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Research Article

Biosorption of chromium(III) by two brown algae *Macrocystis pyrifera* and *Undaria pinnatifida*: Equilibrium and kinetic study

Two brown algae, *Macrocystis pyrifera* and *Undaria pinnatifida*, were employed to remove Cr(III) from aqueous solutions. Both seaweeds were characterized in terms of alginate yields. The alginate contents were 20 and 30% of the dry weight for *M. pyrifera* and *U. pinnatifida*, respectively. Kinetics experiments were carried out at different initial pH values. Cr(III) biosorption was affected by the solution pH. The highest metal uptake was found at pH 4 for both biosorbents. Different models were applied to elucidate the rate-controlling mechanism: pseudo-first-order, pseudo-second-order, external mass transfer and intra-particle diffusion. The application of Langmuir, Freundlich and Dubinin–Radushkevich models to the equilibrium data showed a better fitting to the first model. The maximum Cr(III) sorption capacity (q_m) and the affinity coefficient (b) were very similar for both biosorbents: 0.77 mmol/g and 1.20 L/mmol for *M. pyrifera* and 0.74 mmol/g and 1.06 L/mmol for *U. pinnatifida*. The free energy of the sorption process was estimated using the Dubinin–Radushkevich isotherm. The values indicate that the processes are chemical sorptions. To evaluate the significance of the ion-exchange mechanism, the light metals (Ca^{2+}, Na^{+}, Mg^{2+} and K^{+}) and pH were measured during the experiments.

Keywords: Adsorption / Brown algae / Chromium / Equilibrium / Kinetics

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1 Introduction

Chromium compounds are used for electroplating, the manufacture of dyes and pigments, leather tanning, the production of steel and alloys and wood preserving [1]. Chromium-contaminated natural waters, including surface water and groundwater, have a significant impact, affect all forms of life when entering the food chain through the disposal of wastes into water channels. In the environment, chromium, a redox active metal element, usually exists as Cr(III) or Cr(VI) species. Cr(VI) is a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations. Trivalent Cr is recognized as an essential nutrient required for sugar and fat metabolism, which may exert genotoxic effects in vitro under high exposure conditions. Due to their toxic effects on living systems, US EPA has set the maximum contaminant concentration level for Cr(VI) in domestic water supplies at 0.05 mg/L, while total Cr (including Cr(III), Cr(VI) and its forms) is regulated to below 2.0 mg/L [2].

The conventional method for Cr(VI) removal is its reduction to Cr(III) at pH 2.0 followed by precipitation of $Cr(OH)_3$ by increasing the pH to 9–10 using lime. The disadvantage of precipitation is the disposal of solid waste. Nowadays, adsorption has become by far the most versatile and widely used technology, and activated carbon the most commonly used sorbent. However, activated carbon is expensive, so there has been increased interest in the last years in the use of low-cost adsorbent materials [2]. Algae have been employed as a biosorbent material as well as other kinds of biomass (especially fungi and bacteria) [3], brown algae (Phaeophyta) exhibit high metal uptakes, low cost and are readily available. The main reason for their high metal affinity is the presence of alginate in their cell wall. Alginate is a structural polymer in numerous species of brown seaweed, particularly, members of the genera *Ascophyllum*, *Ecklonia*, *Fusarium*, *Laminaria* and *Macrocystis* constituting between 10 and 40% of the dry solids of these marine algae [4]. As a result of their configuration,

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the polymer chains form electronegative cavities, capable of holding cations via ionic interactions. Due to this ability, alginate has been used for the immobilization of biological material for various purposes, including the removal of heavy metal from wastewater [5].

Macrocystis pyrifera and *Undaria pinnatifida* are the brown algae very abundant in the south coast of Argentina and they could constitute cheap and available biomasses for heavy metal biosorption. There are few previous reports about studies using such biomasses in the removal of lead, cadmium, nickel, copper and mercury [6–9] but none for chromium removal.

Thus, the main objective of this work was to study the uptake of Cr(III) ions from aqueous solutions by *M. pyrifera* and *U. pinnatifida*. The optimum biosorption conditions were found as a function of pH and contact time. Langmuir, Freundlich and Dubinin–Radushkevich models were used to describe equilibrium isotherms. Biosorption mechanisms of Cr(III) were also evaluated in terms of the exchange of the light metals (Ca^{2+}, Na^{+}, K^{+} and Mg^{2+}) and the change of the pH during the batch experiments.

2 Materials and methods

2.1 Biosorbent preparation

The two brown algae used in this work, *M. pyrifera* and *U. pinnatifida*, belong to the Phaeophyta class and the Laminariales order. Both were collected from the coast in Bahía de Camarones and Golfo Nuevo (Patagonia, Argentina). Algae biomass was ground and sieved and the particle size fraction 10–16 mesh (i.e. 1.2–2.0 mm) was retained for sorption experiments. Biomass was washed several times with distilled water (until the electrical conductivity in the washing water was less than 1 mS/cm) and dried. Dried biomass was treated for 24 h with 0.2 mol/L $CaCl_2$ solution at pH 5.0. Then, the biomass was repeatedly washed with distilled water. Finally, the biosorbents were dried in an oven at 50°C for 48 h and stored in desiccators.

