



**HAL**  
open science

## **Biosorption of chromium by alginate extraction products from *Sargassum filipendula*: Investigation of adsorption mechanisms using X-ray photoelectron spectroscopy analysis**

Caroline Bertagnolli, Arnaud Uhart, Jean-Charles Dupin, Meuris Gurgel  
Carlos Da Silva, Eric Guibal, Jacques Desbrieres

### ► To cite this version:

Caroline Bertagnolli, Arnaud Uhart, Jean-Charles Dupin, Meuris Gurgel Carlos Da Silva, Eric Guibal, et al.. Biosorption of chromium by alginate extraction products from *Sargassum filipendula*: Investigation of adsorption mechanisms using X-ray photoelectron spectroscopy analysis. *Bioresource Technology*, 2014, 164, pp.264-269. 10.1016/j.biortech.2014.04.103 . hal-01560495

**HAL Id: hal-01560495**

**<https://hal.science/hal-01560495v1>**

Submitted on 28 Aug 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Biosorption of chromium by alginate extraction products from *Sargassum filipendula*: Investigation of adsorption mechanisms using X-ray photoelectron spectroscopy analysis

Caroline Bertagnolli [a,b,\\*](#), Arnaud Uhart [c](#), Jean-Charles Dupin [c](#), Meuris Gurgel Carlos da Silva [a](#), Eric Guibal [b](#), Jacques Desbrieres [c](#)

<sup>a</sup>School of Chemical Engineering, University of Campinas, Cidade Universitária Zeferino Vaz, 13083-970 Campinas, SP, Brazil

<sup>b</sup>Centre des Matériaux des Mines d'Alès (C2MA/MPA/BCI), Ecole des mines d'Alès, 6 avenue de Clavières, F-30319 Alès Cedex, France

<sup>c</sup>Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux (IPREM), Université de Pau et des Pays de l'Adour, 2 avenue Président Angot, F-64053 Pau, France

## H I G H L I G H T S

- New alternative and renewable adsorbents for the chromium removal were presented.
- The XPS analysis indicated a complex biosorption process for Cr(VI).
- Ion exchange mechanisms are predominating in the removal of Cr(III) by alginate.
- The adsorption results encourage the use of the residue extraction as a sorbent.

## A B S T R A C T

The alginate extraction products from Brazilian brown seaweed *Sargassum filipendula* were studied for chromium biosorption. Batch experiments were conducted at pH 2 and 3 and 20 °C to determine the sorption capacity of this biosorbents for chromium (VI) and (III). The biomass was characterized before and after metal binding by X-ray photoelectron spectroscopy (XPS) in order to determine the mechanisms of chromium biosorption. The residue has a high adsorption capacity, close the value obtained with seaweed and higher than that of alginate for both Cr(III) and Cr(VI). XPS analysis of the biosorbents revealed that carboxyl, amino and sulfonate groups are responsible for the binding of the metal ions. The analysis also indicated that the Cr(VI) bound to the biomass was reduced to Cr(III).

### Keywords:

Biosorption  
Seaweed  
Alginate-extraction  
Chromium  
XPS

## 1. Introduction

Chromium is a hazardous heavy metal found in industrial effluents of electroplating, welding, production of chromium-iron alloys, tannery, metal plating, dyes and varnishes, as well as the use in electronic and metallurgy industries (Mohan and Pittman, 2006). Many studies have shown that they are highly toxic and can seriously damage our aqueous environment (Cieslak-Golonka, 1995; Suwalsky et al., 2008). The trivalent chromium is less toxic than hexa-valent chromium, but a long term exposure to trivalent chromium is

known to cause allergic skin reactions and cancer. The hexavalent chromium has greater mobility and mutagenic and carcinogenic properties. The conventional processes used to remove chromium, like precipitation or ion exchange, are costly due to operational, treatment and sludge disposal costs, so in recent years, biosorption has been proposed as an alternative process.

Removal of chromium from aqueous solutions by biosorption has been studied by several researchers (Calero et al., 2009; Escudero et al., in press), using different bioadsorbents, with advantages such as lower generation of sludge, high efficiency and possibility to use low cost and waste materials. The biosorption of heavy metals by seaweed is related to the properties of its cell wall, enabling the electrostatic attraction and complexation of metal ions (Davis et al., 2003). The brown seaweeds are abundant and do not have vital functions for the marine ecosystem

when torn from their substrates due to tides or their natural life cycle. In the study of hexavalent chromium Park et al. (2006) presented evidence of the combination of adsorption and reduction on the surface of the adsorbent as a mechanism responsible for chromium removal by biomaterials.

Thus, the main objective of this work was to study the uptake of Cr(III) and Cr(VI) ions from aqueous solutions by the alginate extraction products from *Sargassum filipendula*. X-ray photoelectron spectroscopy (XPS) was employed to identify the specific functions involved in chromium binding and allows the elucidation of binding mechanisms.

## 2. Methods

The raw biomass of *S. filipendula* was collected from the coast of northern São Paulo, at Cigarras beach (São Sebastião). The seaweed was washed, dried in an oven at 60 °C for 24 h and grinded and sieved into fractions <1 mm.

