the tenth cycle. It must be emphasized the substantial desorption of copper, whose levels were kept between 80% and 100% from the third to the twentieth cycle.
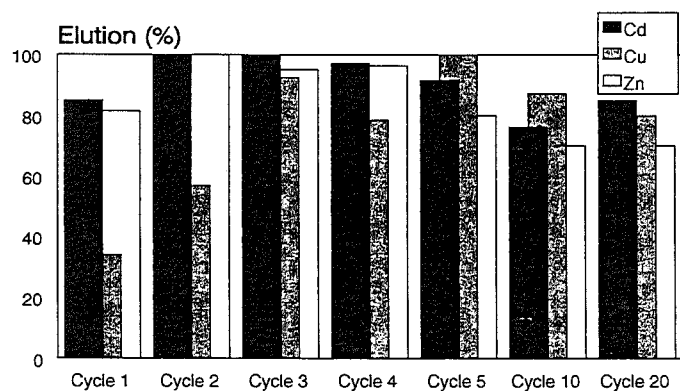
Elution (%)

Eluting solution: CaCl$_2$ (0.1 M/pH < 3,0). Contact time 60 minutes.

Figure 34 - Cd, Cu and Zn desorption.

The re-loading capacity (Figure 35) was decreased in the second and third cycles, being kept constant until the twentieth cycle: 21 mg Cu/ g biomass, 14 mg Cd/ g biomass and 9 mg Zn/ g biomass.

Loading (mg metal/g biomass)
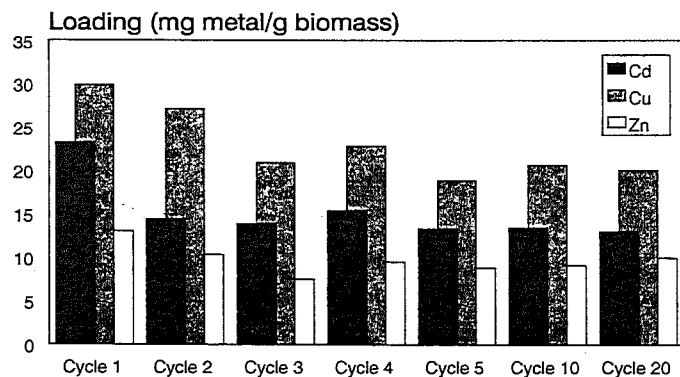
Figure 35 - Cd, Cu and Zn desorption cycles with CaCl$_2$ (0.1 M/pH < 3,0) as eluting solution. Contact time: 60 minutes.

Figures 36 and 37 present similar results with the use of Na$_2$SO$_4$ (0.5 M) solution. Contact time was reduced to 30 minutes based on previous kinetic studies.

From Figures 36 and 37 it can be detached a similar behavior as observed with the use of CaCl$_2$ solution. Copper desorption levels were substantially higher from the first cycle, reaching 95% in further cycles.
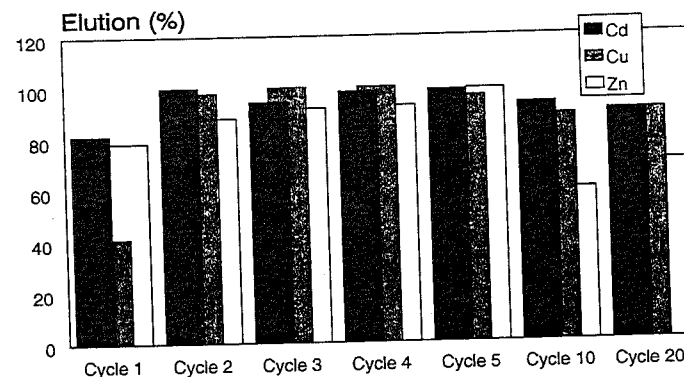
Elution (%)

Figure 36 - Cd, Cu and Zn desorption efficiencies. eluting solution: Na$_2$SO$_4$ (0.5 M/pH < 3,0). Contact time: 30 minutes.