2.2 Extraction and quantification of alginates

The pre-treatment and extraction procedures are based on that of Arvizu-Higuera et al. [10], with several modifications: 10 g of dried, ground and sieved algal samples were placed in vessels with 200 mL of 0.5% formaldehyde agitated at 600 rpm for 30 min. The solutions were drained off, and the algae were washed with distilled water. Then, the algae were put in contact with 150 mL distilled water and the pH value was adjusted to 4.0 using 12 mol/L HCl (at 600 rpm during 15 min). The aqueous solutions were drained off and the algal samples were washed several times with distilled water. The extraction was carried out mixing the washed algae with 250 mL distilled water and adjusting the pH to 10 using 10% w/v Na_2CO_3. The mixtures were kept for 2 h at 70–75°C with continuous agitation. The algal residues were separated from the viscous liquid by filtration with gauze and cotton. About 0.5% v/v HCl was added to the filtered solution up to the completed precipitation of the alginate. The alginic acid fibers were placed in ethanol:water (1:1) to eliminate the excess of acid and others residues. The precipitate was separated by vacuum filtration and mixed with distilled water. About 10% w/v Na_2CO_3 was slowly added to achieve the complete dissolution of the alginic acid. The alginate then was precipitated by drop-wise addition of 10% w/v $CaCl_2$ solution to the stirred alginic acid solution. The precipitates were recovered by filtration and treated with 5% NaClO during 30 min in constant agitation for whitening. Then, they were washed three times with ethanol:water (1:1). To transform the calcium alginate into alginic acid, the fibres were mixed with distilled water and 12 mol/L HCl was slowly added until the pH of the mixture was 2.0. The second wash step was then performed but maintaining the pH at a lower value (1.8) during 15 min. This process was repeated twice. Finally, the fibres were washed with small portions of water, filtered and dried at 30–40°C up to constant weight. The alginate yields were calculated as %w/w, based on the initial dry weight of the algae.

2.3 Cation-exchange capacity (CEC)

The ion-exchange capacity of the biomass to hold cations, i.e. the number of negatively charged sites per unit of biomass mass, could be quantitatively expressed in a measured property known as the CEC. The CEC was measured by cation displacement as described by Hawari and Mulligan [11]. Twenty milliliters of 1 mol/L potassium acetate was added to 1 g of the algae biomass in a 50-mL centrifuge tube. The samples were shaken on a shaker for 30 min at 75 rpm. Then, they were centrifuged for 10 min at 2000 rpm. The clear supernatant was discarded. This process was performed twice. Twenty milliliters of distilled water was added to the biomass and the samples were shaken for 30 min at 75 rpm. Then, they were centrifuged for 10 min at 2000 rpm. The clear supernatant was discarded. This process was performed twice. Twenty-five milliliters of 1 mol/L ammonium acetate was added to the biomass. The samples were shaken for 30 min at 75 rpm and then centrifuged for 10 min at 2000 rpm. The clear supernatant was collected in a clean 50-mL centrifuge tube. This process was repeated twice by pouring the clear supernatant into the same centrifuge tube. The concentration of potassium was measured by atomic absorption. The value for the concentration of potassium is equal to the CEC. The test was performed in triplicate and the average CEC values were 80 ± 4 meq/100 g (*M. pyrifera*) and 69 ± 5 meq/100 g (*U. pinnatifida*).

2.4 Kinetic and equilibrium studies

The kinetic experiments were carried out at different initial pH values (3.0, 4.0 and 5.0) adding 0.1 g of biosorbent to 250-mL Erlenmeyer flasks containing 100 mL of 50 mg/L Cr(III) solution (prepared by dilution of the stock solution of 1000 mg/L Cr(III). Flasks were kept at 20°C in a rotary shaker at 160 rpm. Samples were collected at different time intervals to analyze the chromium remaining in solution.

Chromium sorption isotherms were obtained by mixing 0.1 g of biosorbent with 100 mL of chromium solution (initial concentration varying from 10 to 500 mg/L) at 20°C in a shaker (160 rpm). The initial pH (4.0) and the contact time (4 h) were selected according to the kinetic experiments. At the end of the experiments, Cr(III) and also Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} were analyzed in the solution in order to evaluate ion-exchange mechanisms.

After metal sorption, biosorbents were recovered, washed three times with distilled water and dried in an oven at 50°C for 24 h. Samples were examined using an Environmental Scanning Electron Microscopy (ESEM) (Quanta 200 FEG, FEI, USA), equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. Control biomass (biomass in contact with distillated water at pH 4.0) was also analyzed.

All the experiments were carried out in duplicate. All the chemical reagents were *pro analysi* grade.

2.5 Analytical methods

The initial and final metal concentrations in solution were measured using an absorption atomic spectrophotometer Shimadzu AA-CC6650 (Shimadzu Corporation, Japan). Prior to measurement, samples were filtered through a 0.45-μm membrane. The amount of metal adsorbed was calculated by the mass balance equation

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where q is the solute uptake (mg/g or mmol/g), C_i and C_f the initial and final solute concentrations in solution (mg/L or mmol/L), respectively, V solution volume (L) and m the mass of biosorbent (g, dry weight basis).

