Cr(VI) removal from synthetic and real wastewaters: the use of the invasive biomass *Sargassum muticum* in batch and column experiments

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Abstract

The macroalgae *Sargassum muticum* was selected for the treatment of solutions containing Cr(VI). Very acidic pH values were established as optimal for Cr(VI) reduction. Algae chemical modification reduced equilibrium time to 4 hours. First order kinetic model was used to describe the reduction kinetic of Cr(VI). A column experiment allowed to distinguish the processes occurring during Cr(VI) elimination: its reduction to Cr(III) and the subsequent adsorption of this species formed. Under the selected conditions the biomass was capable of reducing all the incoming Cr(VI) during 77 hours. Industrial wastewaters from chrome plating industry were also tested for chromium removal.

Keywords: Cr(VI); *Sargassum muticum*; environment; kinetics; packed bed; pollution

1. Introduction

Hexavalent chromium is used in many industrial processes such as electroplating, wood preservation, corrosion control or leather tanning, among others. Therefore, several chromium compounds are released into the natural environment, mostly as Cr(VI) and Cr(III) forms [1]. It is well established that Cr(VI) is likely to be carcinogenic, mutagenic and teratogenic to animals and humans via ingestion [2]. During the last decades, the dumping of wastes containing Cr(VI) into natural ecosystems becomes a real concern. Then, is necessary to establish maximum limits for the discharge of this contaminant. The United States Environmental Protection Agency limit for Cr (total) in drinking waters is 0.1 mgL^{-1} [3].

Traditionally, the removal of Cr(VI) from wastewaters has been developed in two steps. The first step is the chemical reduction of Cr(VI) to Cr(III), followed by the precipitation of Cr(III) as $Cr(OH)_3$ [4]. This technique involves some disadvantages like secondary pollution, high chemical and energy requirements or excessive costs. Therefore, several studies can be found in literature related to develop more cheap and efficient processes for Cr(VI) contamination control. Different materials of natural origin have been tested by many authors for Cr(VI) remediation. Seaweeds [5-9], agriculture by-products and wastes [10-14], together with other materials like bracken fern [15] or lignin [16] have been proposed as low cost alternatives to traditional methods.

The extensive study of the interaction between Cr(VI) and natural materials had established that not only biosorption, but also reduction, are the processes responsible for Cr(VI) elimination from solution [17, 18]. Therefore, the use of classic isotherm, like Langmuir or Freundlich models, to describe Cr(VI) removal by biomaterials is

erroneous. These equations have no application for a redox reaction, but they can be applied to describe the total chromium or trivalent chromium removal. In this case, is important to be sure that equilibrium state has been achieved. Park *et al*. [17, 19] have definitively contributed to shed some light on these fundamental aspects.

In this work, various materials have been tested as possible Cr(VI) bio-reductants. The raw and protonated form of the macroalgae *Sargassum muticum* have been selected for a more detailed study. This brown seaweed, originated from Japan, is considered an invasive species in European coast. Their uncontrolled spread produces several damages to environment, fisheries and tourism [20]. During the last decade our group have dedicated a great effort to find a practical application for this biomass as an effective agent in wastewater treatment [21-26]. Following, here are included experiments for the determination of optimum removal pH, biomass dose and kinetic studies centred in hexavalent chromium removal. Moreover, a dynamic test in column has also been carried out. Evidences of Cr(III) retention on the biomass has been found in this column study despite the unfavourable conditions for its adsorption. Finally, the raw and protonated *Sargassum muticum* have been used for the treatment of real wastewaters from an electroplating industry.

2. Experimental methods

2.1 *Biomass*

The materials used in this work: *Sargassum muticum* (brown algae), *Gelidium sesquipedale* and *Chondrus crispus* (red algae), hottentot fig (*Carpobrotus edulis*), bracken fern (*Pteridium aquilinum*), pine cone, pine needles, wild blackberry (*Rubus ulmifolius*) leaves, orange peel and quitin (obtained from spider crab shells [27]), were collected in Galicia (NW Spain). They were washed twice with tap water to eliminate

impurities, oven dried at 60 ºC overnight, crushed with an analytical mill (IKA A 10, Werke GmbH & Co. KG, Staufen, Germany), sieved (size fraction of 0.5-1 mm) and stored in polyethylene bottles until their use.

The raw *S. muticum* biomass was acid-treated in order to obtain its fully protonated form. It was soaked and shacked in a 0.2 $molL^{-1}$ HNO_3 solution using a rotary shaker (175 rpm) during 4 h, at a biomass concentration of 10 gL^{-1}. Afterwards, the material was rinsed thoroughly with deionised water until pH 4.5 was attained. Following filtration, treated biomass was dried in an oven at 60 ºC overnight.

2.2 *Reagents*

The reagents used in this work were HNO_3 and H_2SO_4 from Merck (Merck, Darmstadt, Germany, pro analysis, p.a.), 1,5-diphenylcarbazide from Aldrich (Sigma-Aldrich, Germany) and $K_2Cr_2O_7 \cdot 2H_2O$ p.a. from Panreac (Panreac Química S.A., Barcelona, Spain). All solutions were prepared with deionised water.

2.3 *Analytical techniques*

A standard colorimetric method was employed to determine Cr(VI) concentration in solution [28]. This procedure measures only hexavalent chromium by reaction with 1,5-diphenylcarbazide in acid solution. A red-violet complex is formed and measured spectrophotometrically at 540 nm (Cary 100 Bio UV-visible, Varian, Palo Alto, CA, USA). Total Cr concentration was determined by FAAS (Atomic Absorption Spectrometer- Varian 55B). The concentration of trivalent chromium was calculated as the difference between total chromium and hexavalent chromium concentrations.