The Cr(III) and Cr(VI) solutions were prepared using analytical grade Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck, Germany) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Prolabo, France) dissolved in deionized water. The pH of each solution was adjusted to the required value with diluted HNO<sub>3</sub> or HCl solutions, respectively. Total chromium concentration in aqueous solution was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jobin-Yvon, France) and hexavalent chromium concentration was determined using a colorimetric method (ASTM D1687-02, 2007). The samples were analyzed after complexation with 1,5-diphenylcarbazide by spectrophotometry at 540 nm, and the Cr(III) concentration was then calculated by difference.

### 2.1. Extraction of alginate present in the seaweed and preparation of the biosorbents

The extraction of alginate was performed according to the method described by Mchugh (1987). Fifteen grams of *S. filipendula* were put in contact with sodium carbonate solution (2% w/v) at 60 °C during 5 h before being vacuum-filtered to separate the solid residue and the alginate solution. Then, ethanol was added to the solution for the precipitation of sodium alginate. The seaweed residue, separated during extraction, was exhaustively rinsed in deionized water and dried at 60 °C.

In order to be used in biosorption experiments, the seaweed and the extraction residue were subsequently protonated by the addition of 0.1 mol L<sup>-1</sup> HCl under constant shaking until stabilization at pH 5 (biomass concentration: 10 g L<sup>-1</sup>). The biomass was rinsed with deionized water and then dried in an oven at 60 °C. This step limits pH variation during the sorption. When the sodium alginate extracted was produced calcium alginate beads. A sodium alginate solution, 2% (w/v), was added drop-by-drop, by using a peristaltic pump and a silicone tube with internal diameter 1.6 mm to a CaCl<sub>2</sub> 4% (w/v) stirred solution. The gel beads were kept in the CaCl<sub>2</sub> solution, with gentle agitation, for approximately 24 h for complete gelation. After, calcium alginate beads were exhaustively rinsed with deionized water and air dried for 3 days.

### 2.2. Chromium biosorption

In the kinetic experiments, the biomass (at 2.0 g/L) was added to 1 mmol L<sup>-1</sup> Cr(III) and Cr(VI) solutions adjusted to pH 3 and pH 2, respectively. Samples were taken at periodic time intervals and analyzed using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry, Jobin-Yvon). In the adsorption isotherm experiments, the pH was set as that in the kinetic experiments. The same sorbent dosage was added to the solutions with varying metal concentrations. All flasks were shaken at 150 rpm at 20 °C

for 24 h. The amount of chromium sorbed by biosorbents ( $q$ ) in the sorption system was calculated using the mass balance equation (Eq. (1)):

$$q = \frac{V(C_0 - C_{eq})}{m} \quad (1)$$

where  $V$  is the solution volume (L),  $m$  is the amount of sorbent (g), and  $C_0$  and  $C_{eq}$  (mmol L<sup>-1</sup>) are the initial and equilibrium metal concentrations, respectively.

The Langmuir model (Eq. (2)) was adjusted to the equilibrium data in order to obtain the maximum adsorption capacity ( $q_{max}$ , mmol g<sup>-1</sup>) and the affinity coefficient ( $b$ , L mmol<sup>-1</sup>).

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (2)$$

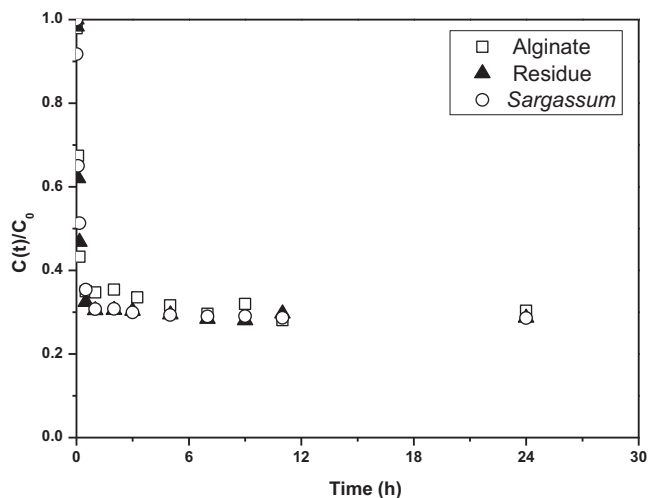
### 2.3. X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy was applied to determine the interactions between the organic functional groups on the biosorbent and the metal adsorbed and the oxidation form of chromium in the biosorbent. The measurements were carried out with a Thermo Scientific K-Alpha spectrometer using a focused monochromatized Al<sub>Kα</sub> radiation ( $h\nu = 1486.6$  eV) operating at 72 W. The analyzed area of the samples was a 400 μm diameter disk. The pressure in the analysis chamber was around  $1 \times 10^{-7}$  mbar. Short-time spectra were recorded before and after each normal long-time experiment and were compared to each other to check that the samples did not suffer from degradation during the measurements. Core peaks were analyzed using a nonlinear Shirley-type background (Shirley, 1972) and peak positions and areas were obtained by a weighted least square fitting of model curves (70% Gaussian and 30% Lorentzian combination). Quantification was performed on the basis of Scofield's photoionization cross-sections (Scofield, 1976). The compounds Cr<sub>2</sub>S<sub>3</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (Alfa Aesar), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Cr<sub>2</sub>O<sub>3</sub> (Aldrich) were used as references for chromium bonds in the biomass.