Kinetic information is required for modeling and design of the adsorption processes. In order to investigate the mechanism of biosorption and the potential rate-controlling step, the following kinetic models have been used to test experimental data.

The integrated pseudo-first-order equation (PFORE) [12] and can be expressed as

$$\ln\left(1 - \frac{q_t}{q_{eq}}\right) = -k_1 t \quad (2)$$

where q_{eq} (mg/g) is the sorption capacity at equilibrium (experimental value), k_1 (min^{-1}) is the pseudo-first-order rate constant.

The integrated pseudo-second-order rate equation (PSORE) [12] can be expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (3)$$

where q_{eq} (mg/g) is the sorption capacity at equilibrium (calculated value from experimental data), k_2 ($g\,mg^{-1}\,min^{-1}$) is the pseudo-second-order rate constant.

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process. The solid–liquid sorption process can be divided into three steps: (i) mass transfer of the adsorbate from the bulk liquid to the particle surface (boundary-layer diffusion), (ii) adsorption at an exterior site, (iii) intra-particle diffusion. Thus, the uptake of chromium ions can be controlled by either the mass transfer through the boundary film of liquid or by the intra-particle mass transfer. The external mass transfer coefficient, β_L (cm/s) of Cr(III) in the liquid film boundary can be evaluated using the equation proposed by Gupta et al. [13]

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mk_a}\right) = \ln\left(\frac{mk_a}{1+mk_a}\right) - \left(\frac{1+mk_a}{mk_a}\right)\beta_L.S_s t \quad (4)$$

where C_t and C_0 (both in mg/L) are the concentration of sorbent at time t and 0, respectively, k_a (L/g) is a constant obtained by multiplying the Langmuir constants q_m and b, m (g/L) and S_s (cm^2/L) are the adsorbent mass and surface area per unit of volume of solution, respectively. The mass transfer coefficient β_L (cm/s) can be calculated from the slope of the regression line: $\ln[(C_t/C_0)-(1/1+mk_a)]$ versus t.

The intra-particle diffusion was explored by using the following equation:

$$q_t = K_{dif} t^{1/2} + C \quad (5)$$

where C is the intercept and K_{dif} is the intra-particle diffusion rate constant. The value of q_t correlated linearly with values of $t^{1/2}$ and the rate constant K_{dif} was directly evaluated from the slope of the regression line [13].

Equilibrium relationships between sorbent and sorbate are described by sorption isotherms. Many models have been proposed for the adsorption of solutes from liquid solutions onto a solid surface. Langmuir model is probably the most popular isotherm model due its simplicity and its usually good agreement with experimental data. According to this model, uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate [14]. The Langmuir isotherm is represented by the following equation:

$$q_{eq} = \frac{bq_m C_{eq}}{1+bC_{eq}} \quad (6)$$

where q_{eq} is the metal uptake at the equilibrium (mmol/g); q_m is the maximum Langmuir uptake (mmol/g); C_{eq} is the final concentration at the equilibrium (mmol/L); b is the Langmuir affinity constant (L/mmol). The parameters of the model were determined after linearization of Eq. (6) (i.e. C_{eq}/q_{eq} versus C_{eq}).

The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is:

$$q_{eq} = K\,C_{eq}^{1/n} \quad (7)$$

where K is a constant related to the biosorption capacity and $1/n$ is an empirical parameter related to the sorption intensity of the adsorbent, which varies with the heterogeneity of the material. The parameters were obtained by linear regression after linearization ($\ln q_{eq}$ versus $\ln C_{eq}$).

The equilibrium data were also analyzed with the Dubinin–Radushkevich (D-R) isotherm model to characterize the nature of the biosorption processes as physical or chemical. The linear representation of D-R isotherm equation is expressed by [15]

$$\ln q_{eq} = \ln q_m - \beta\epsilon^2 \quad (8)$$

where q_{eq} is the amount of metal ions sorbed on per unit weight of biomass (mol/g), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol/J) and ε is the Polanyi potential ($\varepsilon = RT\ \ln(1+1/C_{eq})$). The sorption energy ($E$; kJ/mol) was calculated as follows [15]:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

3 Results and discussion

3.1 Extraction and quantification of alginates

Alginic acid occurs in all brown algae. It may be present both in the cell wall matrix and in the mucilage or intercellular material and can constitute between 10 and 40% of the dry weight of the algae [16]. Its abundance depends on the depth at which the algae are grown, in which part of life cycle it is, the health state and it also displays seasonal variations. The yields of alginate founded with the protocol applied in this work were 20 ± 5 and 30 ± 4.5% of the dry weight for *M. pyrifera* and *U. pinnatifida*, respectively. The difference in the alginate amount could be attributed to the biomass growth conditions and the moment of the life cycle when it was harvested.