Loading (mg metal/g biomass)
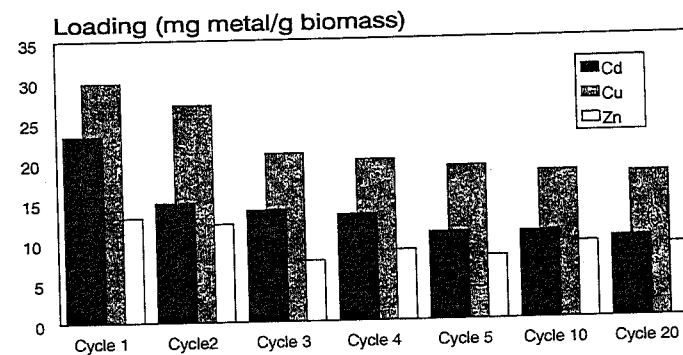
Figure 37 - Cd, Cu and Zn desorption efficiency with Na$_2$SO$_4$ (0.5 M/pH < 3,0). Contact time: 30 minutes.

The loss of biosorbent during the cycles was also observed, and the results are presented in Figure 38.

As can be observed, the biomass eluted with Na_2SO_4 presented a much higher loss, achieving 60% of loss in comparison to 17% of loss for the biomass eluted with $CaCl_2$.
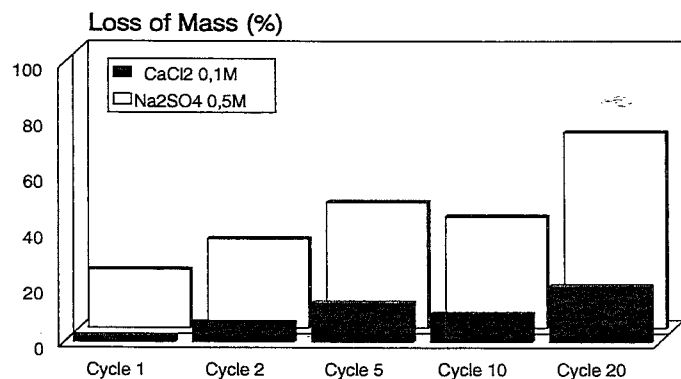
Figure 38 - Loss of *Sargassum sp.* biomass after twenty sorption/desorption cycles

Beyond the remarkable loss of mass observed, the biomass, after elution with Na_2SO_4 presented a paste-like aspect, differently from what was observed with $CaCl_2$, whose structural integrity was kept. It can be concluded that $CaCl_2$ solution is the most suitable metal desorption agent for the process, allowing the re-use of the biomass and with a reasonable loss, compatible with the operation.

4.10.1   Adsorption studies with the treated biomass-Cadmium adsorption isotherms with cross-linked biomass

Cadmium adsorption isotherms, obtained with native and immobilized (formaldehyde and glutaraldehyde) *Sargassum sp.* are presented in Figure 39.
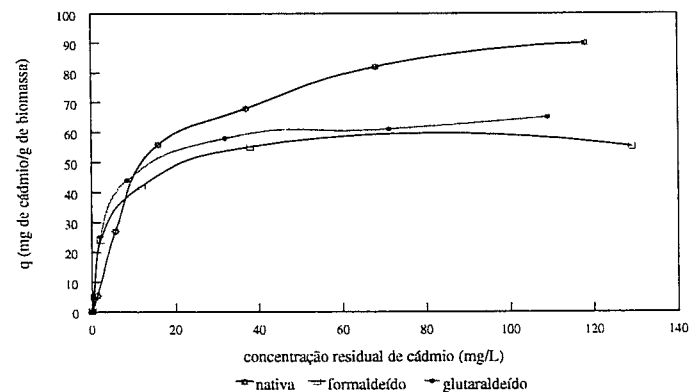
Figure 39 - Cd adsorption isotherms, at 29°C, for native and chemically treated *Sargassum sp.*

From Figure 39 it is observed that *Sargassum sp.* presented a cadmium uptake capacity around 90 mg metal/g biomass, for the native sample, demonstrating to be a good cadmium biosorber. However, when the biomass was treated with glutaraldehyde and formaldehyde, the seaweed presented a decreased cadmium uptake capacity, in comparison with the native biomass. Both isotherms, however, were closely similar for the treated biomasses. The maximum cadmium uptake capacity was around 60 mg cadmium/g biomass. This decrease, however, was associated to an enhancement in the mechanical strength of the *Sargassum sp.* biomass.

