



Organic leaching and metal removal with *Sargassum filipendula*

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ABSTRACT. The biosorption process with algae is usually carried out with a concomitant alginate leaching process. Alginate is identified as the main functional group, responsible for generating the most active sites. Biomass chemical and thermal pretreatment is an alternative process for reducing organic leaching. Experiments with different pH rates were performed to analyze the leaching process of pretreated (contact time: 24, 48 and 72 hours) and non-pretreated biomass of *Sargassum filipendula*. The concentrations of calcium, magnesium, sodium and potassium ions, as well as total organic carbon, were determined to evaluate the biomass sorption capacity. Capacities of native and pretreated biomass to remove the heavy metal ions Cr and/or Ni from solutions of different concentrations were compared. The ion competition effect on removal capacity was studied. The biosorbent had a higher affinity with chromium ion.

Keywords: biosorption, chromium, nickel, seaweed, total organic carbon.

Lixiviação orgânica e remoção de metais usando *Sargassum filipendula*

RESUMO. A biossorção, utilizando algas marinhas, geralmente é acompanhada do processo de lixiviação de alginatos, identificado como o principal grupo funcional responsável por disponibilizar a maior parte dos sítios ativos. Uma alternativa para reduzir a lixiviação é o pré-tratamento químico e térmico da biomassa. Experimentos em diferentes pH foram realizados para analisar a lixiviação da biomassa de *Sargassum filipendula* pré-tratada (tempo contato: 24, 48 e 72-h) e *in natura*. As concentrações dos íons cálcio, magnésio, sódio e potássio bem como do carbono orgânico total foram determinados para avaliar a capacidade de sorção da biomassa. A capacidade da biomassa *in natura* e pré-tratada em remover os íons cromo e/ou níquel nas diferentes concentrações de soluções foram comparadas. O efeito de competição entre os íons foi estudado em relação à capacidade de remoção, apresentando o biossorvente maior afinidade pelo íon cromo em solução.

Palavras-chave: biossorção, cromo, níquel, alga marinha, carbono orgânico total.

Introduction

Many effluents contain several metallic species that must be removed before disposal in the environment. Studies have shown that the biosorption process, which uses materials of biological origin as adsorbents, such as bacteria, fungi and algae, for the passive removal of diverse metallic ions, is an efficient and low-cost technology compared when to conventional processes (VOLESKY, 1990). The biosorption process may combine one or more of the given mechanisms: ion exchange, complexation, physical and/or chemical adsorption, coordination, quelation and inorganic micro-precipitation (SÂG; KUTSAL, 1996). Recently, considerable attention has been directed towards the use of low-cost, naturally occurring biosorbents. Among these processes, ion exchange is considered the most important mechanism in the removal of metallic ions by algal biosorbents.

Aquatic contamination by heavy metals is extremely harmful since these elements are not degradable in the environment and may accumulate in living organisms (VEIT et al., 2009). Chromium is one of the most important heavy metals (Gazola et al., 2006) and wastewater discharge from electroplating industry contains concentrations of chromium, copper, zinc, nickel, cadmium and lead ions which cause serious water pollution (VEIT et al., 2009).

Brown seaweeds (*Phaeophyta*) species' ability in removing several metallic elements is attributed to the biochemical constituents of the cell wall, composed basically of three biopolymer types: alginate, fucoidan and cellulose, which provide several functional groups on the linking sites. According to Davis et al. (2003), the capacity of the brown seaweed for the removal of heavy metals from aqueous solutions is mainly due to the presence of carboxylic groups in the alginate

biopolymer. The alginate is usually found in the seaweed cell walls, as calcium, magnesium, sodium and potassium salts, derived from the interaction between alginic acid and alkaline or alkaline earth elements found in seawater (ANTUNES et al., 2003). According to Costa et al. (2001), these elements are efficient ion exchangers for the removal of heavy metals from aqueous solutions. Alginic acid is found in all brown seaweeds in amounts that range from 10% to 40% of algal dry weight (untreated), depending on the alga type and the environmental conditions that stimulate its biosynthesis (DAVIS et al., 2003).

Biosorption is generally accompanied by the alginate leaching process from the biomass structure into the solution (KRATOCHVIL; VOLESKY, 1998; FIGUEIRA et al., 2000), which decreases the biosorbent adsorption capacity. It is important to investigate alternatives to modify the biomass of marine algae before their use as biosorbents. Chemical and thermal pretreatment of the biomass is an effective method to reduce organic leaching from the biosorbent structure and to increase its stability (MATHEICKAL et al., 1999; MATHEICKAL; YU, 1999).