3.2 Kinetics of Cr(III) removal

The study of the sorption kinetic is not only useful for elucidating sorption mechanism and determining the rate-controlling steps (the resistance to film diffusion, intra-particle diffusion or the

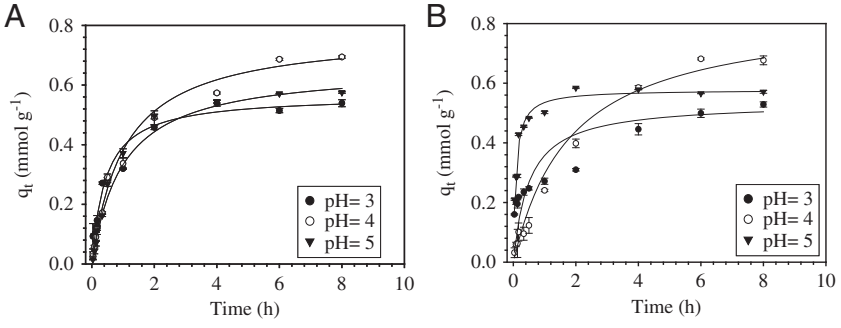

Figure 1. Evolution of chromium uptake at different initial pH values using (A) *M. pyrifera* and (B) *U. pinnatifida*. The lines represent the fitting with the PSORE kinetic model.

Table 1. Kinetic constants for the adsorption of Cr(III) onto *M. pyrifera* and *U. pinnatifida* at different initial pH values

Parameters	*M. pyrifera*			*U. pinnatifida*		
	pH 3	pH 4	pH 5	pH 3	pH 4	pH 5
Pseudo-first-order						
K_1 (min^{-1})	9.63×10^{-3}	0.0109	0.0137	0.0104	0.0049	0.019
R^2	0.92	0.95	0.95	0.89	0.90	0.74
Pseudo-second-order						
q_{eq} (mmol/g)	0.57	0.77	0.66	0.54	0.85	0.57
K_2 (g mmol^{-1} min^{-1})	0.067	0.021	0.025	0.062	0.010	0.36
R^2	0.996	0.995	0.994	0.98	0.95	0.999
External mass transfer						
βL (m/s)	5.9×10^{-4}	8.7×10^{-4}	1.4×10^{-3}	2.5×10^{-4}	4.5×10^{-4}	6.8×10^{-4}
R^2	0.96	0.98	0.98	0.93	0.97	0.98
Intra-particle diffusion						
K_{id} (mmol g^{-1} min$^{-1/2}$)	0.025	0.031	0.031	0.01	0.01	0.02
R^2	0.93	0.94	0.91	0.95	0.93	0.85

$C_o = 50$ mg/L; $T = 20^\circ$C; biomass concentration = 0.1 g in 100 mL.

chemical reaction rates), but also for evaluating the optimum conditions (including equilibrium time) for batch adsorption experiments. The evolution of chromium uptake at different initial pH values using *M. pyrifera* and *U. pinnatifida* is shown in Fig. 1. The plots show that at least 6 h were needed to reach the equilibrium in both biosorbents. This contact time was later used for equilibrium studies. Acidity of the solution is frequently one of the most important factors affecting biosorption of heavy metal ions. Solution pH affects both: chemically active sites onto the biomass and the speciation of the metal in solution [17]. It is well known that Cr(III) cations in water can undergo hydrolysis and/or complexation reactions, the extent of which depends primarily on the total Cr(III) concentration, the pH, and the type of anions presents in the solution. The simple hydrolysis of Cr(III) can be written as follows [18]:

$$Cr^{3+} + H_2O \longleftrightarrow Cr(OH)^{2+} + H^+ \qquad (10)$$

Cr^{3+} and $Cr(OH)^{2+}$ were major species at pH values lower than 5.0, whereby $Cr(OH)_2^+$ was found to be negligible [19]. The adsorption of Cr(III) by biosorbents was mainly due to the

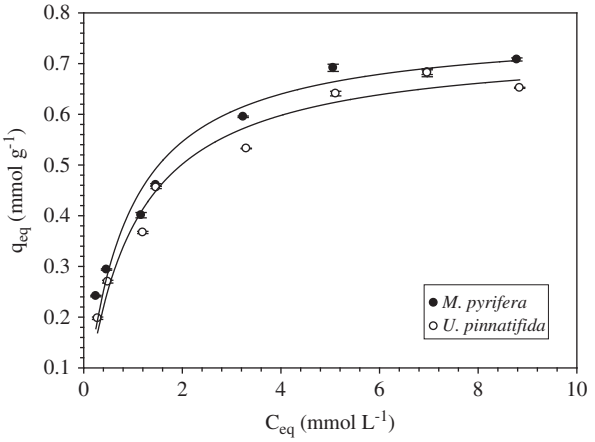

Figure 2. Adsorption isotherms of Cr(III) using *M. pyrifera* (●) and *U. pinnatifida* (○) as biosorbents at pH 4.0. Continuous lines represent the adjustment with the Langmuir model.