4.10.2 Copper adsorption isotherms with cross-linked biomass

Copper adsorption isotherms for *Sargassum sp.*, native, formaldehyde and glutaraldehyde treated are presented in Figure 40.
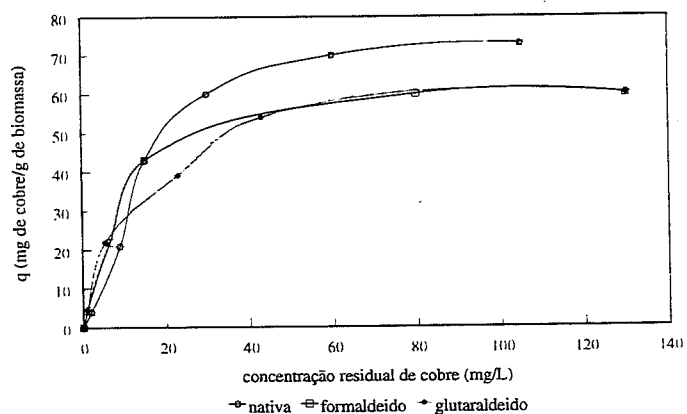
Figure 40 - Cu adsorption isotherms, at 29 °C, for native and chemically treated *Sargassum sp.*

The results also reveal a decrease in copper uptake capacity, not so pronounced as previously observed for cadmium (70 mg copper/g biomass in comparison to 60 mg copper/g biomass). Again, an improvement in the hardness of the biomass was observed.

4.10.3 Zinc adsorption isotherms with cross-linked biomass

Accordingly, zinc adsorption isotherms are presented in Figure 41 for the same protocol of experiments.

From this Figure 41 it is possible to check that the maximum uptake capacity, for zinc, decreased from 50 to 36 mg zinc/g

biomass, the same behavior previously observed for cadmium and zinc.

The extent to which the cross-linking treatments jeopardized the structure of the seaweeds deserves intensive investigation, in order to select, in the near future, cross-linking agents more suitable for the process, but with equivalent enhancement in the physical structure of selected biomasses.
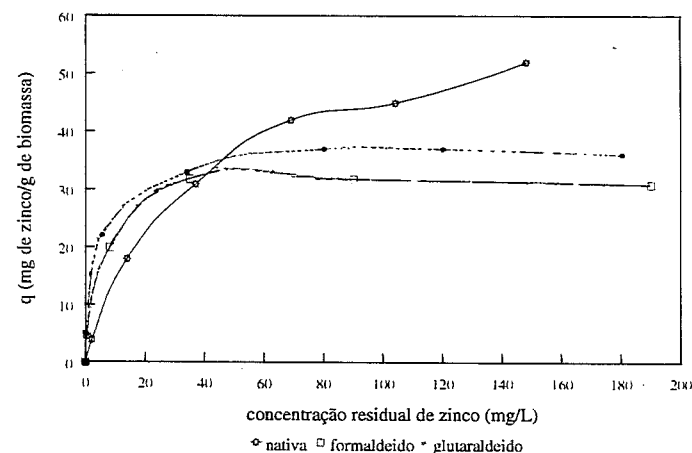
Figure 41 - Zn adsorption isotherms, at 29° C, for native and chemically treated *Sargassum sp.*

5. SCALE-UP AND ECONOMIC EVALUATION

The economic evaluation of the process will be performed based on the composition of the effluent from "Companhia Paraibuna de Metais", as most of the experiments previously done considered its composition. One has to have in mind that a wide variability in its composition is observed during summer and winter time, mainly due to evaporation and precipitation during summer and precipitation periods. These differences are reflected in their heavy metals content, being not so important their alkaline and alkaline-earth elements content in the different seasons. For the purpose of scale-up and economic evaluation the average composition of the effluent during summer will be considered, because it is much more concentrated in heavy metals than the equivalent winter effluent.

The final solution to be treated by biosorption is placed in a stabilization lagoon and the treatment unit will consider the treatment of 1.0 m^3/day, pumped from the stabilization pond to the heavy metals treatment unit. For the design of a pilot unit for this purpose, several assumptions must be done, as not all the information are readily available or easily obtained.

Beyond some theoretical considerations, it will be designed a treatment unit consisting of fixed-bed reactors for the treatment of a heavy metal-containing effluent and the complete effluent from "Paraibuna de Metais"; that means, some calculations will be performed considering solely the presence of heavy metals, while some other will consider the whole spectrum of metals present in the effluent.

5.1 Case 1: presence of heavy metal ions only

The first assumption to be done is that the concentration of heavy metals is the same as listed in Table 2, and, based on the adsorption results reported in Figure 19 (considering only 1 Liter of heavy metals solution):

[Zn] = 385 mg/L, 25% adsorption, 96.2 mg Zn recovered

[Cd] = 18 mg/L, 55% adsorption, 9.9 mg Cd recovered

[Cu] = 10.1 mg/L, 92% adsorption, 9.3 mg Cu recovered

[Al] = 1.2 mg/L, 68% adsorption, 0.8 mg Al recovered.