Fourier Transform Infrared (FTIR) spectroscopy was used to identify the chemical groups present in the raw and protonated *Sargassum muticum*. The samples were

examined within the range 350-4000 cm^{-1} using a Bruker spectrophotometer (model Vector 22) equipped with a Speac Golden Gate ATR (attenuated total reflection) device. This technique allowed analysing the samples (fine powder) directly without KBr grinding.

2.4 *Screening*

Hexavalent chromium solutions of 100 mgL^{-1} were prepared dissolving exact quantities of $K_2Cr_2O_7 \cdot 2H_2O$ in deionised water. 0.1 g of biomass was putted in contact with 40 mL of the chromium salt solution. A pH value of 1 was achieved and maintained during the experiments with small volumes of HNO_3 65%. The mixtures were stirred in a rotary shaker (175 rpm) during 24 hours and then, they were analysed to determine the Cr(VI) concentration in solution.

The Cr(VI) removal percentages were calculated from the expression:

$$Removal\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

Where C_i is the initial Cr(VI) concentration and C_f is the Cr(VI) concentration after 24 hours of contact time.

2.5 *Biomass dose*

These studies were carried out in order to estimate the optimum biomass dose for maximum elimination of Cr(VI) from solution. Different amounts of raw biomass, varying between 0.5 and 7.5 mgL^{-1}, were equilibrated with 40 mL of Cr(VI) solution (100 mgL^{-1}) during 24 h. The solution pH was fixed at 1.

2.6 *Effect of pH on metal reduction*

The dependence of Cr(VI) elimination on solution pH was studied in batch experiments in the pH range from 1 to 6. For this purpose 0.1 g of biomass were placed in Erlenmeyer flasks with 40 mL of metal solution (100 mgL^{-1}). The mixtures were stirred on a rotary shaker at 175 rpm for 24 h (room temperature). The pH was adjusted by addition of NaOH and HNO_3 (Merck p.a.) solutions. The hexavalent chromium concentration was calculated as mentioned above.

2.7 *Kinetic studies*

The experiments were performed in a thermostated vessel (25.0 ± 0.1 ºC). 0.25 g of *Sargassum muticum* were mixed under agitation with 100 mL of Cr(VI) solution of different concentrations: 20, 50, 100 and 200 mgL^{-1} (raw biomass) or 50 and 100 mgL^{-1} (protonated biomass). The pH was maintained at a constant value of 1. Several aliquots were collected at different times in order to determine the Cr(VI) concentration.

2.8 *Column experiment*

The column experiment was carried out in a glass column of 3 cm internal diameter and 40 cm length, filled with 30 g of protonated *Sargassum muticum*. A porous sheet was attached at the bottom of the column in order to support the biomass, and to ensure uniform inlet flow and a good liquid distribution into the column. The top of the bed was closed by a 10 cm height layer glass beds (1 mm diameter), which avoid the loss of biomass and also ensure a closely packed arrangement. A 50 mgL^{-1} Cr(VI) solution was fed through the bed in up-flow mode at 10 $mLmin^{-1}$ using a peristaltic pump (Watson Marlow) connected at the bottom of the column. The pH of the incoming solution was fixed at 1. Samples were collected periodically. The concentrations of the chromium species in solution were determined as mentioned above.

2.9 *Industrial wastewaters*

Batch experiments were also carried out to treat wastewaters from a chrome plating industry. The materials used in this study were: the raw and protonated algae *Sargassum muticum* and the bracken fern biomass. They were putted into contact with 40 mL of the wastewaters during 48 h at the optimal dose. After this time, Cr(VI), Cr(III) and total Cr concentrations were determined. Two pH values were tested, natural (not fixed) and 1.

3. **Results and discussion**

3.1 *Screening*

Chromium removal from wastewaters using biomaterials is well stated as an adsorption-coupled reduction process [17]. In order to favour the reduction reaction of the hexavalent chromium a very acidic pH was selected. Very low pH values could avoid operating a system based on this technology. Nevertheless, it can be directly applied, for example, at the end of some acidic washing cuvettes in chromium plating plants, where solution pH values are lower than 2.

Different materials were studied at pH 1 in order to evaluate their potential use in Cr(VI) removal processes. Figure 1 shows the Cr(VI) elimination percentages obtained for each biomass. Most of the selected materials in this screening were able to remove high quantities of Cr(VI). In fact, only two of them (*Chondrus crispus* and chitin) presented removal percentages lower than 40%. The brown seaweed *Sargassum muticum*, both raw and acid treated forms, along with bracken fern, hottentot fig and *Rubus ulmifolius* present removal percentages close to 100%. Therefore, these materials could be considered for their use in Cr(VI) decontamination technologies, considering the good removal results.

Regarding the chemical composition of these materials, we can find a wide variety of compounds and many structural differences. The main structural polysaccharide present

in most of them is cellulose (1-4 linked β-D-glucose). *Sargassum muticum* is an example of brown algae, which are formed by different kinds of polysaccharides, mainly alginates (1-4-linked β-D-mannuronate and α-L-guluronate) and fucoidans (α-L-fucose). *Gelidium sesquipedale* and *Chondrus crispus* are red algae constituted by carrageenans (3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose) and agar (L,D-(3-6)-anhydro-α-galactopyranose). All these macroalgae also contain a great number of hydroxyl groups that form part of the polysaccharide structure and an internal cell wall composed by cellulose [29, 30]. The other materials are basically composed by lignin (methoxylated monolignol monomers), cellulose and hemicellulose, or acetylglucosamine (2-Acetylamino-2-deoxy-D-glucose), in the case of the chitin. Nevertheless, they all share the ability to reduce Cr(VI) to Cr(III) due to the presence of a great number of chemical entities, such as phenols or amino groups, that act as electron donors.