Table 2. Langmiur, Freundlich and Dubinin–Radushkevich parameters for the adsorption of Cr(III) on *M. pyrifera* and *U. pinnatifida*

Isotherm model	*M. pyrifera*	*U. pinnatifida*
Langmuir		
q_m (mmol/g)	0.77	0.74
b (L/mmol)	1.20	1.06
R^2	0.996	0.994
Freundlich		
K_f (mmol/g)	0.41	0.37
N	4.00	3.66
R^2	0.948	0.924
D-R Isotherm		
E (kJ/mol)	14.14	13.35
q_m (mmol/g)	0.91	0.89
R^2	0.88	0.86

Table 3. Comparison of biosorption capacity and affinity for Cr(III) with different biomaterials

Adsorbents	q_m (mmol/g)	b (L/mmol)	References
Chorella miniata	0.79	–	[28]
Carrots residues	0.86	–	[25]
Parmelina tiliaceae	1.00	–	[27]
Citrus cinensis	0.77	11.45	[24]
Eggshells	3.00	–	[29]
Yellow passion-fruit shell	1.63	–	[30]
Spirulina sp.	3.05 (pH 7)	–	[30]
Hylocomium splendens	0.8	–	[1]
Rhodococcus opacus strain	1.40	1.08	[14]
Fucus vesiculosus	1.21	1.88	[31]
Fucus spiralis	1.17	1.77	[31]
Ulva lactuca	0.71	1.98	[31]
Ulva sp.	1.02	1.38	[31]
Palmaria palmate	0.57	4.94	[31]
Polysiphonia lanosa	0.65	1.34	[31]

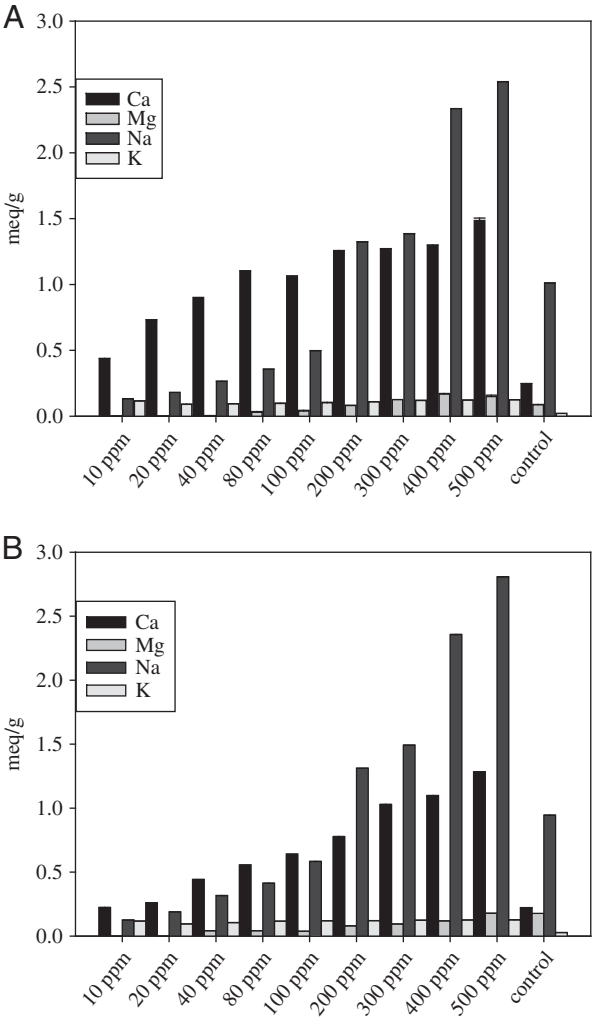

Figure 3. Light metals released during the adsorption experiments as a function of the initial Cr(III) concentration using: (A) *M. pyrifera*; (B) *U. pinnatifida*. Error bars represent the standard deviation for two replicates.

complexation of Cr(III) species. In general, the optimum pH for Cr(III) adsorption was in the range of 4.0–6.0. The high removal efficiency of Cr(III) from solution at pH > 6.0 was mainly due to the precipitation of chromium hydroxide $Cr(OH)_3$ [20, 21]. Under neutral to basic conditions (between pH 6.0 and 10.5), Cr(III) will tend to precipitate out, while under acid conditions it will tend to solubilize [22]. In addition, Cr(III) is more easily oxidized at higher pH value [23]. Regarding the biosorbent, carboxylic groups (−COOH), important groups for metal uptake, are deprotonated and negatively charged at pH values higher than 3.0, and the attraction of positively charged metal ions would be enhanced [24]. Due to the Cr(III) speciation and the existence of deprotonated carboxylic groups, pH 4.0 was selected for the equilibrium studies in this work.

Kinetics data were fitted with the PFORE, PSORE, mass transfer and the intra-particle diffusion equations. Table 1 shows the corresponding parameters derived from each model at the three pH values assayed with both biosorbents. These results are in agreement with others found in the literature, which report that most of the sorption systems follow a pseudo-second-order kinetic model [25–27]. These results suggest that the rate-limiting step is a chemical sorption process between the metal cation and the algal biomass. The correlation coefficients found for external film diffusion and intra-particle diffusion are lower than those found for the PSORE model, indicating that in the cases studied in this paper, both process can be assumed not significant. When the biomass is employed as a free suspension in a well-agitated batch system, the effect of external film diffusion on biosorption rate can be considered as not significant. The fact that the adsorbate diffusion into the adsorbent particle is not a limiting factor during metal uptake can be associated with a large available surface area of the biomass because of the small particle size used.

3.3 Cr(III) sorption isotherms in mono-component solutions

The adsorption equilibrium defines the distribution of a solute between the liquid and solid phases after the adsorption process reached the equilibrium condition at constant temperature. Figure 2 shows the equilibrium data for the adsorption of Cr(III) on both algae at pH 4.0. As it can be seen, there is no significant difference in the chromium adsorption on both biosorbents.