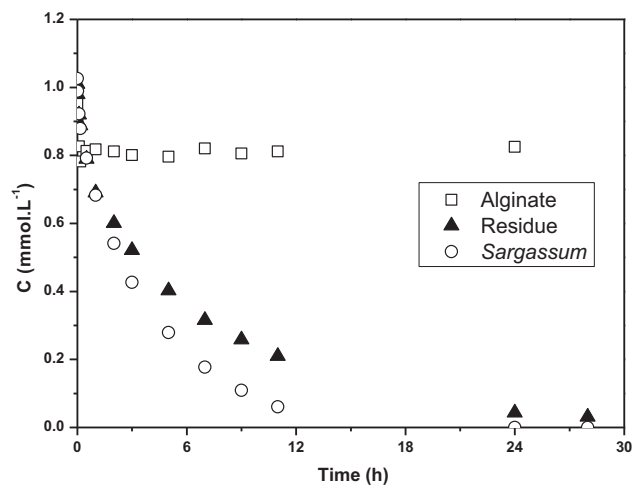
## 3. Results and discussion

### 3.1. Biosorption experiments

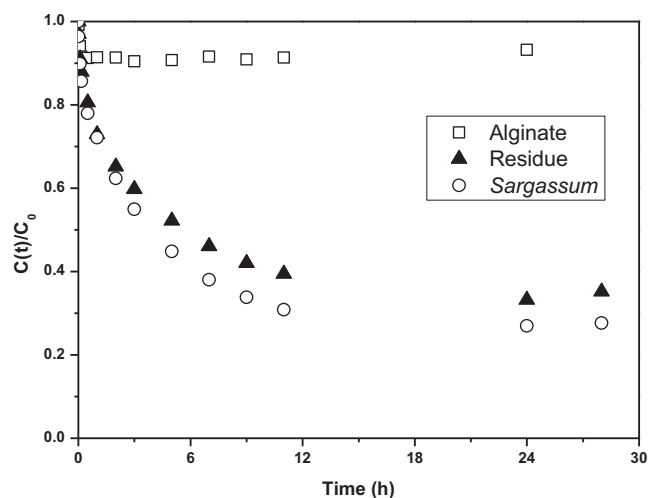
Fig. 1 illustrates the equilibrium time required for the uptake of chromium species by the different biosorbents. Faster biosorption kinetics can be observed on the biosorbents with the trivalent chromium. The equilibrium balance was reached within one hour (Fig. 1a), while for total chromium 24 h contact time was necessary (Fig. 1b). The disparities in equilibrium time between Cr(III) and Cr(VI) illustrates are reflex of the differences in the adsorption mechanisms. The alginate presents poor interaction with the hexavalent form of chromium. Indeed, the egg-box structure of calcium-gelled alginate beads cannot involve electrostatic interactions or ion exchange with anionic forms of chromium (chromate anions). This mechanism is supposed to be responsible for the adsorption of met-als cation with alginate (Davis et al., 2003). In the study chromium sorption (either Cr(III) and Cr(VI)) the different chromium species were measured in solution (Fig. 2). With time, the concentration of Cr(VI) decreases, until getting closer to zero, while the Cr(III) concentration increases. In equilibrium, practically all chromium present in solution is found in its trivalent form, indicating its reduction during biosorption. The presence of Cr(III) in the solution indicates that sea-weed materials can reduce Cr(VI) to Cr(III) under the current experimental conditions. Cui et al. (2011) studied chromium sorption using the byproduct of beer production, observed the same behavior during uptake kinetics: Cr(III) concentrations increased with an



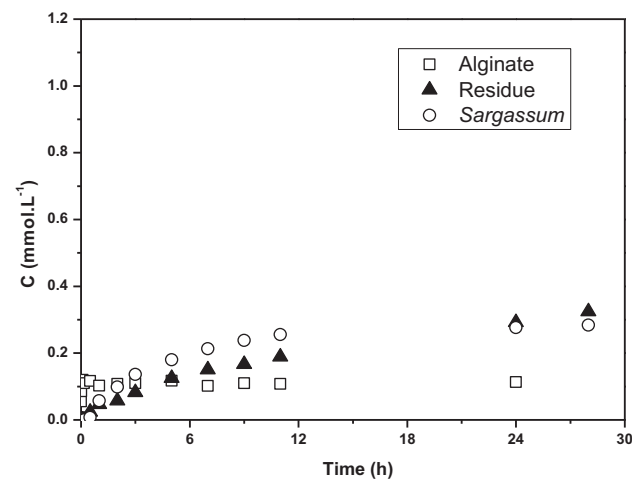
(a)



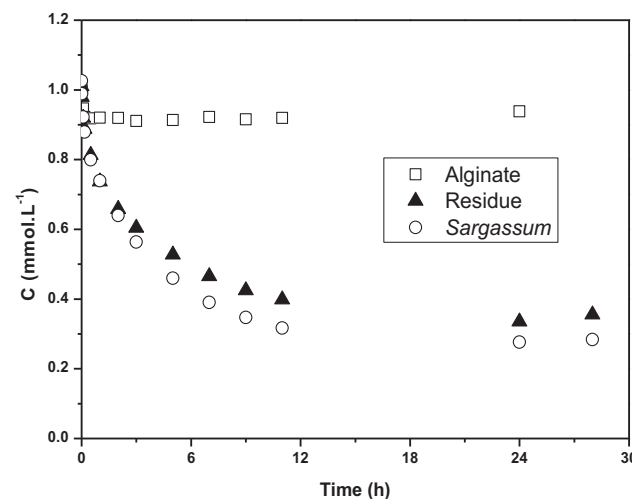
(a)



(b)



(b)



(c)

**Fig. 1.** Uptake kinetics for chromium removal from (a) Cr(III) and (b) Cr(VI) solutions using alginate extraction products from *Sargassum filipendula*.

increase in contact time. For alginates, the hexavalent chromium is stable during all kinetics, and there is no reduction reaction and only a little adsorption.