As stated in the introduction section, *Sargassum muticum* was selected not only for its good removal results but also for its abundance and problems associated with its spread. The treatment of the algae is also significant in order to obtain stable biomass suitable for industrial use. As in many parts of the world, this macroalgae is also considered an invasive species in Galician coats, which implies an important environmental hazard and also a risk for the aquaculture industry, with a great importance in this Spanish region. These problems require the removal of the algae from the sea and its treatment as a waste. Therefore, the search for an application regarding this seaweed is of great importance. Nevertheless, some limitations concerning optimal operation pH, stabilization of the material or processing of the generated metal-biomass should be taken into account.

FTIR spectroscopy was used to identify the chemical groups present in raw and protonated *S. muticum*. The results are showed in Figure 2. The broad band at 3276-3332 cm^{-1} shows the presence of free and intermolecular bounded –OH and –NH groups. The band that appeared at 2923-2935 cm^{-1} indicates the existence of –CH stretching. Carboxyl ions present in these materials, give rise to two bands: a strong asymmetrical stretching band at 1614-1621 cm^{-1} and a weaker symmetrical band at 1415-1503 cm^{-1}. Moreover, the peak at 1250 cm^{-1} could be ascribed to –SO3 stretch. The peaks at 1020-1029 cm^{-1} were due to the –C–O stretching of alcoholic groups. It is remarkable the fact that the intensity of this peak is greater than the corresponding to carboxyl groups especially for protonated *S. muticum*. This could mean that –OH groups are more abundant than carboxyl ones. Moreover, when the alga was protonated some differences appear in FTIR spectra: great increase in the peak due to –C–O stretching of alcoholic groups; displacement of the weaker stretching symmetrical band and splitting of the strong asymmetrical stretching band, due to the presence of carboxyl ions. The FTIR spectroscopy does not provide quantitative information about the algae surface chemistry but this analysis can even identify the main chemical groups.

3.2 *Biomass dose*

The minimum dose of *Sargassum* biomass necessary to achieve maximum chromium elimination was studied increasing the biomass concentration. Figure 3 shows the removal percentages of Cr(VI) from solution. Percentages close to 100% were obtained for a biomass dose greater than 2 gL^{-1}. These results allowed us to select a biomass concentration of 2.5 gL^{-1} as optimum for further experiments.

3.3 *pH dependence studies*

We have already mentioned that hexavalent chromium removal is mainly due to reduction and adsorption processes, both of them highly pH dependent. Then, pH studies were carried out in order to determine the best experimental conditions for maximum Cr(VI) removal. Figure 4 shows the Cr(VI) elimination as a function of pH for raw and protonated *Sargassum muticum*. In both cases at low pH values the Cr(VI) removal efficiency was high. Nevertheless, as the pH was increased the removal percentages were considerably reduced. Maximum removals of 100% were observed at pH 1. Moreover, when the protonated form of the alga was studied, Cr(VI) maximum removal was also observed at pH 2, which is important for practical application. The elimination efficiency in the range of pH from 2 to 5.5 decreases, but removal percentages observed for the protonated algae were always better than those reported for raw *Sargassum muticum*.

Speciation calculations show that hexavalent chromium in solution mainly exists as hydrogen chromate ion ($HCrO_4^-$) in the pH interval studied [31]. This anion, in contact with the electron donor groups of the biomass, is reduced to Cr(III) with the subsequent oxidation of the functional groups in the biomass surface.

The proposed indirect mechanism for this reaction involves three steps [32]: (1) sorption of $HCrO_4^-$ anions onto the biomass (2) reduction of Cr(VI) to Cr(III) and (3) adsorption of Cr(III) onto the biomass. This mechanism and also its variant, considering the direct reduction of Cr(VI) on solution, are now widely accepted. It was confirmed by the study of the interaction of hexavalent chromium with the biomass by several techniques, like X-ray photoelectron spectroscopy [33] and recently by X-ray absorption fine structure spectroscopy [18].

Then, according to this mechanism, low pH values will favour the Cr(VI) reduction by two different ways: on the one hand the *Sargassum* surface will be more positively charged, which favours the adsorption of $HCrO_4^-$; on the other hand, the presence of great amounts of protons in solution favours the reduction reaction, in agreement with the following equation:

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad E^0 = +1.35\ V \qquad (2)$$

According to this relationship, acidic conditions produce an increase in the reduction potential $HCrO_4^-/Cr^{3+}$, thereby strengthening the oxidising character of $HCrO_4^-$ ions with respect to the biomass. When the solution pH increases the reduction potential decreases, so Cr(VI) stays in hexavalent form [5]. So that, pH 1 was selected as optimum for Cr(VI) elimination. More detailed studies were performed at this pH value.