The equilibrium data were analyzed using three isotherm models: Langmuir, Freundlich and D-R isotherms. The corresponding calculated parameters are listed in Table 2. According to the correlation coefficients, Langmuir model ($R^2 = 0.99$) represents better the biosorption of Cr(III) onto *M. pyrifera* and *U. pinnatifida* biomasses than the D-R and Freundlich models, indicating that the sorbed Cr(III) ions form a monolayer on the adsorbent surface. The D-R isotherm

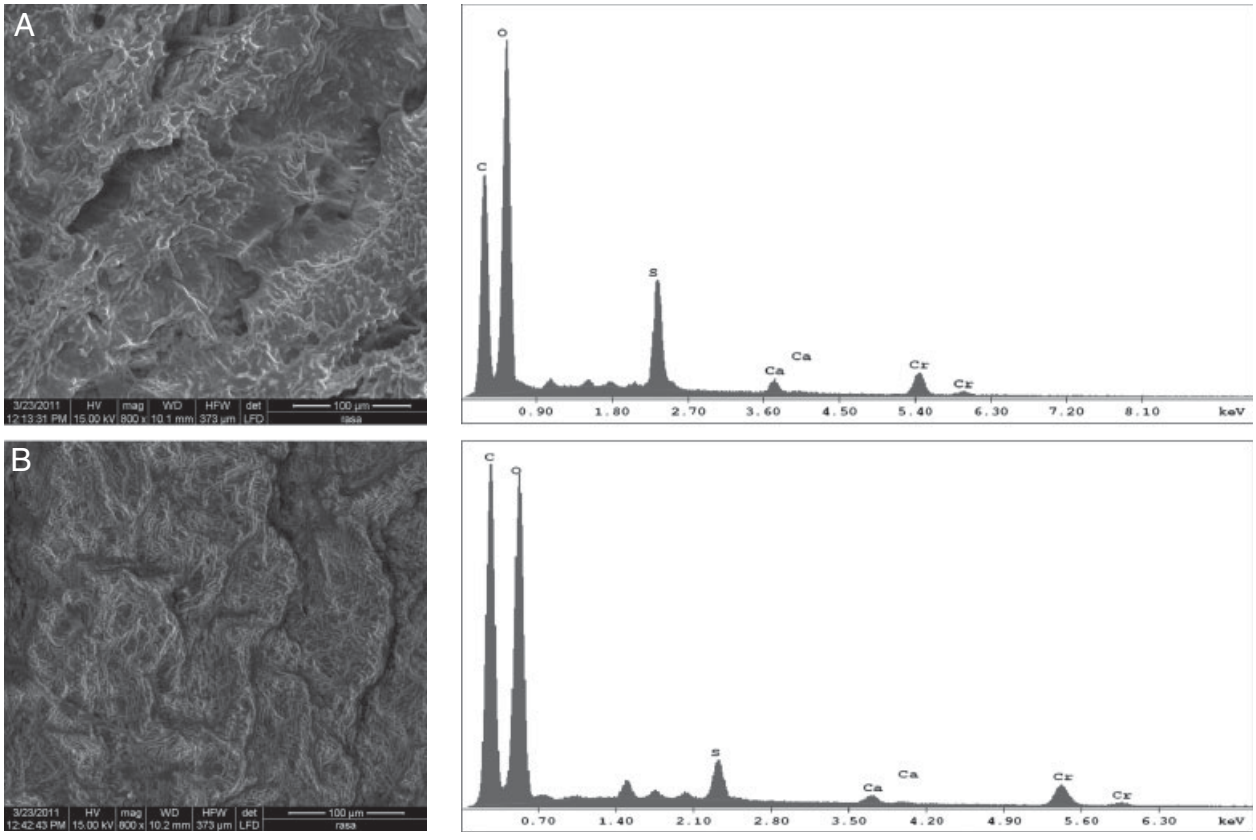

Figure 4. ESEM–EDX analysis corresponding to Ca-treated biosorbent particles loaded with Cr(III): (A) *M. pyrifera*; (B) *U. pinnatifida*.

model is useful to estimate the value of the free energy involved in the sorption process, which depends whether the process is physisorption or chemisorption. A free energy lower than 8 kJ/mol indicates that the interaction between the sorbent and the sorbate is weak, typical of a physic process, while higher E values indicate that chemisorption is involved [15]. According to the values found in our case the adsorption of Cr(III) on both algae is a chemical adsorption.