Current investigation (i) evaluates the effect of biomass pretreatment contact time (24, 48 and 72 hours) by using a calcium chloride solution; (ii) evaluates, in a batch operation, the effects of pretreatment on the biomass sorption capacity for metallic ions and the resultant organic leaching from the exposition of the biosorbent samples to acid media.

Material and methods

Biomass chemical pretreatment

The biomass in current assay was the brown seaweed *Sargassum filipendula*, commonly found along the Brazilian coast. The algae were washed with tap water, rinsed with deionized water and dried at 60°C for 24 hours. The biomass pretreatment was carried out as follows: 10 g of the native biomass were treated with 400 mL of 0.2 M CaCl_2 solution for three different contact times (24, 48 and 72 hours) under slow agitation at room temperature ($\cong 25^\circ\text{C}$). Initial pH of CaCl_2 solution was adjusted at 5.0 using 0.1N HCl solution. After every 24 hours of treatment, the biomass was submitted to successive washings with deionized water and placed again in contact with 400 mL of 0.2 M CaCl_2 solution. Finally, all pretreated biomass samples were dried at 60°C for 24 hours and stored.

Metallic solutions

The salts used in the preparation of metallic solutions were $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The concentrations of Cr and Ni used in the sorption experiments were 2 and 7 mequiv g L^{-1} (meq L^{-1}). The pH values were adjusted with 0.1 M NaOH, 0.1 N and 1.0 N HCl. All experiments were performed in duplicate and deionized water was used.

Identification of the metallic ions present in the native structure of the algae

To determine qualitative and quantitatively the metallic ions present in the biomass structure, an acid digestion of the native biomass (0.5 g) was performed on a hot plate by using 10 mL of HNO_3 and HCl 1:1 (v v^{-1}) mixture, followed by a slight evaporation (just a few milliliters). Concentrations of Zn, Ca, Fe, K, Cu, Cr, Ni, Mn, Mg and Na ions were determined by atomic absorption spectrophotometry (Varian Spectr AA-10 Plus).

Adsorption and release of metallic ions in aqueous acid media

Experiments were carried out with deionized water with and without initial pH correction (1.5, 2, 3, 4, 5 and 6) by using native and pretreated *S. filipendula* biomass (24, 48 and 72 hours treatments) with the following conditions: biomass concentration 3 g L^{-1} (dry basis), initial solution volume 100 mL, temperature 30°C and rotation speed 150 rpm. Tests were conducted during 100 hours and samples filtered with a 0.45 μm membrane filter (Millipore). Sorption experiments with Cr and Ni metallic ions and their mixtures were carried out in pH = 3 only for the 24h-pretreated biomass, using the same experimental conditions previously described. Chromium and nickel concentrations as well as those of calcium, magnesium, sodium and potassium ions released from the biomass structure were determined by atomic absorption spectrophotometry (Varian Spectr AA – 10 Plus). Solubility analyses were carried out by the measurement of total organic matter in the aqueous phase by Shimadzu TOC-5000A.

Scanning Electron Microscopy (SEM)

Samples of stipes and blades of the native and 24h-pretreated biomass were analyzed. Each sample (dry basis) was attached to a 10 mm diameter metal support. The sample on the support was then put into a sealed unit where coating of the biomass with gold took place under vacuum condition (Shimadzu IC-50 Ion Coater). Afterwards, the support containing the covered biomass was introduced into a scanning electron microscopy unit (Shimadzu SS-550 - Superscan Scanning Electron Microscope) and a certain pressure was set up. The biomass structure could then be observed in detail and the digital images of interest were obtained.

Results and discussion

An acid digestion of the native alga was performed to determine which metal ions were present in its structure. Results obtained by using *S. filipendula* biomass are shown in Table 1. Biomass contained a significant amount of calcium ion in its structure when compared to the other elements.

Table 1. Metallic ions present in the *Sargassum filipendula* biomass structure.

Metal ion	Quantity in the biomass (mg g ⁻¹ biomass)
Iron	0.93 ± 0.01
Magnesium	11.20 ± 0.76
Calcium	43.97 ± 1.69
Potassium	7.33 ± 0.05
Sodium	4.53 ± 0.19

The metals Cu, Cr, Ni, Zn and Mn were not detected in the samples.