It is important to remember that these adsorption rates were achieved for a 2 g/L fixed concentration of biomass. For other biomass concentrations, different solid/liquid equilibria will be stablished, but, for these preliminary calculations, these rates will be considered.

From Figure 19, it can be calculated the loading capacity of the biomass, and this will be done considering 1 Liter of metals solution and the total mass of metal recovered, not the individual rates of uptake.

The total mass of heavy metals recovered was 116.2 mg (for 1 Liter); so, the total loading capacity is equivalent to 58.1 mg heavy metals/g biomass. However, this loading capacity did not promote a complete removal of the heavy metals. As a matter of convenience for the calculation, the complete removal (or adsorption) will be considered as the ideal treatment. Thus, 100% of heavy metals recovery will be the basis for the calculation. One liter of the heavy metals solution contains 414.3 mg of heavy metals (for 1 Liter of solution); so:

58.1 mg metals ——— 1 g biomass

414.3 mg metals ——— x

x = 7.13 g biomass

The above value is the theoretical mass of *Sargassum* sp. needed to treat, with 100% efficiency, 1 Liter of heavy metals solution, in the concentrations found in the summer effluent. However, the pilot unit will be designed to treat 1 m^3/day, so:

7.13 g biomass —— 1 L solution

y —— 1,000 L solution

y = 7,130 g = 7.1 kg biomass

The above value is the amount of biomass needed to accumulate the heavy metal content from 1 m^3 of solution.

If we consider that $CaCl_2$ 0.1 N will be used as the desorbing agent after the saturation of the biomass, it can be used during 20 biosorption/desorption cycles, with à loss of biomass around 20% (Figure 38). So, it is necessary to have an overestimation of the amount of sorbent to be used, taking into account this loss, which gives an amount of **8.52 kg biomass.**

If, however, Na_2SO_4 0.5 M is used, the loss of biomass during 20 biosorption/desorption cycles is much greater, around 70%. Thus, **14.48 kg biomass** must be used in the reactor.

Another consideration must be done, regarding the efficiency of the elution; the elution rates obtained for the desorption of the heavy metals are around 90%, so, from cycle to cycle 10% of metals remain on the biomass. That means that each sorption cycle starts with a pre-loaded biomass. So, it must be considered that a certain portion of the biomass in the reactor will not participate in the process. It is thus advisable to have a 10% increase in the amount of biomass due to pre-loading, and also a 10% increase to ensure any disturb in the process.

This way, considering $CaCl_2$ 0.1 N as desorbing agent **10.22 kg biomass** are needed while for Na_2SO_4 0.5 N as desorbing agent **17.37 kg biomass** must be used.

These amounts of biomass would be sufficient to treat 1 m^3/day of the heavy metals solution, during 20 cycles taking into account partial desorption of the metals and also the losses of

sorbent. That means that in 24 hours of continuous operation the bioreactor would be saturated giving place to the desorption step.

As the adsorption and desorption cycles are usually short-term cycles, it is advisable to have more than one reactor for the adsorption, including a stand-by reactor for continuous operation of the treatment unit.

In order to predict the design of the reactor, some variables must be considered, such as:

(i) The amount of fluid per unit time;

(ii) The amount of metals to be adsorbed;

(iii) The uptake capacity of the adsorbent;

(iv) The allowable pressure drop through the bed;

(v) The duration of the adsorption cycle; and,

(vi) The time required to reactivate the adsorbent.

Even though all these parameters markedly affect the design of the reactor (usually a fixed-bed column), parameters (ii), (iii) and (v) affect the amount of adsorbent to be used. On the other hand, parameters (i) and (iv) affect the diameter and depth of the adsorbing bed.

The duration of the cycles of adsorption and desorption can be determined by an economical balance and mainly based on previous judgement or experience in the process. In the present case, solid/liquid equilibria reported from batch experiments will be considered, even though it is known that different solid/liquid ratios affect this parameter.

As regards the desorption step, if the reactivation time is smaller than one adsorption cycle, then only 50% of the adsorbers can be on stream in a continuous operation. However, if the bed is reactivated in less than one-third of the time required for adsorption, then, 3 to 4 adsorbers can be on stream (supposing they are of the same design).