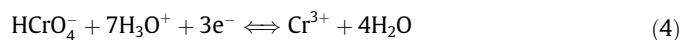
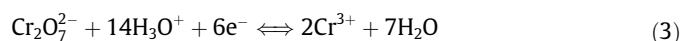
The isotherms at 20 °C for the different products obtained during the extraction of alginate were adjusted to the Langmuir model. A greater adsorption capacity of "total" chromium can be seen (*Sargassum*  $q_{\max} = 1.046 \text{ mmol g}^{-1}$   $b = 1.799 \text{ L mmol}^{-1}$   $R^2 = 0.992$ ; Residue  $q_{\max} = 0.819 \text{ mmol g}^{-1}$   $b = 2.604 \text{ L mmol}^{-1}$   $R^2 = 0.988$ ), but the higher values of  $b$  show a great affinity of the adsorbents for trivalent chromium (*Sargassum*  $q_{\max} = 0.657 \text{ mmol g}^{-1}$   $b = 60.051 \text{ L mmol}^{-1}$   $R^2 = 0.926$ ; Residue  $q_{\max} = 0.635 \text{ mmol g}^{-1}$   $b = 166.154 \text{ L mmol}^{-1}$   $R^2 = 0.793$ ; Alginate  $q_{\max} = 0.411 \text{ mmol g}^{-1}$   $b = 22.140 \text{ L mmol}^{-1}$   $R^2 = 0.974$ ). The maximum adsorption capacities for residue are close to those obtained by algae and higher than alginate for both Cr(VI) and Cr(III) forms. This confirms that the residue can be valorized as a sorbent while the alginate can be used for elaborative valuable products for industries such as food and pharmaceutical.

The pH of the solution was measured after biosorption ( $\text{pH}_{\text{eq}}$ ) in order to help understanding the biosorption mechanisms. "Total" chromium biosorption was performed in pH 2 while trivalent chromium was studied at pH 3, defined according to metallic speciation and other works (Leyva-Ramos et al., 1995; Bertagnoli et al., 2014).

**Fig. 2.** Effect of time on the adsorption and reduction of Cr(VI) (a) Cr(VI); (b) Cr(III); (c) "total" Cr.

For total chromium, the pH variation during biosorption ( $\Delta\text{pH} = \text{pH}_{\text{eq}} - \text{pH}_{\text{initial}}$ ) systematically increase with the concentration, regardless of the biosorbent. The reduction of chromium is eased by the low working pH and the phenomenon causes the consumption of  $\text{H}_3\text{O}^+$  in the solution, leading to pH increase.

Eqs. (3) and (4) show the reduction reactions for the chromium species that predominate in the working pH.



By the Nernst equation, the redox potential of  $\text{HCrO}_4^-/\text{Cr}^{3+}$ , dominant species at pH = 2, is calculated by Eq. (5). The redox potential  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  increases with the decrease in pH and consequently, inducing a greater reduction of Cr(VI) to Cr(III).

$$E(\text{HCrO}_4^-/\text{Cr}^{3+}) = E^0(\text{HCrO}_4^-/\text{Cr}^{3+}) + 1.97 \times 10^{-2} \log(\text{HCrO}_4^-/\text{Cr}^{3+}) - 0.138\text{pH} \quad (5)$$

$E^0$ : standard redox potential.

For trivalent chromium, pH variation is less significant: an increase is observed at low concentrations while at higher concentration the  $\Delta\text{pH}$  is stable. This behavior is similar to the trivalent chromium solutions before pH adjustment.

### 3.2. X-ray photoelectron spectroscopy

This technique contributes to the understanding of the mechanisms involved in chromium removal: determination of functional groups, evaluations of the oxidation state of the metal (Dupont and Guillon, 2003).

Table 1 reports the elemental composing of the biosorbents. XPS analyzes were not performed for alginate material showing little adsorption for hexavalent chromium. An increase in the concentration of carbon can be observed after the adsorption for all biosorbents in the study: this means that the metal has a strong interaction with the different organic groups. Silicon, with bonding energy between 103 and 104 eV, was found in the  $\text{SiO}_2$  form (Edgell et al., 1986), indicating the presence of alga diatoms in the residue. Some traces of Si were also found in alginate. Nitrogen from the amino groups from proteins present in algae and the sulfur from fucoidan were also detected and variations were observed in their concentrations after adsorption (at.% N slightly rises up from 3.4 to 5.0 while at.% S increases four times after adsorption). The concentration of these functional groups and compounds on chromium removal was already reported by Bertagnolli et al. (2014) using FTIR analysis. This was also confirmed by several studies evaluating the interaction of heavy metals with seaweeds (Fourest and Volesky, 1996; Yang and Chen, 2008). The presence of small amounts of both sulfur (at.% = 0.5) and nitrogen (at.% = 0.7) indicates the difficulty to selectively extract alginate from the seaweed: fucoidan biopolymer and alga proteins remained in the extracted material.