The sequence found for the metal concentration present in the biomass structure was Ca > Mg > K > Na. Costa et al. (2001) obtained the same sequence of elements for *Sargassum* sp. biomass considering stipes and blades. However, rates obtained in current assay for the concentration of calcium (43.97 mg g⁻¹) and magnesium (11.20 mg g⁻¹) ions were higher than those of calcium (25.71 and 20.79 mg g⁻¹) and magnesium (5.96 and 5.51 mg g⁻¹) concentrations found by Costa et al. (2001) in the stipes and blades, respectively.

Organic leaching and ions released by native and pretreated biomass were investigated at the following initial pH rates in the aqueous medium: 1.5, 2, 3, 4, 5 and 6, which were adjusted with 0.1 and 1.0 N HCl and 0.1 M NaOH solutions. An experiment was also performed without pH correction. Figure 1 shows the organic leaching behavior of the native and pretreated biomass (24, 48 and 72h treatments) for different initial pH rates.

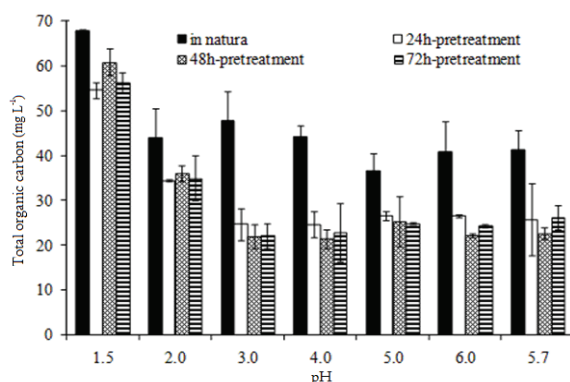


Figure 1. Total organic carbon leaching from native and pretreated biomass of *S. filipendula* at different pH rates in aqueous medium.

Since results of total organic carbon content for the pretreated biomass samples were lower when compared to those obtained for native biomass for

all pH rates, a leaching reduction was suggested. According to Matheickal et al. (1999), biomass stability means larger mechanical resistance and allows its use in fixed bed columns that operate in cycles. According to Leusch et al. (1995), the native biomass, when chemically reinforced, has improved mechanical stability and resistance to pressure, which is a requested condition for the application in sorption columns.

Figure 1 reveals that for the lowest pH values (1.5 and 2) the leaching degree was higher for the native and the pretreated biomass samples. Organic leaching probably occurred because of the change in alginate components solubility when exposed to strongly acidic medium, affecting the ionic biomass form as well as its chemical stability and physical properties. Total organic carbon reduction obtained in pretreated biomass samples is presented in Table 2, where the experimental rates obtained with the native biomass in each pH condition were chosen as reference. It is clear that in all the investigated cases the pretreatment process provided a significant leaching reduction especially in pH range between 3.0 and 4.0. The time increase of the biomass chemical treatment did not cause marked changes on the total organic carbon reduction, and therefore the 24h-treatment became more adequate.

Table 2. Percent reduction of total organic carbon obtained for the treated biomass in different acid solutions, related to results obtained with the native biomass in each condition.

pH	Treatment (hours)			
	24	48	72	Average
1.5	19.55	10.26	16.91	15.57 ± 4.79
2.0	21.85	18.27	20.44	20.19 ± 1.81
3.0	48.36	54.05	53.54	51.98 ± 3.15
4.0	44.28	51.46	48.34	48.03 ± 3.60
5.0	27.33	30.76	31.84	29.98 ± 2.35
6.0	34.85	45.49	40.26	40.20 ± 5.32
5.7	37.43	44.95	36.28	39.55 ± 4.71

Consequently, 24-h contact time pretreatment was selected for scanning electron microscopy experiments. The condition in which there was a great reduction of the total organic carbon in the leachate lay between pH 3 and 4; so pH 3 was chosen for the operational conditions to perform the chromium and nickel biosorption experiments (isolated or combined) by native or 24h-pretreated biomass. The concentrations of alkaline and alkaline earth elements released in the solution by native and pretreated biomass as a function of different pH values are provided in Figure 2 (a, b, c and d).

Results show that the native seaweed provided a significant alteration in the concentration of all ions (Ca²⁺, Mg²⁺, Na⁺ and K⁺), while the pretreated biomass samples had a significant alteration only in the calcium ion concentration.