From previous experience, the desorption step is much faster than the adsorption step; thus, if one considers the operation of a bioreactor plus a stand-by reactor, just one can be used for adsorption. When the former saturates with heavy metals, then the operation is transferred to the stand-by reactor, while desorption of heavy metals is accomplished.

Returning to the calculations, it is the purpose of the scale-up to treat 1 m³/day of the stored effluent. This way:

1,000 L effluent —— 24 hours

z —— 1 hour

z = 41.6 L

In order to achieve the goal of treating 1 m3/day, it is necessary to treat 41.6 L/hour. From laboratory results, it is known that 70 g of the *Sargassum* sp. biomass can completely fill in a bioreactor with a volume of 4.85 L, with a good packing and without the creation of preferential chanelling. In order to have the dimensions of the reactor and the residence time in the reactor the following calculations must be done:

70 g biomass —— 4.85 L

10,220 g biomass* —— w

w = 708 L

* Considering $CaCl_2$ 0.1 N as desorbing agent

So, the reactor must have a total volume of 708 L to support 10.2 kg of the biomass. With this number, it is possible to estimate the radius and the Height of the column, keeping the same height/diameter ratio previously used, equal to 5.0.

$V = \pi R^2 H$, where

V = Volume of the reactor

R = Radius of the basis of the reactor

H = Height of the reactor.

Thus,

$708 \text{ dm}^3 = \pi R^2 (10R)$

R = 2.8 dm ⇨ R = 28 cm ⇨ D = 56 cm (where D = internal diameter)

As H = 5D ⇨ H = 280 cm.

However, the density of the biomass has to be considered, in order to estimate the working volume of the reactor. From previous experimentations it was observed that 18 g of *Sargassum* sp. biomass displaced 1 L of solution inside a reactor, considering its very high swelling capacity. Thus:

18 g biomass —— 1 L

10,220 g biomass —— k

k = 567 L

Based on this displacement, that corresponds to the density of the biomass, the working volume of the reactor is:

V = (708 - 567) L = **140 L**

As it is expected to have a flow-rate of 41.6 L/hour, and based on the working volume of 140 L, the residence time of the solution in the reactor is **3.36 hours**. This is far beyond of what is needed for a contact time for an effective biosorption process.

There are some viable alternatives for not misusing the uptake capacity of the biomass or not to have an overestimated energy consumption: Instead of 3.36 hours of residence time a 10 min contact time can be used, based on previous experimentations with *Sargassum* sp. biomass. This means that a much higher flow-rate can be used, instead of 41.6 L/hour, predicted in the beginning of these calculationsn; another alternative is to treat a much higher volume of solution per day, instead of 1 m³/day. As a last suggestion, instead of using a big bioreactor, several smaller bioreactors could be used, performing together the total volume of 708 L and keeping the same working volume, for the whole adsorption system. This

seems to be a feasible alternative that can decrease energy costs due to the need of less potent pumps to feed the effluent and also can help in the desorption step, while several adsorbing columns can continue the treatment operation.

All these alternatives deserve further investigation, as well as a detailed study on the hydraulic conditions that will govern the system. However, this preliminary approach already considers accessory designs.

Now, another set of similar calculations can be performed considering the use of Na_2SO_4 0.5 M as desorbing agent

70 g biomass —— 4.85 L

17,370 g biomass* —— w

w = 1203 L

* Considering Na_2SO_4 0.5 M as desorbing agent

So, the reactor must have a total volume of 1203 L to support 17.37 kg of the biomass. With this number, it is possible to estimate the radius and the height of the column, keeping the same height/diameter ratio previously used, equal to 5.0.

$V = \pi R^2 H$, where

V = Volume of the reactor

R = Radius of the basis of the reactor

H = Height of the reactor.

Thus,

$1203\ dm^3 = \pi R^2(10R)$

R = 3.4 dm $\Rightarrow$ R = 34 cm $\Rightarrow$ D = 68 cm (where D = internal diameter)

As H = 5D $\Rightarrow$ H = 340 cm.

However, the density of the biomass has to be considered, in order to estimate the working volume of the reactor. From previous experimentations it was observed that 18 g of *Sargassum* sp. biomass displaced 1 L of solution inside a reactor, considering its very high swelling capacity. Thus:

18 g biomass —— 1 L

17,370 g biomass —— k

k = 965 L

Based on this displacement, that corresponds to the density of the biomass, the working volume of the reactor is:

V = (1203 - 965) L = **238 L**

As it is expected to have a flow-rate of 41.6 L/hour, and based on the working volume of 238 L, the residence time of the solution in the reactor is **5.72 hours**. This is far beyond of what is needed for a contact time for an effective biosorption process.