Table 1 also shows the presence of chromium in the contaminated samples and highlights the contribution of ionic exchange

mechanisms in the removal of both Cr(III) and Cr(VI), regardless of the biosorbent. The reduction or disappearance of ions such as Ca, Mg, Na and Fe after contact with the metal obviously confirms this ion exchange mechanisms. For alginates, the participation in the ionic exchange for removing trivalent chromium is even more important, with a great reduction in the percentages of calcium and sodium ions. The guluronic acids in alginates trap cations by means of ionic interactions with the electronegative cavity formed by the egg-box structure (Grant et al., 1973). The removal of divalent cations such as those of Cu, Zn, Ni, Pb and Cd by alginate has been investigated by several researchers who propose the exchange of  $\text{Ca}^{2+}$  with these ions (Davis et al., 2003; Papageorgiou et al., 2006). For trivalent chromium, there are very few papers, but the study by Araújo and Teixeira (1997) showed the exchange of  $\text{Ca}^{2+}$  with  $\text{Cr}^{3+}$  and/or  $\text{Ca}^{2+}$  with  $\text{CrOH}^{2+}$ , while (Cazón et al., 2012) observed a significant exchange of  $\text{Cr}^{3+}$  with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ .

Binding energy (BE) profiles of chromium atom (Cr 2p), carbon atom (C 1s), and oxygen atom (O 1s) in the biosorbents before and after metal biosorption are shown in Table 2. The C 1s spectra of all the samples show a common component with BE of 285.0 eV, which is attributed to the bond C—C—H; this peak is usually set up in energy for calibrating the energy scale of the spectrometer (Brundle and Baker, 1980). The remaining observed peaks can be attributed to alcohols (C—O), ethers (O—C—O) and carboxyl groups (O=C—O) with BEs of  $286.5 \pm 0.2$  eV,  $288.0 \pm 0.3$  eV and  $289.2 \pm 0.2$  eV, respectively (Moulder et al., 1992). These organic functions are typical of algae polysaccharides and the small variations in the C1s BE are due to small changes in electronic densities of the groups in relation with their local environment (Chen et al., 2002).

The spectra for O 1s present components encompassing the 530–533 eV region, whose peak identification is presented in Table 2. They are associated to several functional groups present in the biosorbents (ether, alcohol, carboxylic acid and hydroxyl). BE peaks of about  $531.9 \pm 0.2$ ,  $532.9 \pm 0.2$  and  $534.2 \pm 0.4$  eV can be assigned to metal hydroxide, C=O, and C—O (carboxyl and ether), respectively (Moulder et al., 1992). For alginate, a peak at 530.7 eV appears after contact with chromium (Table 2); this peak confirms the presence of chromium oxide at the surface of the sorbent. Dambies et al. (2001) observed the appearance of this peak while studying the chemical interactions of chromium with chitosan.

The binding of chromium on the biosorbents is characterized by the appearance of typical bands. High intensity Cr 2p<sub>3/2</sub> peaks are generally recorded to discriminate Cr(III) form from Cr(VI) state as usually reported in the literature (e.g., Wagner et al., 1979). Kushwaha et al. (2012) performed thermal and chemical treatments on palm husks for manufacture a chromium biosorbent. They observed peak contributions of Cr 2p<sub>3/2</sub>, correlated to BE for

**Table 1**  
Elemental composition of raw and Cr-loaded biosorbents as determined using XPS.

Elements	Average atomic concentration (%)							
	<i>Sargassum</i>	<i>Sargassum</i> + Cr(III)	<i>Sargassum</i> + Cr(IV)	Residue	Residue + Cr(III)	Residue + Cr(VI)	Alginate	Alginate + Cr(III)
Al2p	–	–	–	0.3	1.0	0.9	–	–
C1s	52.3	62.9	61.9	63.3	61.5	61.6	44.9	87.5
Ca2p	–	–	–	0.3	–	0.1	7.6	–
Cl2p	–	–	–	–	–	–	21.7	–
Fe2p	–	–	–	0.1	–	–	–	–
Mg1s	–	–	–	0.2	–	0.1	3.3	–
N1s	3.4	5.0	5.0	2.4	2.9	2.6	1.3	0.7
Na1s	–	–	–	1.9	–	–	6.6	–
O1s	32.9	27.5	28.3	28.9	30.3	30.7	13.9	10.7
S2p	0.5	1.6	2.0	1.3	1.7	1.6	0.2	0.5
Si2p	10.9	2.6	2.3	1.3	2.0	1.7	0.5	0.4
Cr2p	–	0.4	0.5	–	0.6	0.7	–	0.2