3.4 *Kinetic studies*

Kinetic studies allow establishing the necessary time to achieve the equilibrium. Figures 5 and 6 show the variation of Cr(VI) concentration with time for the selected biomaterials. The reduction kinetics of Cr(VI) by raw *S. muticum* is relatively fast, achieving the 50 % in less than 50, 85 and 90 minutes, when the initial chromium concentration is 20, 50 and 100 mgL^{-1}, respectively. When the protonated alga was utilized, the kinetic was considerably faster, achieving a 50 % reduction in the initial metal concentration, 50 and 100 mgL^{-1}, in less than 40 and 50 minutes, respectively. When the initial Cr(VI) concentration was 100 mgL^{-1}, the equilibrium was achieved in 14 h for raw *S. muticum*. The chemical modification of this alga has a significant impact in the equilibrium time, reducing it to a value close to 200 min. These equilibrium times are comparable or even better than the obtained in previous works for the elimination of

Cr(VI) with bracken fern [15], grape stalks and yohimbe bark [13] or activated carbons [34].

Kinetic studies also proved that the reduction depends on the initial Cr(VI) concentration. Moreover, it can be noted that complete removal of Cr(VI) is obtained if contact time is long enough.

As stated in the above section, at pH 1 it can be assumed the irreversible reduction of Cr(VI) to Cr(III) due to the reducing organic matter present in the alga. Therefore, the disappearance of Cr(VI) in solution can be examined, as a first approximation, using a simple first order kinetic model (Eq. 3).

$$\frac{d[Cr(VI)]}{dt} = -k[Cr(VI)] \rightarrow [Cr(VI)]_t = [Cr(VI)]_0 e^{-kt} \quad (3)$$

where *k* is a pseudo-first order rate constant for the reduction of Cr(VI) that includes the effect of protons and the concentration of oxidable organic matter.

Figures 5 and 6 show the kinetic of Cr(VI) elimination by raw and protonated *S. muticum*, respectively, at different initial metal concentrations and also the data fit to Eq. 3. The kinetic constants obtained and the coefficients of correlation for each fit are showed in Table 1. The *k* values found are much higher in the case of the protonated algae.

There is no clear relation between the kinetic constants and the initial chromium concentrations studied. Similar *k* values were obtained for 50 and 100 mgL^{-1} of initial Cr(VI) concentration, but for the lowest one tested the metal reduction is more rapid. This last value is similar to the obtained with the protonated alga at 100 mgL^{-1} of initial Cr(VI) concentration (Table 1).

The presence of Cr(III) could alter the kinetic of Cr(VI) reduction, probably inhibiting its adsorption and blocking the access to reducing sites. This is in agreement with the reduction mechanisms proposed by Park *et al*. for the removal of Cr(VI) by biomaterials [32]. The kinetic constant, *k*, includes the equivalent organic compounds capable of reducing Cr(VI), then, some modification in these groups due to the presence of different quantities of Cr(III) ions in solution and adsorbed in the algae could explain its changes. The adsorption of the formed Cr(III), that normally occurs based on electrostatic interactions, and contribute to the biomass modification, should be small in this case due to the very acidic pH of the solution, but not negligible.

3.5 *Column experiment*

The column experiment was developed in order to determine the capacity of acid treated *S. muticum* to remove Cr(VI) from solution in continuous tests. These studies allowed to distinguish the two processes occurring during Cr(VI) elimination: its reduction to Cr(III) and the subsequent adsorption of this species formed. Batch experiments indicated that low pH favours the reduction reaction, so a pH value of 1 was maintained in the column inlet.

The data plotted in Figure 7 shows the evolution of Cr(VI), Cr(III) and total Cr concentration during the time that the column was working. Under the selected conditions of bed depth and flow rate, 30 g of acid treated *S. muticum* was capable of reducing 100% the incoming Cr(VI) during 77 h, when the breakthrough point was attained. In this case, it was established as the time when Cr(VI) concentration in the outlet is 10% of the initial concentration. At that moment 46.2 L of contaminated solution were treated.

After breakthrough point the Cr(VI) concentration in solution was increased very fast during 50 h, when the Cr(VI) concentration in the outlet reached 30 mgL^{-1}. After this point, it started a very slow increase until the initial concentration of 50 mgL^{-1} was reached. Regarding the curve of Cr(III) it can be observed that, at first, 34 % of total Cr was retained by the biomass. Once Cr(VI) started to appear in the outlet solution (77 hours), no more adsorption of Cr(III) was observed. While Cr(VI) is totally reduced, the adsorption of the Cr(III) formed is observed, despite of the unfavourable pH conditions for this process [24]. Evidences of the Cr(III) adsorption but not Cr(VI) at pH 1 on *Sargassum* species were found by Zheng *et al*. [18].

Figure 7 allow us to analyse the properties of this kind of biomass for reducing and also adsorbing the two forms of Cr present in solution. At first, treated *S. muticum* is capable of act as reductant, eliminating 100% of Cr(VI). In addition, this alga also acts as an adsorbent, removing 34% of total Cr. This fact can be explained taking into account that at low times the functional groups of the algae were involved in two processes, reduction and adsorption. As the biomass is able to reduce 100% of Cr(VI), total Cr in the outlet increases, which could imply that the functional groups involved in Cr(III) adsorption are the same that those involved in Cr(VI) reduction. This fact is also supported by the work of Zhang *et al.* where it is showed that Cr(III) ions coordinate with the oxygen atoms of carboxyl and hydroxyl groups present in the alga. Moreover, when Cr(VI) appears in the outlet, the capacity of the biomass for adsorbing Cr is over and the biomass acts only as a Cr(VI) reductant.