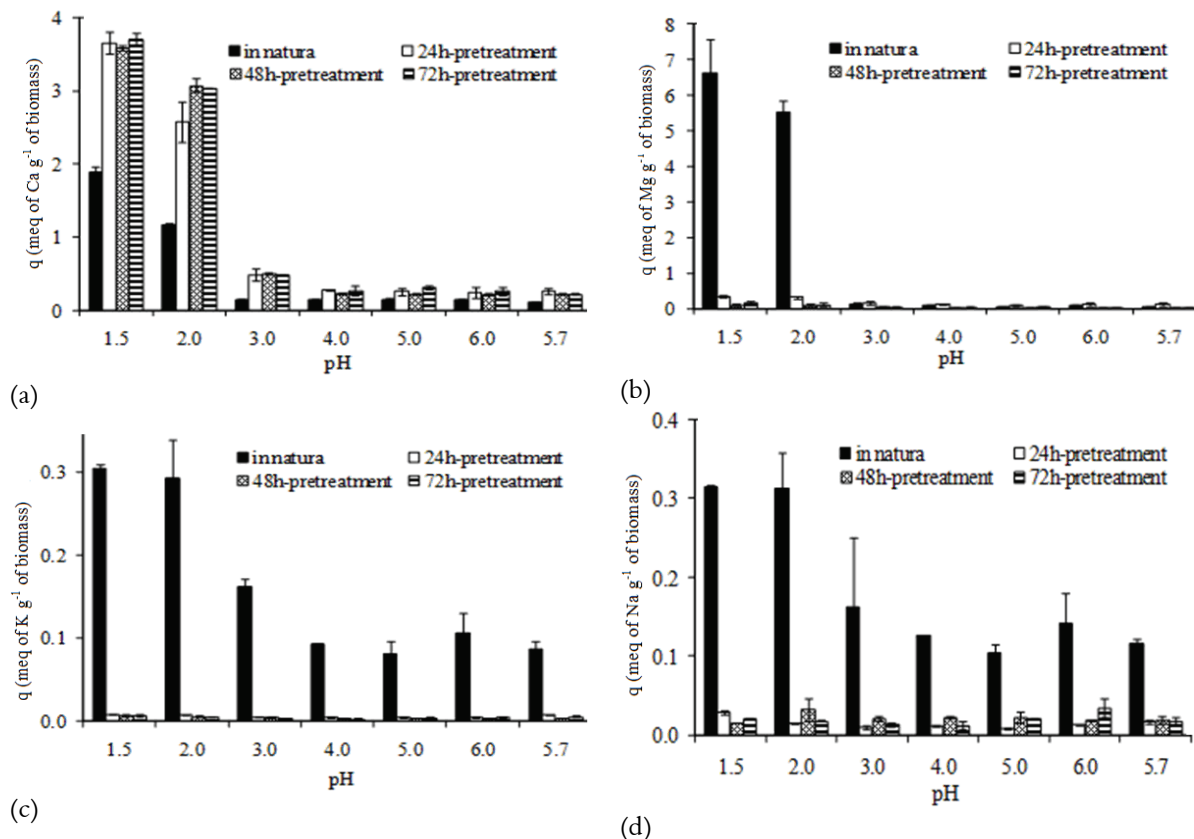


Figure 2. Quantity of ions released from the native and pretreated biomass at different pH values: (a) calcium, (b) magnesium, (c) potassium, (d) sodium.

These phenomena were expected because the untreated biomass contained the above-mentioned ions naturally linked to the acid functional groups, while the treated biomass presented chemical alterations generated by the contact with high calcium concentration solution, with most of its sites occupied by calcium ions. The native and the 24h-pretreated *Sargassum filipendula* biomass samples were analyzed by scanning electron microscopy and the images obtained are shown in Figure 3.