Analogously, alternative parameters must be considered such as an increase in the flow-rate or in the amount of solution to be treated daily.

5.2 Case 2: presence of heavy metal ions and alkaline/ alkaline-earth elements, in the concentration they are present in the effluent

The first assumption to be done is that the concentration of heavy metals is the same as listed in Table 2, and, based on the adsorption results reported in Figure 19 (considering only 1 Liter of heavy metals solution).

Here, the adsorption rates were also achieved for a 2 g/L fixed concentration of biomass. These rates will be considered.

[Zn] = 385 mg/L, 12,5% adsorption, 48.1 mg Zn recovered

[Cd] = 18 mg/L, 47.5% adsorption, 8.5 mg Cd recovered

[Cu] = 10.1 mg/L, 92% adsorption, 9.3 mg Cu recovered

[Al] = 1.2 mg/L, 30% adsorption, 0.4 mg Al recovered.

From Figure 19, it can be calculated the loading capacity of the biomass, and this will be done considering 1 Liter of metals solution and the total mass of metal recovered, not the individual rates of uptake.

The total mass of heavy metals recovered was 66.3 mg (for 1 Liter); so, the total loading capacity is equivalent to 33.2 mg heavy metals/g biomass. However, this loading capacity did not promote a complete removal of the heavy metals. As a matter of convenience for the calculation, the complete removal (or adsorption) will be considered as the ideal treatment. Thus, 100% of heavy metals recovery will be the basis for the calculation.

One liter of the heavy metals solution contains 414.3 mg of heavy metals (for 1 Liter of solution); so:

33.2 mg metals ——— 1 g biomass

414.3 mg metals ——— x .

x = 12.47 g biomass

The above value is the theoretical mass of *Sargassum* sp. needed to treat, with 100% efficiency, 1 Liter of heavy metals solution, in the concentrations found in the summer effluent. However, the pilot unit will be designed to treat 1 m³/day, so:

12.47 g biomass ——— 1 L solution

y ——— 1,000 L solution

y = 12,470 g = 12.47 kg biomass

The above value is the amount of biomass needed to accumulate the heavy metal content from 1 m³ of solution.

If we consider that $CaCl_2$ 0.1 N will be used as the desorbing agent after the saturation of the biomass, it can be used during 20 biosorption/desorption cycles, with a loss of biomass around 20% (Figure 38). So, it is necessary to have an overestimation of the amount of sorbent to be used, taking into account this loss, which gives an amount of **14.96 kg biomass**.

If, however, Na_2SO_4 0.5 M is used, the loss of biomass during 20 biosorption/desorption cycles is much greater, around 70%. Thus, **21.19 kg biomass** must be used in the reactor.

Another consideration must be done, regarding the efficiency of the elution; the elution rates obtained for the desorption of the heavy metals are around 90%, so, from cycle to cycle 10% of metals remain on the biomass. That means that each sorption cycle starts with a pre-loaded biomass. So, it must be considered that a certain portion of the biomass in the reactor will not participate in the process. It is thus advisable to have a 10% increase in the amount of biomass due to pre-loading, and also a 10% increase to ensure any disturb in the process.

This way, considering $CaCl_2$ 0.1 N as desorbing agent **17.95 kg biomass** are needed while for Na_2SO_4 0.5 N as desorbing agent **25.43 kg biomass** must be used.

These amounts of biomass would be sufficient to treat 1 m³/day of the complete effluent, during 20 cycles taking into account partial desorption of the metals and also the losses of sorbent. That means that in 24 hours of continuous operation the bioreactor would be saturated giving place to the desorption step.

As the adsorption and desorption cycles are usually short-term cycles, it is advisable to have more than one reactor for the adsorption, including a stand-by reactor for continuous operation of the treatment unit.

In order to predict the design of the reactor, some variables must be considered, such as:

(i) The amount of fluid per unit time;

(ii) The amount of metals to be adsorbed;

(iii) The uptake capacity of the adsorbent;

(iv) The allowable pressure drop through the bed;

(v) The duration of the adsorption cycle; and,

(vi) The time required to reactivate the adsorbent.

Even though all these parameters markedly affect the design of the reactor (usually a fixed-bed column), parameters (ii), (iii) and (v) affect the amount of adsorbent to be used. On the other hand, parameters (i) and (iv) affect the diameter and depth of the adsorbing bed.