Regarding to the capacity of the biomass to reduce Cr(VI) different behaviours can be observed. Once the biomass is not able to reduce 100% of the inlet Cr(VI) a sharp rise was observed corresponding with the decrease in the groups that are oxidized in the biomass. After 125 h, the increase in the Cr(VI) concentration becomes slower, which

can be attributed to the remaining oxidizable groups which reduce Cr(VI) during 300 h. These groups are able to reduce Cr(VI) ions for a long time, so large amounts of contaminated solution can be treated.

Finally, the increase in total Cr concentration observed at the end could be assigned to the Cr(III) desorption that was retained in the column in the firsts hours of operation, due to some lose of the biomass structural consistence. This fact was observed during all the time that the column was working, at first the outlet solution had a brown colour characteristic of this kind of alga, and the biomass inside the columns started to become colourless. At the end of the operation time all the algae had a white-yellow colour, that can be ascribed to de loss of the main pigments (chlorophyll and fucoxantin) present in the biomass due to their oxidation by Cr(VI) [5].

3.6 *Industrial wastewaters*

Industrial wastewaters from a chrome plating plant were tested in this part of the study. These wastewaters were fully characterized. The results are showed in Table 2.

Cr(VI) and Cr(III) elimination from these real wastewaters were essayed in batch experiments. Table 3 shows the removal percentages of Cr(VI), Cr(III) and total Cr in solution after 48 h of contact time. When the pH was not fixed, the raw *Sargassum muticum* presents elimination percentages lower than 40%, while the protonated algae is capable of removing higher percentages of the two chromium forms present in solution. According with the previous experiments, the acid treatment of *S. muticum* also improves the capacity of this biomass for Cr(VI) reduction in the real wastewater tested.

The presence of Cr(III), Al and nitrate ions in solution makes the interaction of Cr(VI) with the biomass oxidized groups more difficult. At the pH of the real wastewater solution carboxylate groups present in the algae structure are ionized, so the interactions

of these groups with cations are favoured. So that, Cr(VI) reduction could be partially inhibited due to the great diminution in positive charge of the chemical entities, and also to possible inhibition in the organic groups oxidation.

In order to improve conditions for the reduction, a set of experiments were developed adjusting the pH to 1. The summary is showed in Table 3. As expected, taking into account the result obtained in batch experiments with synthetic water, Cr(VI) removal percentages were improved considerably, reaching almost 100% in both cases. The increase is particularly significant for raw *S. muticum*. Concerning Cr(III) results, it was found that the drop in pH value greatly diminish its adsorption due to the less favourable interaction with the protonated groups of the biomass. Therefore, at pH 1 Cr(VI) is completely removed from solution, but some Cr(III) from reduction and initially present remains in solution, so Cr(III) is not eliminated. In the case of total Cr, the best results were obtained with the protonated algae at natural pH.

As a brief resume it can be said that *Sargassum muticum* seaweed could be a good alternative to the traditional methods for chromium species elimination from real wastewaters of a plating plant. Control of solution pH is of great importance. Then, depending on the objectives of the treatment, the pH should be fixed to a determinate value.

4. Conclusions

The macroalgae *Sargassum muticum* was found to be extremely efficiency for Cr(VI) removal in solutions with very low pH. The kinetics of the process is relatively fast and can be described using a first order model. The protonation of the algae considerably increase its Cr(VI) removal qualities. Elimination of Cr(VI) through its reduction to Cr(III) and the subsequent adsorption of this species formed, was clearly stated in a

simple column experiment. Industrial wastewaters from a chrome plating plant were successfully tested for chromium removal using this biomass.

5. Acknowledgements

The authors wish to thank Ministerio de Educación y Ciencia for financial support through the research project CTM2010-18114. P. Lodeiro gratefully acknowledges financial support through Angeles Alvariño project AA 10.02.56B.44.0 (from Xunta de Galicia) co-funded by 80% with European Social Funds.

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FIGURE CAPTIONS

Figure 1. Percentage of chromium removal by different biomasses in deionised water. Initial concentration of Cr(VI) 100 mg L^{-1}, pH 1 and biomass dose 2.5 g L^{-1}.

Figure 2. FTIR spectra for raw (solid line) and protonated (dashed line) *S. muticum*.

Figure 3. Removal percentage of Cr(VI) as a function of biomass dose. Initial concentration of Cr(VI) 100 mg L^{-1}, pH 1 and 24 h of contact time.

Figure 4. pH dependence studies for the elimination of Cr(VI) using raw (squares) and protonated (circles) *Sargassum muticum*. Contact time 24 h, biomass concentration of 2.5 g L^{-1} and initial Cr(VI) concentration 100 mg L^{-1}.

Figure 5. Kinetics of Cr(VI) elimination for raw *Sargassum muticum*. Biomass concentration 2.5 gL^{-1}, Cr(VI) initial concentration 20 (circles), 50 (squares), 100 (up triangles) and 200 (down triangles) mgL^{-1}. T= 25 ± 0.1 ºC and pH 1. The lines correspond to the fit to Eq. 3.

Figure 6. Kinetics of Cr(VI) elimination for acid treated *Sargassum muticum*. Biomass concentration 2.5 gL^{-1}, Cr(VI) initial concentration 50 (squares) and 100 (up triangles) mgL^{-1}. T= 25 ± 0.1 ºC and pH 1. The lines correspond to the fit to Eq. 3.

Figure 7. Column experiment at pH 1, using 30 g of acid treated *Sargassum muticum*, Initial Cr(VI) concentrations 50 mgL^{-1} and flow rate of 10 $mLmin^{-1}$. The symbols represent Cr(VI) concentration (circles), Cr(III) concentration (triangles) and total Cr concentration (squares).