**Table 2**  
Summary of binding energies for the adsorbents.

Elements	Energy position (eV)								Identification
	<i>Sargassum</i>	<i>Sargassum</i> + Cr(III)	<i>Sargassum</i> + Cr(VI)	Residue	Residue + Cr(III)	Residue + Cr(VI)	Alginate	Alginate + Cr(III)	
C 1s	285.0	285.0	285.0	285.0	285.0	285.0	285.0	285.0	C—C/H
	286.4	286.4	286.6	286.6	286.5	286.6	286.6	286.7	C—O
	288.2	287.8	288.0	287.9	287.8	288.1	287.7	—	C=O, O—C—O
	289.4	289.0	289.1	289.0	289.2	289.2	289.0	289.0	COO
	—	—	—	290.1	290.8	—	—	—	$\pi/\pi^*$ transition
O 1s	—	—	—	—	—	—	—	530.7	M—O (ex.: Cr <sub>2</sub> O <sub>3</sub> /CrO <sub>3</sub> )
	531.7	531.9	531.7	531.8	531.9	532.1	531.7	531.7	M—OH (ex.: Cr(OH) <sub>3</sub> )
	533.1	532.9	532.8	532.9	532.9	533.1	532.9	532.9	C=O, —SO <sub>3</sub> , SiO <sub>2</sub> C—O
	534.6	534.0	533.8	534.0	534.3	534.4	533.9	533.9	Cr <sub>2</sub> O <sub>3</sub> /Cr(OH) <sub>3</sub>
	—	577.5	577.6	—	577.6	577.7	—	576.5	Cr(VI)
	—	579.4	579.4	—	579.6	579.5	—	580.5	Cr—S
	—	575.2	575.4	—	574.4	575.0	—	574.7	—
	—	—	—	—	—	—	—	—	—

Cr(III) in the range 577.2–577.8 eV, while the peak contributions of Cr 2p<sub>3/2</sub> related to BE for Cr(VI) ranged between 578.9 and 581.7 eV (in relation with local atoms environments).

With the objective of assessing the type of bond formed between chromium and the biosorbent, references materials like Cr<sub>2</sub>S<sub>3</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Cr<sub>2</sub>O<sub>3</sub> were assessed by XPS. Cr(III)—S, Cr(III)—O and Cr(VI)—O bonds have then been respectively associated with Cr2p<sub>3/2</sub> BE of 575.0 eV, 577.7 eV and 580.8 eV these results confirm data published by Yuan et al.(2013). Comparing the binding energies of the reference spectra with the Cr2p spectra for the residue and the seaweed contaminated with chromium, two forms of the metal can be identified. Chromium (III) bonded to sulfur (BE Cr2p<sub>3/2</sub>: 574.2 eV) and chromium (III) in oxide and/or hydroxide environment (BE Cr2p<sub>3/2</sub>: 577.6 eV) are observed. Approximately 13% of the whole chromium present in the biomass is bound with sulfur both for *Sargassum* + Cr(III) and for *Sargassum* + Cr(VI); for the residue + Cr(VI), the percentage went down to 7.5%, while for residue + Cr(III) this percentage rose up to 29%. These results confirm the fucoidan contribution for metal uptake by seaweed products.

Similar system test and analysis were performed on a commercial alginate sample for comparison. XPS data have shown, in this case, that the little amount of sulfur present in the alginate (~0.2 at.%) was partially associated with chromium (via Cr—S bonds), contributing to the effective removal of chromium (III). However, the interactions between chromium and alginate organic functions seem to operate in a slightly different way as the recorded Cr 2p<sub>3/2</sub> BEs are different from those noticed after the *Sargassum* and the residue extraction processes. This is certainly due to additional electronic effects produced by residual chemical entities incompletely released out after the biosorbent initial procedure of washing.

All these considerations are corroborated by the S2p spectra in which a Cr—S environment is clearly visible after the extraction of chromium with algae (S2p doublet located at 163.5–164.6 eV). These specific BEs were previously identified in commercial Cr<sub>2</sub>S<sub>3</sub>, which exhibits an additional intense doublet at 161.3–162.5 eV. Those environments correspond respectively to the presence of monosulfide S<sup>2-</sup> and disulfide pairs S<sub>2</sub><sup>-</sup> interacting with Cr(III). A partial oxidation of the surface of the material grains has been noticed when analyzing commercial Cr<sub>2</sub>S<sub>3</sub> and leads to the appearance at high energy side of a third doublet (169.0–170.1 eV) assigned to sulfates (as confirmed by the XPS analysis of commercial Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). The same doublet is also observed for *Sargassum* + Cr(III). The assumption of interactions between chromium and sulfate groups cannot be totally rejected. The Cr2p<sub>3/2</sub> component of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O standard was recorded at 578.4 eV and cannot be discerned in the experimental profiles, between Cr(III)—O and Cr(VI)—O environments. The metal complexation

with sulfate groups in the biomass had been already commented by Figueira et al. (1999) during the extraction of iron by *Sargassum*.

The XPS results show the presence of both Cr(III) and Cr(VI) forms in the adsorbents contaminated with metal. The presence of hexavalent chromium was not detected in the liquid phase in the chromium (III) nitrate solutions before or after biosorption. However, but depending on the redox potential of the system, the oxidation of trivalent chromium to hexavalent chromium could have happened on the adsorbent surface. The thermodynamic diagram for the redox potential (Eh) versus pH (Pourbaix diagram) present the chromium species in a contaminated medium. The distribution of Cr(III) and Cr(VI) species in the environment depends on the chemical reactions with the components present on the sorbent and on the redox conditions of the medium (Richard and Bourg, 1991). At pH 3 (corresponding to the operating pH) chromium can be present in its hexavalent form for high redox potentials (i.e., >0.9 V).