The duration of the cycles of adsorption and desorption can be determined by an economical balance and mainly based on previous judgement or experience in the process. In the present case, solid/liquid equilibria reported from batch experiments will be considered, even though it is known that different solid/liquid ratios affect this parameter.

As regards the desorption step, if the reactivation time is smaller than one adsorption cycle, then only 50% of the adsorbers can be on stream in a continuous operation. However, if the bed is reactivated in less than one-third of the time required for adsorption, then, 3 to 4 adsorbers can be on stream (supposing they are of the same design).

From previous experience, the desorption step is much faster than the adsorption step; thus, if one considers the operation of a bioreactor plus a stand-by reactor, just one can be used for adsorption. When the former saturates with heavy metals, then the operation is transferred to the stand-by reactor, while desorption of heavy metals is accomplished.

Returning to the calculations, it is the purpose of the scale-up to treat 1 m^3/day of the stored effluent. This way:

1,000 L effluent —— 24 hours

z —— 1 hour

z = 41.6 L

In order to achieve the goal of treating 1 m3/day, it is necessary to treat 41.6 L/hour. From laboratory results, it is known that 70 g of the *Sargassum* sp. biomass can completely fill in a bioreactor with a volume of 4.85 L, with a good packing and without the creation of preferential chanelling. In order to have the dimensions of the reactor and the residence time in the reactor the following calculations must be done:

70 g biomass —— 4.85 L

17,950 g biomass* —— w

w = 1243 L

* Considering $CaCl_2$ 0.1 N as desorbing agent

So, the reactor must have a total volume of 1243 L to support 17.95 kg of the biomass. With this number, it is possible to estimate the radius and the Height of the column, keeping the same Height/diameter ratio previously used, equal to 5.0.

$V = \pi R^2 H$, where

V = Volume of the reactor

R = Radius of the basis of the reactor

H = Height of the reactor.

Thus,

$1243\ dm^3 = \pi R^2 (10R)$

R = 3.4 dm ⇨ R = 34 cm ⇨ D = 68 cm (where D = internal diameter)

As H = 5D ⇨ H = 340 cm.

6. COSTS

The associated costs include the construction of the column reactors (main column and a stand-by column), pump, desorbing agents and acquisition of the biomass. These costs constitute just a preliminary evaluation; costs associated to construction, maintenance as well as interests due to the possible recycling of the metals will not be here considered.

When made possible the costs were based on international prices. Costs associated to the acquisition of the reactors and biomass will be described based on the costs estimated by Brazilian companies.

Tables 8 and 9 present the estimated costs for the scaled-up unit using $CaCl_2$ 0.1 N or Na_2SO_4 0.5 M as desorbing agents, respectively, and considering the sole presence of heavy metals in solution, without the presence of alkaline and alkaline-earth elements in solution. For all the calculations, it was considered that the volume of desorbing solution is equal to two working volumes of the reactor, and considering that the biomass is going to be used for twenty times.

Table 8 - Estimated costs for the continuous unit (CaCl2 0.1N) - Heavy metals containing solution

Item	Unit Cost (US$)	Amount	Total Cost (US$)
Investments Costs			
Column acrylic reactor	1,000	2	2,000
Pump *			
Pump drive mod. H-07591-00	1,070	1	1,070
Tubing size 73, Tygon	200.00	1 set of 15.2 m	200.00
CaCl2 solution**	0.12/L	140 L	336.00
Biomass (seaweed)	1/kg	10.22 kg	10.22
Total			3,616.22

* Variable-flow modular pump system. Model Masterflex I/P, 0.2 to 13 lpm

** This value can reach US0.50/Kg depending on the season of the year

Table 9 - Estimated costs for the continuous unit (Na_2SO_4 0.5N) - heavy metals containing solution

Item	Unit Cost (US$)	Amount	Total Cost (US$)
Investments Costs			
Column acrylic reactor	1,000	2	2,000
Pump *			
Pump drive mod. H-07591-00	1,070	1	1,070
Tubing size 73, Tygon	200.00	1 set of 15.2 m	200.00
CaCl2 solution**	1.03/L	238 L	4,902.80
Biomass (seaweed)	1/kg	17.37 kg	17.37
Total			4,920.17

* Variable-flow modular pump system. Model Masterflex I/P, 0.2 to 13 lpm

** This value can reach US0.50/Kg depending on the season of the year

Tables 10 and 11 present the estimated costs for the scaled-up unit using $CaCl_2$ 0.1 N or Na_2SO_4 0.5 M as desorbing agents, respectively, and considering the whole effluent solution, that means, including alkaline and alkaline-earth elements.