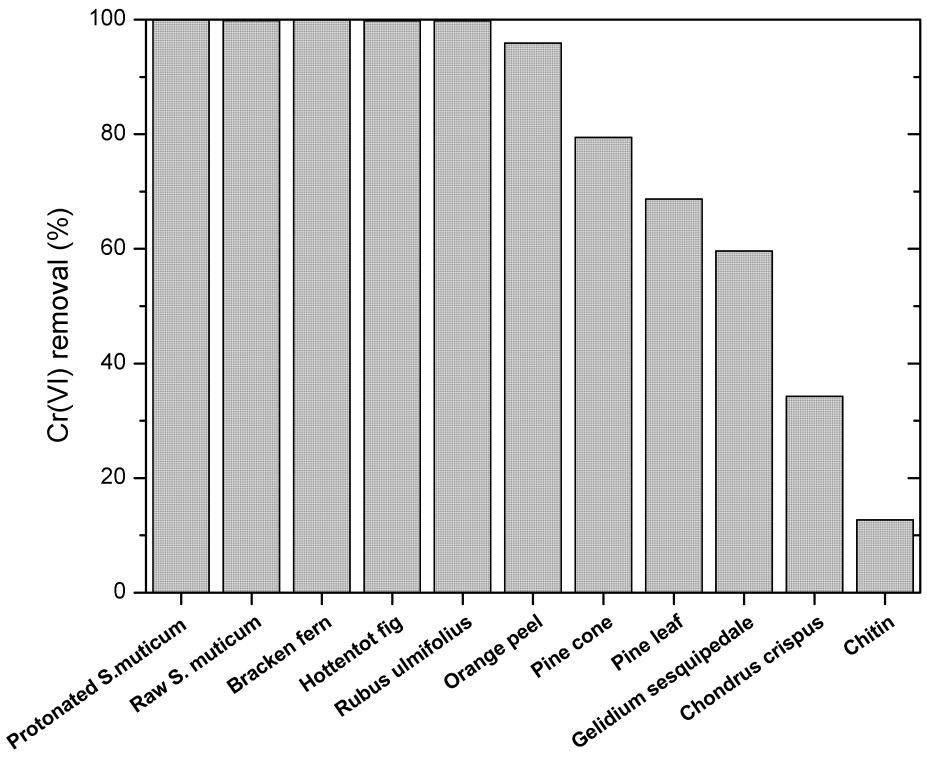

Figure 1

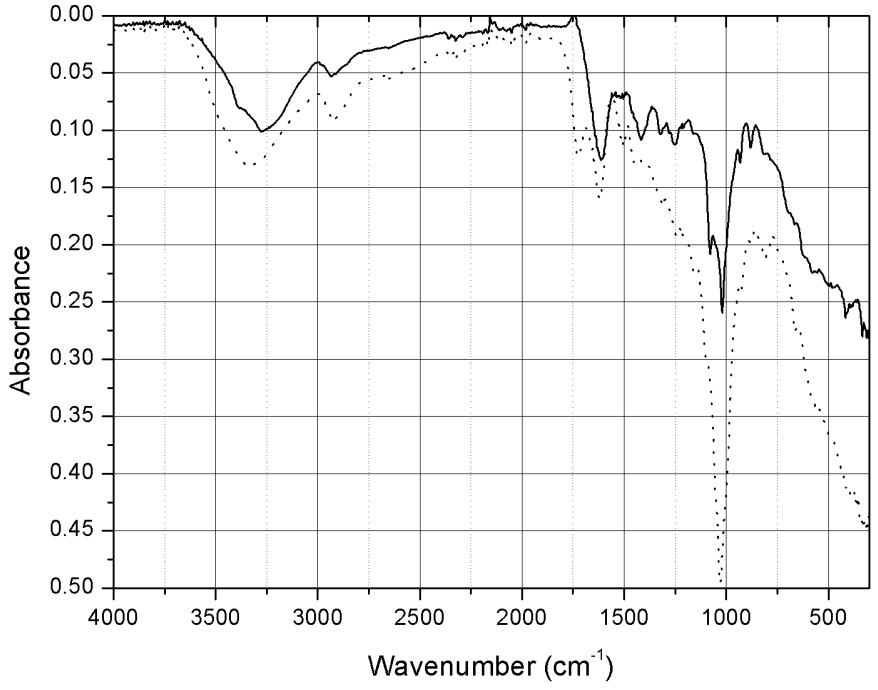

Figure 2

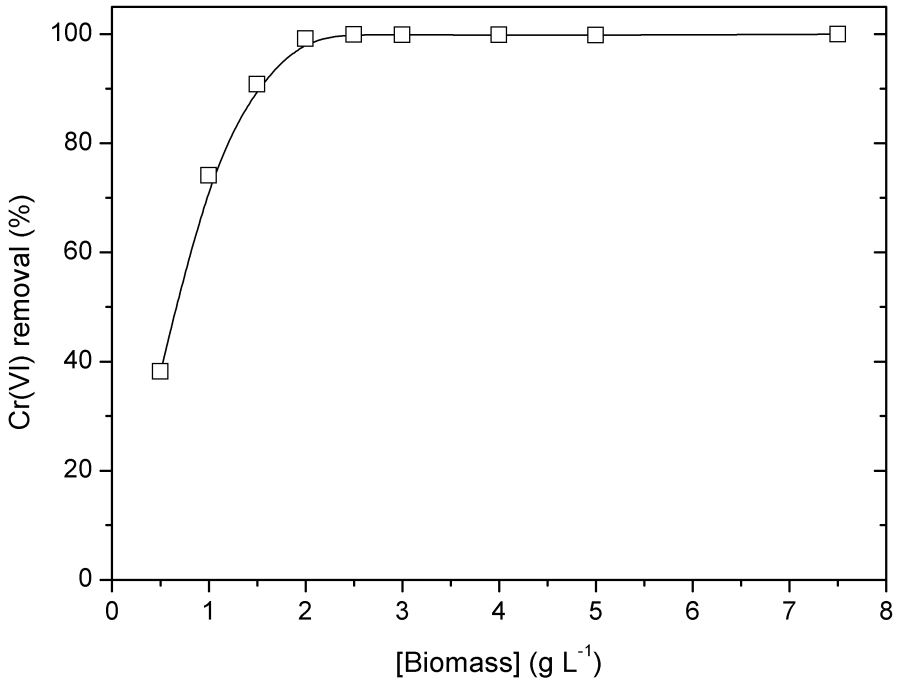

Figure 3

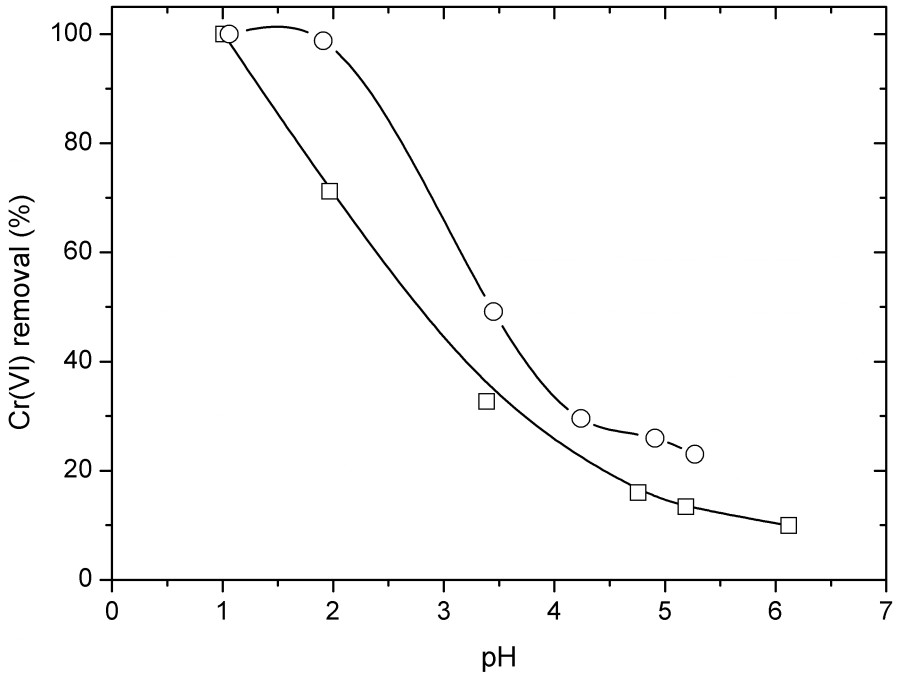

Figure 4

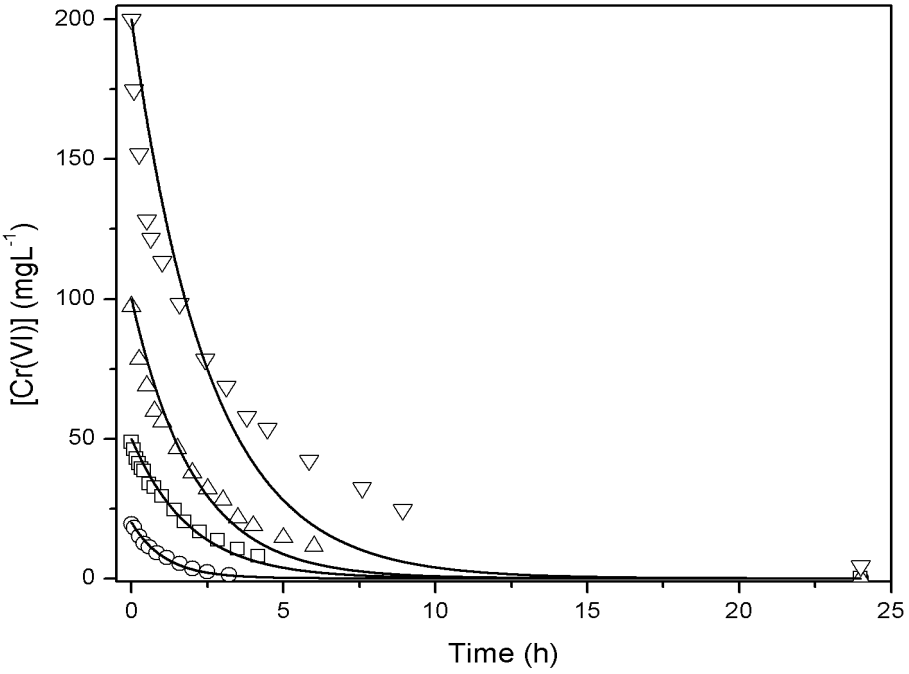

Figure 5

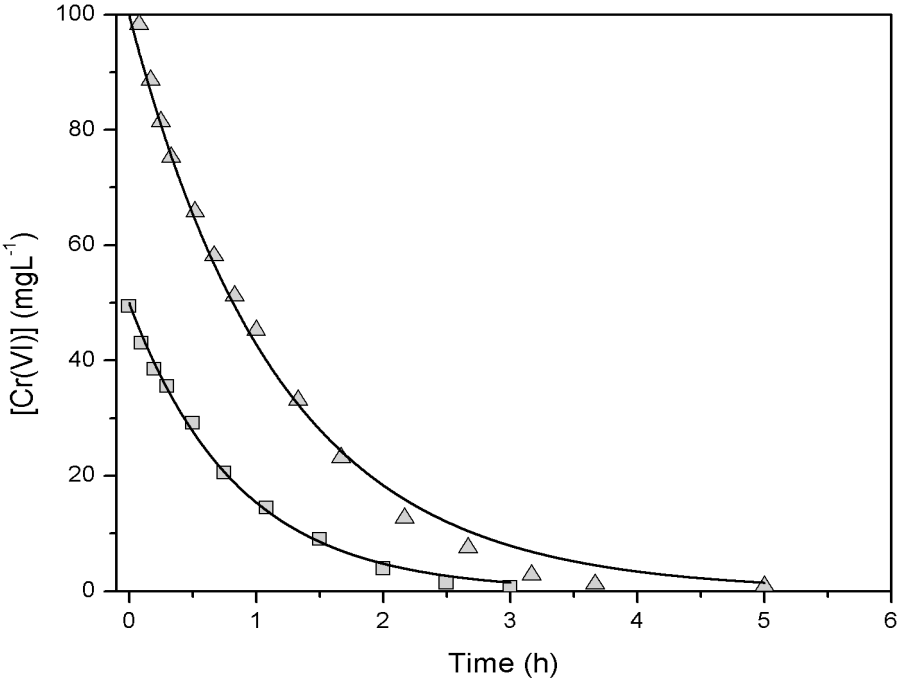

Figure 6

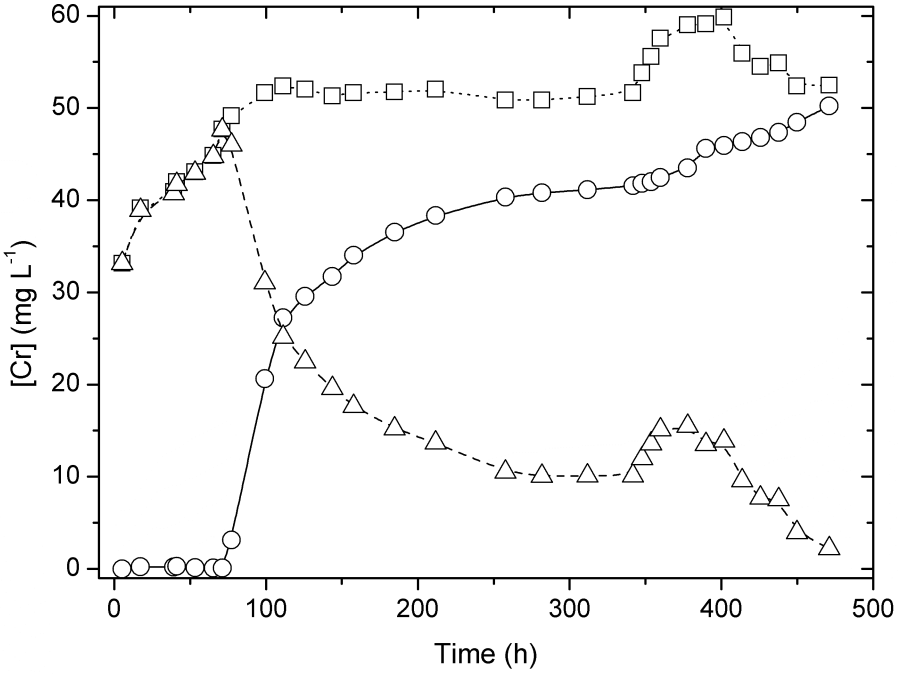

Figure 7

TABLES

Table 1. Kinetic rate constants for Cr(VI) elimination by raw and protonated *Sargassum muticum* at several