According to Yu et al. (2000), for application purposes, it is important to know the biosorbents internal structure since the binding mechanisms are still not well understood. Analyzing the images presented in Figure 3, one may observe the structure of the porous particles featuring great variations in size and extensive interconnections, with an entangled appearance, particularly in the blades of the native biomass. When the image of the native biomass (Figure 3a) is compared with the pretreated one (Figure 3c), the microstructures are clearly different. It may also be observed that the arrangement of the structural fibers of the chemical and thermal pretreated biomass samples is more organized and uniform. This is mainly attributed to

the biosorbent saturation with calcium ions which, according to Yu et al. (2000), may increase the stability of the biomass. As for the images in Figure 3b and d, no significant difference was observed with regard to the arrangement of the structural fibers between the stipes of the biomass samples because the native biomass already presented those fibers evenly distributed along the stipe. The stipe structure of the pretreated biomass was saturated with calcium ions. According to Matheickal et al. (1999), the addition of calcium ions to alginate results in a cooperative association of long regions of polymer chains, with an 'egg box' structure type, which improves the stability of the polymers. The 'egg box' behavior seems to be the same verified in current research for $CaCl_2$ -pretreated biomass (Figure 3c). According to these authors, the decrease of organic leaching from chemically and thermally pretreated biomass is mainly due to the cross linking reaction that occurs in the alginate molecules.

Organic leaching from native and 24h-pretreated biomass was studied with high and low initial concentrations of Cr and Ni ions in solution and the proportional combination of both.

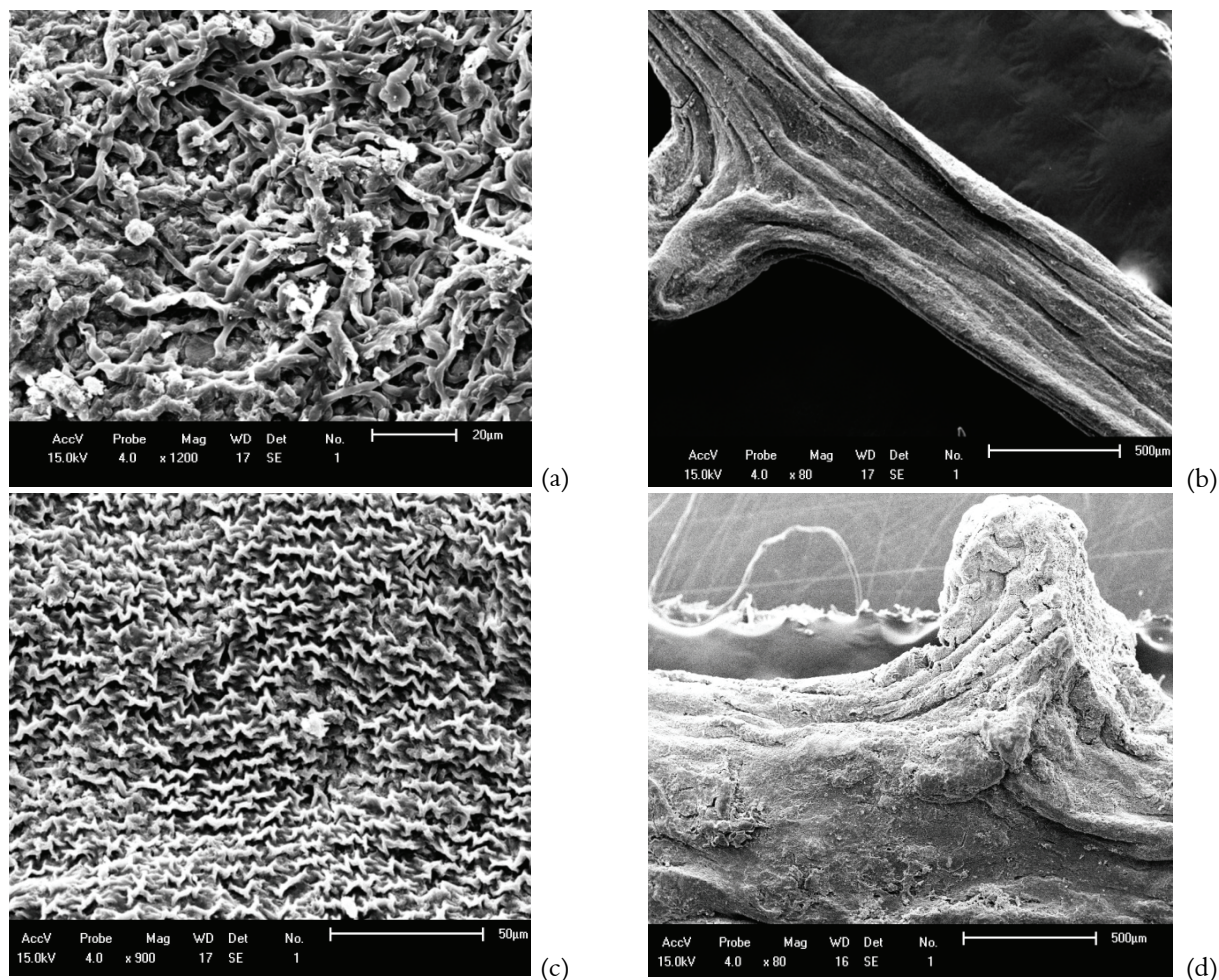


Figure 3. Scanning electron microscopy images of algal biomass: (a) native-blades; (b) native-stipes; (c) pretreated-blades; (d) pretreated-stipes.