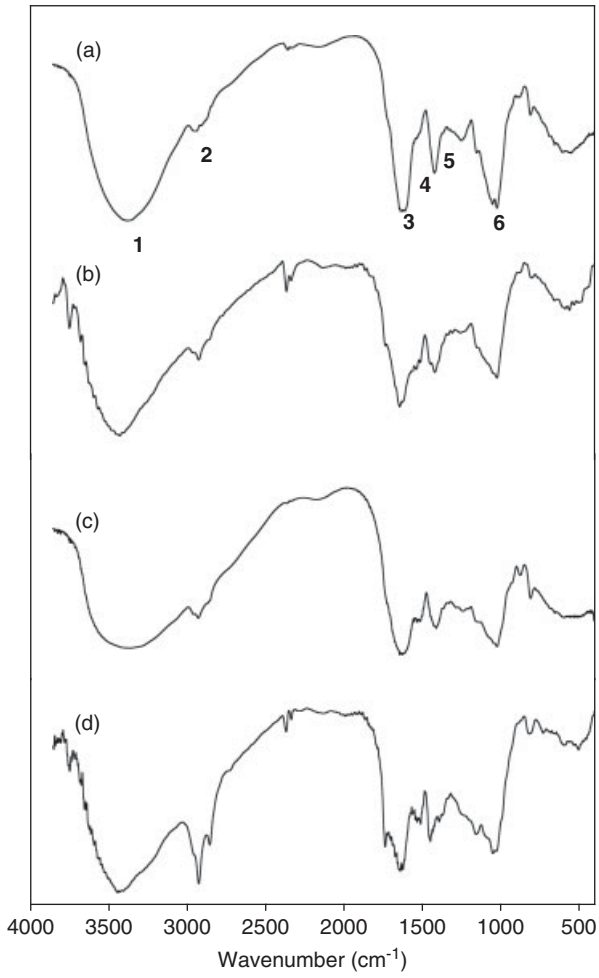

Figure 5. FTIR spectra of both biosorbents with and without metal. (A) *M. pyrifera* pH 4.0; (B) *M. pyrifera* pH 4.0, with Cr(III); (C) *U. pinnatifida* pH 4.0; (D) *U. pinnatifida* pH 4.0, with Cr(III).The most relevant peaks are numbered: 1, NH stretching (amine); 2, OH stretching (COOH); 3, asymmetric COOH stretching; 4, OH bending (COOH); 5, CO stretching(COOH); 6, CN stretching (amine) [32, 33].

The maximum adsorption capacity (q_m) of Cr(III) by both algae are very similar: 0.77 mmol/g for *M. pyrifera* and 0.74 mmol/g in the case of *U. pinnatifida*. The same occurred in the case of Hg(II) adsorption, *M. pyrifera* and *U. pinnatida*, had the same maximum adsorption capacity ($q_m = 0.8$ mmol/g) [9]. The values of b (affinity coefficient) were 1.20 L/mmol (*M. pyrifera*) and 1.06 L/mmol (*U. pinnatifida*) indicating a slightly higher affinity for Cr(III) by *M. pyrifera*. Table 3 shows a summary of Cr(III) maximum adsorption capacity (q_m) reported in the literature using different biomaterials. The q_m values range from 0.57 to 3.00 mmol/g, clearly this parameter depends on the nature of the biosorbent but also on their growing conditions, health state at the moment of collection, pretreatment and the experimental conditions for biosorption. When comparing the adsorption capacity for Cr(III) obtained with other algae, it possible to say that *M. pyrifera* and *U. pinnatifida* are better adsorbents for Cr(III) than *Palmaria* sp. but had lower adsorption capacity than *Ulva* sp. (Table 3). Probably the high adsorption capacity for Cr(III) by *Spirulina* sp. ($q_m = 3.00$ mmol/g at pH 7) [30] was due to Cr(III) precipitation because it is well-documented Cr(III) tend to precipitate as chromium hydroxide at the pH employed in those experiments [1, 18].

Ion-exchange is an important concept in biosorption, because it can explain many of the observations made during heavy metal uptake experiments, especially regarding the key role of alginate in biosorption, as it has been shown that ion-exchange takes place between metals when binding to alginate [31]. Untreated biomass generally contains light metal ions, such as K^+, Na^+, Ca^{2+} and Mg^{2+}, acquired from seawater, acting as counterions of the alginate groups. In this work, biomass was treated with Ca^{2+}. So, it is expected that the majority of the active sites were occupied by calcium ions. Calcium, magnesium, sodium and potassium concentrations in solutions were measured in the equilibrium experiments, in order to investigate their release during the uptake of Cr(III), associated with ion-exchange mechanisms. The meq/g of each ion released as a function of the initial Cr(III) concentrations is shown in Fig. 3A and B. It can be seen in the figures that Ca^{2+} and Na^+ were the main ions involved in cationic exchange, except in control studies. Control experiments showed that there was a release of ions (Ca^{2+}, Na^+, Mg^{2+}) when mixed with deionised water. In the absence of metal, the biosorbents

Table 4. Wave numbers (cm^{-1}) of the dominat peaks obtained in the FT-IR spectra of control and Cr(III) loaded biomass

	M. pyrifera (pH 4)	*M. pyrifera* (pH 4)+Cr(III)	*U. pinnatifida* (pH 4)	*U. pinnatifida* (pH 4)+Cr(III)
1: N–H stretching (amine)	3403	3400	3387	3403
2: O–H stretching (COOH)	2942	2925	2930	2926
3: N–H bending (amine) C–O stretching (amide)	1653	1650	1653	1647
4: O–H bending (COOH)	1429	1425	1429	1440
5: C–O stretching (COOH)	1255	–	–	–
6: C–N stretching (amine)	1031	1033	1034	1038

release Na^+ and adsorb H^+ from the solution: in those systems the pH increases from 4.0 to 4.8. In the presence of Cr(III), specially at low concentration, Ca^{2+} was the main ion released by the biosorbents, whereas $Cr(OH)^{2+}$ (the dominant species of chromium at pH 4) was bound to them. Regarding the final pH of the solutions, it was found that, at high concentration of Cr(III), the pH decreased up to 3.6; at this pH, Cr(III) and $Cr(OH)^{2+}$ coexist but Cr(III) becomes the dominant specie in solution. In those cases, not only Ca^{2+}, but Na^+ become the main ions released from the biosorbent and exchange with Cr(III) from the solution