The ratio between the amounts of Cr(III) and Cr(VI) present in the alga and in the residue was calculated based on the binding energies at 577.6 eV and 579.5 eV, respectively, and their own *shake-up* satellites. The seaweed contaminated with total chromium present a Cr(III)/Cr(VI) ratio of 2.22 and the residue a value close to 1.90, indicating that the amount of chromium in the trivalent form present at the surface of the seaweed is more than the double of the amount of hexavalent chromium. The result confirms the occurrence of chromium reduction on the surface of the adsorbent, associated to its adsorption on the biomass and also its release in the liquid phase, as observed in the quantification of chromium species after kinetics (Fig. 1).

Park et al. (2008), studying the brown alga *Ecklonia* sp., verified by XPS analysis the complete reduction of Cr(VI) to Cr(III), attributing to the oxygen-binding compounds on the material the removal of trivalent chromium (resulting from the reduction of the hexavalent chromium). The authors also state that a low concentration of protons on the biomass could only cause a partial reduction of Cr(IV); this is consistent with the results in this study.

Murphy et al. (2009) assessed, by means of XPS, the biosorption of trivalent and total chromium in brown, green and red seaweed. They observed the reduction of chromium hexavalent to trivalent form. They also observed that the chromium bond affects the relative amounts of carboxylic group and alcohols in the polysaccharides (contained in the biomass). The variation depends on the metal but confirms the involvement of these groups in the removal of “total” Cr. Consistently with this was the reduction of Cr(VI) to Cr(III) was partial, with Cr(III)/Cr(VI) ratios varying 1.79 and 2.22. For trivalent chromium, it is believed that the ionic exchange mechanisms were responsible for metal removal.

The difficulty in forecasting the interactions between natural organic adsorbents and metallic ions is due to the great chemical

heterogeneity of the biomass, and the electrostatic interactions between their load and the metallic ions (Bouanda et al., 2002). Assessing the present results and literature, (Yang and Chen, 2008; Park et al., 2006, 2008) the removal of total chromium, present in solution in anionic form, is a complex process involving both the reduction of the metal (forming of complexes at the surface of the adsorbent) and ion exchange. Hexavalent chromium can form complexes with the protonated functional groups on the acidified surface of both seaweed and residue, such as  $-\text{COOH}$ ,  $-\text{NH}_2$  and  $-\text{SO}_3\text{H}$ . Cr(VI) can also oxidize the secondary alcohol groups in the biosorbent, while it is reduced to Cr(III). Trivalent chromium, formed from the redox reaction of Cr(VI), or from the study with chromium (III) nitrate, interact by ion exchange with alkali metal ions, such as  $\text{Ca}^{2+}$  present in biosorbents. Cr(III) can also form complexes due to the coordination reactions (Chen and Yang, 2005), especially in sulfonate and carboxylic groups.

When assessing the experiments, especially for “total” chromium, it can be noticed that the biosorption mechanism is strongly dependent on the system. A low working pH facilitates removal of “total” chromium, and the phenomenon causes a consumption of  $\text{H}^+$  in the solution, leading to an increase in the pH. The hexavalent chromium might be a partial or total reduction to trivalent form, depending of the initial concentration of chromium in solution and the protons on the surface of the biosorbent.

#### 4. Conclusions

This paper presents new alternative and renewable adsorbents for the removal of heavy metals, especially chromium in its different forms, also encouraging the industrial use of a Brazilian alginate and reusing the residue of its extraction.

The XPS analysis indicated a complex biosorption process for Cr(VI), with carboxyl, amine and sulfonic groups involved, and the reduction of Cr(VI) to Cr(III) during biosorption. The removal of trivalent chromium by the alga and the residue also involved the carboxyl, amine and sulfuric groups and ionic exchange mechanisms. Ion exchange mechanisms are predominating in the removal of trivalent chromium by alginate.

#### Acknowledgements

Caroline Bertagnolli acknowledges her Doctoral fellowship supported by CNPq – Brazil.

#### References

Araújo, M.M., Teixeira, J.A., 1997. Trivalent chromium sorption on alginate beads. *Int. Biodeterior. Biodegrad.* 40, 63–74.

ASTM D1687–02, 2007. Standard Test Methods for Chromium in Water. ASTM International, West Conshohocken.

Bertagnolli, C., da Silva, M.G.C., Guibal, E., 2014. Chromium biosorption using the residue of alginate extraction from *Sargassum filipendula*. *Chem. Eng. J.* 237, 362–371.

Bouanda, J., Dupont, L., Dumonceau, J., Aplincourt, M., 2002. Use of a NICA-Donnan approach for analysis of proton binding to a lignocellulosic substrate extracted from wheat bran. *Anal. Bioanal. Chem.* 373, 174–182.

Brundle, C.R., Baker, A.D., 1980. *Electron Spectroscopy: Theory and Technical Applications*, fourth ed. Academic Press, New York.

Calero, M., Hernández, F., Blázquez, G., Tenorio, G., Martín-Lara, M., 2009. Study of Cr(III) biosorption in a fixed-bed column. *J. Hazard. Mater.* 171, 886–893.