Figure 4 shows the total organic carbon leaching results.

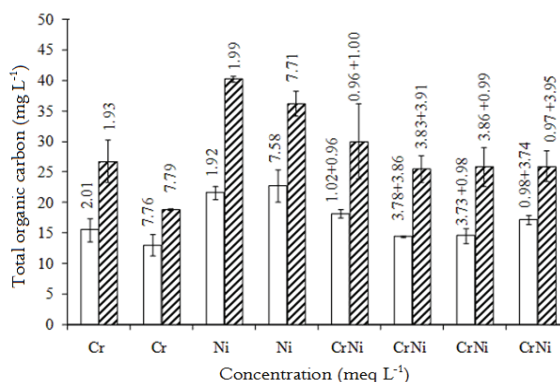


Figure 4. Total organic carbon leaching from biomass at high and low initial metal concentrations and its combinations: ▨ native; □ 24h-pretreated.

Results provided in Figure 4 demonstrate that all systems (mono and binary) containing high chromium concentration presented the lowest rates

of total organic carbon, with a 23.5 mg L⁻¹ average native alga and 14 mg L⁻¹ for the pretreated alga. The mono and binary systems containing low chromium concentration presented intermediary TOC rates with an average value of 27.7 and 17 mg L⁻¹ for the native and pretreated biomass, respectively. Highest TOC rates were observed for the mono-component systems containing low and high nickel concentration with an average rate of 38.3 mg L⁻¹ for the native biomass and 22.2 mg L⁻¹ for the pretreated biomass.

Matheickal and Yu (1999) carried out experiments with CaCl₂-pretreated seaweed biomass samples of *Durvillaea potatorum* and *Ecklonia radiata* at different initial pH values (1, 3 and 5) and initial Pb (II) and Cu (II) concentrations from 0.4 to 4.5 mM. The organic leaching rates obtained for different pH conditions were lower than 20 mg L⁻¹ when using *D. potatorum* at different concentrations of Pb (II) and lower than 10 mg L⁻¹ when using *E. radiata* species at different concentrations of Cu (II).

Reduction percentage of TOC obtained for the 24h-pretreated (Figure 4) relative to the experimental values obtained with native biomass for high and low concentrations of Cr and/or Ni and its combination is shown in Figure 5.

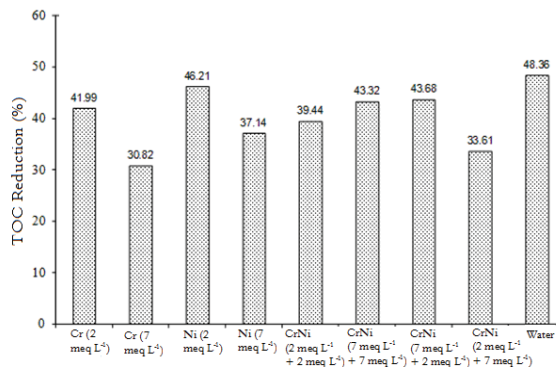


Figure 5. Percent reduction of total organic carbon (TOC) obtained for the pretreated biomass at different initial concentrations of metal ions.

Biomass pretreatment provided a significant reduction of organic leaching in all systems, with a maximum reduction for the mono-component system with low nickel concentration (46.21%). Comparing these results with the percentage reduction of TOC in Table 2 for pH 3.0, one may observe that TOC reduction for different concentrations of metallic ion solutions was lower than the rate obtained for the 24h-pretreated biomass using the native biomass in water medium as reference (48.36%).

Figure 6 shows chromium and/or nickel ions biosorption and calcium, magnesium, sodium and potassium ions released per unit mass of biosorbent. In the case of the two biomass samples, the higher metal removal levels were obtained for chromium rather than for nickel in all systems (mono and binary), except for the binary system with low chromium and high nickel concentrations. The above, shows that chromium is preferentially captured by the biomass in the competition between the metallic ions.