initial metal concentrations (T=298 K, pH= 1), obtained by fitting experimental data to Equation 3.

C_i (mg·L^{-1})	k (h^{-1})	r^2
Raw *Sargassum muticum*		
200	0.39 ± 0.05	0.86
100	0.49 ± 0.03	0.96
50	0.52 ± 0.02	0.98
20	0.92 ± 0.03	0.992
Protonated *Sargassum muticum*		
100	0.85 ± 0.02	0.995
50	1.18 ± 0.03	0.997

Table 2. Composition of wastewater from a chrome plating plant.

Parameter	
pH (18.9 ºC)	4.88
Conductivity (25 ºC) / μScm^{-1}	157.3
Solved Cr(VI) / mgL^{-1}	25.3
Solved Cr(III) / mgL^{-1}	12.8
Solved Al / mgL^{-1}	22.6
Total Cr / mgL^{-1}	38.1
Total Al / mgL^{-1}	24.1
Nitrate / mgL^{-1}	16.0
Cyanide / mgL^{-1}	< 0.5

Table 3. Elimination percentages of chromium species by raw and protonated *Sargassum muticum* at pH 1 and natural pH. Contact time 48 h, biomass dose 2.5 gL^{-1}.

	Sargassum muticum		Protonated *S. muticum*	
%	pH 1	natural pH	pH 1	natural pH
Cr(VI)	99.3	39.4	99.2	84.3
Cr(III)	-	30.4	-	33.2
Cr total	32.9	36.4	32.9	67.1