Cazón, J.P., Bernardelli, C., Viera, M., Donati, E., Guibal, E., 2012. Zinc and cadmium biosorption by untreated and calcium-treated *Macrocystis pyrifera* in a batch system. *Bioresour. Technol.* 116, 195–203.

Chen, J.P., Hong, L., Wu, S., Wang, L., 2002. Elucidation of interactions between metal ions and calcium-based ion-exchange resin by spectroscopic analysis and modeling simulation. *Langmuir* 18, 9413–9421.

Chen, J.P., Yang, L., 2005. Chemical modification of *Sargassum* sp. for prevention of organic leaching and enhancement of uptake during metal biosorption. *Ind. Eng. Chem. Res.* 44, 9931–9942.

Cieslak-Golonka, M., 1995. Toxic and mutagenic effects of chromium(VI). A review. *Polyhedron* 15, 3667–3689.

Cui, H., Fu, M., Yu, S., Wang, M.K., 2011. Reduction and removal of Cr(VI) from aqueous solutions using modified byproducts of beer production. *J. Hazard. Mater.* 186, 1625–1631.

Dambies, L., Guimon, C., Yiacomou, S., Guibal, E., 2001. Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy. *Colloids Surf. A Physicochem. Eng. Aspects* 177, 203–214.

Davis, T.A., Volesky, B., Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* 37, 4311–4330.

Dupont, L., Guillon, E., 2003. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environ. Sci. Technol.* 37, 4235–4241.

Edgell, M.J., Baer, D.R., Castle, J.E., 1986. Biased referencing experiments for the XPS analysis of non-conducting materials. *Appl. Surf. Sci.* 26, 129–149.

Escudero, C., Fiol, N., Villaescusa, I., Bollinger, J.-C., in press. Effect of chromium speciation on its sorption mechanism onto grape stalks entrapped into alginate beads. *Arab. J. Chem.* <http://dx.doi.org/10.1016/j.arabcj.2013.03.011>.

Figueira, M.M., Volesky, B., Mathieu, H.J., 1999. Instrumental analysis study of iron species biosorption by *Sargassum* biomass. *Environ. Sci. Technol.* 33, 1840–1846.

Fourest, E., Volesky, B., 1996. Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*. *Environ. Sci. Technol.* 30, 277–282.

Grant, G.T., Morris, E.R., Rees, D.A., Smith, P.J.C., Thom, D., 1973. Biological interactions between polysaccharides and divalent cation: the egg-box model. *FEBS Lett.* 32, 195–198.

Kushwaha, S., Sreedhar, B., Sudhakar, P.P., 2012. A spectroscopic study for understanding the speciation of Cr on palm shell based adsorbents and their application for the remediation of chrome plating effluents. *Bioresour. Technol.* 116, 15–23.

Leyva-Ramos, R., Fuentes-Rubio, L., Guerrero-Coronado, R.M., Mendonza-Barron, J., 1995. Adsorption of trivalent chromium from aqueous solutions onto activated carbon. *J. Chem. Technol. Biotechnol.* 62, 64–67.

McHugh, D.J., 1987. *Production, Properties and Uses of Alginates*. FAO, Rome.

Mohan, D., Pittman, C.U., 2006. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J. Hazard. Mater.* 137, 762–811.

Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D., 1992. *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*. Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie.

Murphy, V., Tofail, S.A.M., Hughes, H., McLoughlin, P., 2009. A novel study of hexavalent chromium detoxification by selected seaweed species using SEM-EDX and XPS analysis. *Chem. Eng. J.* 148, 425–433.

Papageorgiou, S.K., Katsaros, F.K., Kouvelos, E.P., Nolan, J.W., Le Deit, H., Kanellopoulos, N.K., 2006. Heavy metal sorption by calcium alginate beads from *Laminaria digitata*. *J. Hazard. Mater.* 137, 1765–1772.

Park, D., Yun, Y.-S., Park, J.M., 2006. Comment on the removal mechanism of hexavalent chromium by biomaterials or biomaterial-based activated carbons. *Ind. Eng. Chem. Res.* 45, 2405–2407.

Park, D., Yun, Y.-S., Park, J.M., 2008. XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption. *J. Colloid Interface Sci.* 317, 54–61.

Richard, F.C., Bourg, A.C.M., 1991. Aqueous geochemistry of chromium: a review. *Water Res.* 25, 807–816.

Scofield, J.H., 1976. Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. *J. Electron Spectrosc. Relat. Phenomena* 8, 129–137.

Shirley, D.A., 1972. High-resolution X-Ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B* 5, 4709–4714.

Suwalasky, M., Castro, R., Villena, F., Sotomayor, C.P., 2008. Cr(III) exerts stronger structural effects than Cr(VI) on the human erythrocyte membrane and molecular models. *J. Inorg. Biochem.* 102, 842–849.

Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F., 1979. *Handbook of X-ray Photoelectron Spectroscopy*. Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie.

Yang, L., Chen, J.P., 2008. Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum* sp. *Bioresour. Technol.* 99, 297–307.

Yuan, S., Liang, B., Zhao, Y., Pehkonen, S.O., 2013. Surface chemistry and corrosion behaviour of 304 stainless steel in simulated seawater containing inorganic sulphide and sulphate-reducing bacteria. *Corrosion Sci.* 74, 353–366.