A slightly higher chromium removal capacity has also been verified for all systems (mono and binary) by using the pretreated biomass, when compared to the employment of the native one. Highest removal capacities, observed for the mono-component system of high chromium ion concentration, were 1.67 and 1.84 meq g⁻¹ for the native and pretreated biosorbent, respectively. In the case of the binary system with high chromium ion concentration, the removal capacities were 1.08 and 1.40 meq g⁻¹, respectively for the native and pretreated samples.

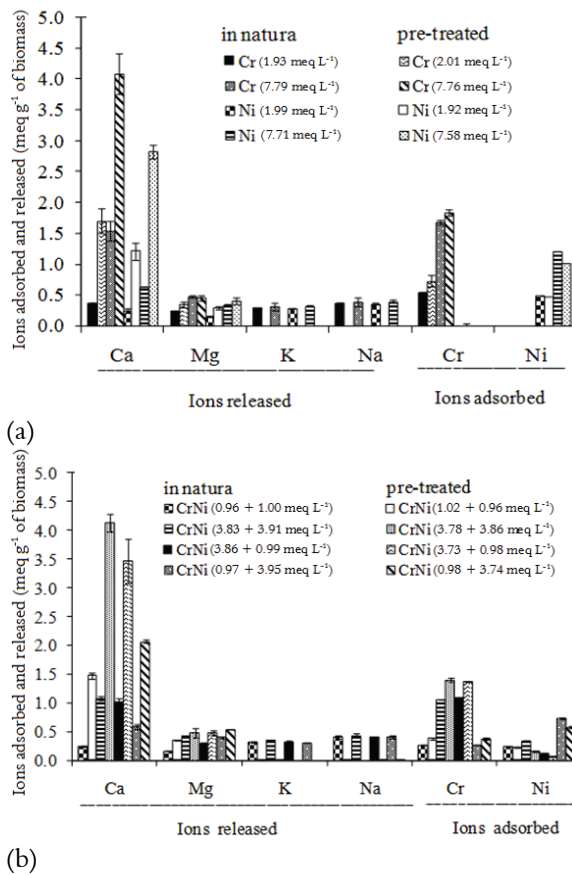


Figure 6. Sorption (Cr and Ni) and release (Ca, Mg, Na and K) of metal ions by native *Sargassum filipendula* and pretreated biomass: (a) mono-component systems and (b) binary systems.

As for nickel removal, the native biomass presented a higher capacity, corresponding to 1.20 meq g⁻¹ and 0.73 meq g⁻¹ for mono-component and binary systems, respectively. Seolatto et al. (2007) observed that the pre-treatment of *Sargassum filipendula* biomass too did not influence the nickel biosorption for mono-component system.

The results of individual and combined biosorption of chromium and nickel showed that adsorbent material sites have a stronger preference for chromium observed by other authors when they employed different biosorbents: Sharma et al. (2007) with unmodified shelled *Moringa oleifera* seeds (SMOS); Oliveira et al. (2005) with raw rice bran and Tsui et al. (2006) with Ca-treated *Sargassum* biomass.

The concentration of calcium ions released by the biomass samples was considerable, mainly for the mono- and binary-systems, with high chromium ion concentration. Calcium and magnesium ions released in the systems are probably related with the ion exchange properties of the biosorbents during chromium and/or nickel removal. According to Sæg and Kutsal (1996), the biosorption process may involve a combination of mechanisms, such as ion

exchange, complexation, physical and/or chemical adsorption, coordination, chelation and inorganic micro-precipitation. The presence of mono-valent ions (Na^+ and K^+) in solutions was insignificant since, according to Costa et al. (2001), these ions were only present in small amounts in the biomass. In fact, chemical treatment demonstrated that most sites were occupied by calcium ions.

Conclusion

The results of this study in different acid media showed that the pretreatment procedure was efficient in TOC reduction. However, there was no large variation between the three treatment times. Scanning electron microscopy analysis showed a more organized and uniform arrangement of the structural fibers of the chemically pretreated biomass when compared with that of the native alga. Biomass samples had a higher affinity for chromium than for nickel ions. Results show that biomass samples may be used in Cr and/or Ni ions removal from acid wastewaters. However, kinetic studies must be performed to optimize the removal process.

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