Table 10 - Estimated costs for the continuous unit (CaCl2 0.1N) - Effluent

Item	Unit Cost (US$)	Amount	Total Cost (US$)
Investments Costs			
Column acrylic reactor	1,000	2	2,000
Pump *			
Pump drive model H-07591-00	1,070	1	1,070
Tubing size 73, Tygon	200.00	1 set of 15.2 m	200.00
CaCl2 solution**	0.12/L	246 L	590.40
Biomass (seaweed)	1/kg	17.95 kg	17.95
Total			3,878.35

* Variable-flow modular pump system. Model Masterflex I/P, 0.2 to 13 lpm

** This value can reach US0.50/Kg depending on the season of the year

Table 11 - Estimated costs for the continuous unit
(Na$_2$SO$_4$ 0.5N) - Effluent

Item	Unit Cost (US$)	Amount	Total Cost (US$)
Investments Costs			
Column acrylic reactor	1,000	2	2,000
Pump *			
Pump drive mod. H-07591-00	1,070	1	1,070
Tubing size 73, Tygon	200.00	1 set of 15.2 m	200.00
CaCl$_2$ solution**	1.03/L	349 L	7,189.40
Biomass (seaweed)	1/kg	25.43 kg	25.43
Total			10,484.83

* Variable-flow modular pump system. Model Masterflex I/P, 0.2 to 13 lpm

** This value can reach US0.50/Kg depending on the season of the year

From the previous calculations it can be seen that, when using CaCl$_2$ 0.1 N as desorbing agent, the increase in the price of the treatment is around 7% for treating heavy metals solution and the complete effluent. However, when using Na$_2$SO$_4$ 0.5 N as desorbing agent, this increase is around 113%, for the same operational conditions.

From these preliminary calculations it can be estimated the annual costs for the operation of a small treatment plant. The possible recycling of metals, that would markedly reduce the costs of the treatment plant, will not be here considered, deserving, however, special attention in order to reduce the costs of the treatment plant to close the circuit in order to reach a completely clean technology.

7. GENERAL CONCLUSIONS

The technique of biosorption able to separate heavy metals present in waste waters from other compounds in a reasonable manner. The exceptions are waste waters with high contents of alkaline-earth elements.

The enrichment factors observed indicate the possibility of integrating the process to a further step with a view of recycling the metals, for instance by electrochemical methods or selective precipitation. However, some drawbacks must be overcome, such as the deleterious effect of non-toxic elements on the uptake of heavy metals by the biomass and the need to improve the hardness of the biomass to support a greater number of biosorption and desorption cycles.

An important feature of the method is that there is no need for any pre-treatment, except, in certain cases, the need to adjust the pH. However, the possibility of recycling the metals gives the choice for a real decontamination of the environment. The „group selectivity" of the extraction permits a heavy metal recycling by electrochemical methods or selective precipitation. The advantages of electrochemistry is the missing of addition of any chemicals. Some preliminary work on electroprecipitation is done, but deserves a much deeper investigation to be linked at both methods.

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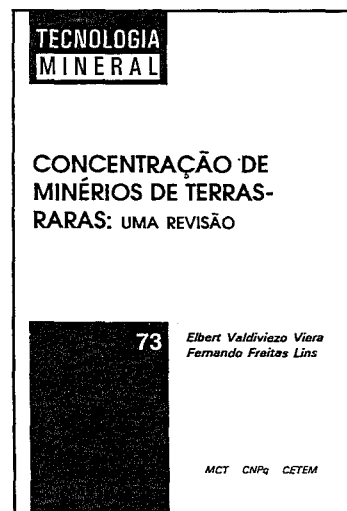
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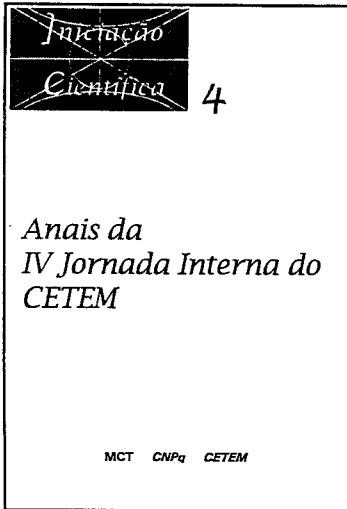
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