3.4 Biomass characterization

The morphology of the biosorbent particles can be seen in the ESEM micrographs shown in Fig. 4A (*M. pyrifera*) and B (*U. pinnatifida*). In both cases, after biosorption, chromium was uniformly distributed over the alga surface and no physical change was visible after metal binding. The right side of both figures presents representative X-ray maps of the surface showing the presence of chromium, sulfur and calcium peaks.

The major binding sites in brown algae are usually attributed to the carboxylic groups of the alginates and other acid polysaccharides [28]. However, other less abundant functional groups such as sulfonic groups from fucoidans and, to a lesser extent, N- and S-containing groups from proteins may also be important for metal ion binding. FT-IR was used to analyze the functional groups in the biomass involved in metal binding. As shown in Fig. 5, the FT-IR spectra of control and Cr(III)-loaded biomass display a number of adsorption peaks, indicating the complex nature of the biomass tested. The FT-IR spectrum exhibits the following peaks (Table 4): 3400 and 3387 cm^{-1}, due to the stretching vibration of bonded –OH and –NH groups. The peaks at 2942, 2925, 2930 and 2926 cm^{-1} are the indicator of alkyl chains –CH stretching vibration. The typical amide I band, C=O stretching vibration appears strongly at 1653, 1650 and 1647 cm^{-1}. The absorbance peaks at 1429, 1425 and 1440 cm^{-1} are to due N–H bending (cis form), $–CH_2$ scissoring or $–CH_3$ antisymmetrical bending vibration and O–H deformation. The C–O (carboxyl) stretch at about 1255 cm^{-1} was detected only in the control spectrum of *M. pyrifera* biomass. The peaks at 1184 and 1056.8 cm^{-1} may be attributed to C–N stretching vibration of amine groups. Hence, the absorption peaks at 1031, 1033, 1034 and 1038 cm^{-1} can be assigned to –C–O– or –C–N– groups. These changes in the FT-IR spectra of biosorbents have also been observed in other biosorption studies using marine algae as biosorbents [9, 14, 30]. Also, a decrease in the peak intensities was detected after biosorption of Cr(III), indicating that those groups are involved in the binding of Cr(III).

4 Concluding remarks

M. pyrifera and *U. pinnatifida* have the same considerable potential for removing Cr(III) from aqueous solutions. Although their alginate content in the cell wall is different (20 and 30% for *M pyrifera* and *U. pinnatifida*, respectively), their adsorption capacities for Cr(III) are very similar. Kinetic studies showed that the adsorption equilibrium of Cr(III) took place after at least 4 h and the optimum pH was 4.0. Experimental data could be described adequately by pseudo-second-order kinetic. Equilibrium data were better represented by the Langmuir model. The value obtained for maximum sorption capacity (q_m) was 0.7 mmol/g for both biomaterials and the affinity coefficient (b) were 1.20 and 1.06 L/mmol for *M. pyrifera* and *U. pinnatifida*, respectively. The free energy, estimated by the D-R isotherm, was typical for chemical sorption. The exchange of Cr(III) by light metals is one of the possible mechanisms involved. Carboxylic groups is the main functional group involved in Cr(III) binding, although the participation of amine group was also demonstrated by FT-IR. The chromium adsorption did not provoke any significant physical change in the biomasses.

Practical Application

Industry is compelled to treat their waste waters in order to minimize their heavy metal contents. Traditional technologies for waste water treatment (chemical precipitation, ion exchange, membrane processes, etc.) normally have high operational costs or low removal efficiencies. Due to its simplicity and efficiency, adsorption is considered as a better technology. The search for low cost, easily available and effective adsorbent is one of the main objectives of biosorption studies. In this manuscript, we used two brown algae as biosorbents. Both are very abundant in the south coast of Argentina, where they arrive with the tide, causing a negative impact at tourist activities. Besides, *U. pinnatifida* is an invasive species that caused ecological problems. The results of the lab-scale experiments presented show that both algae are suitable for the removal of Cr(III), a contaminant presents in the wastewater of tannery industries.

Nomenclature

q	[mg/g] or [mmol/g]	solute uptake (Eq. 1)
C_i	[mg/L] or [mmol/L]	initial solute concentration in solution (Eq. 1)
C_f	[mg/L] or [mmol/L]	final solute concentration in solution (Eq. 1)
M	[g]	biosorbent mass (dry weight basis) (Eq. 1)
q_m	[mmol/g]	maximum Langmuir metal uptake (Eq. 6)
q_{eq}	[mmol/g]	metal uptake at the equilibrium (Eq. 6)
B	[L/mmol]	Langmuir affinity constant (Eq. 6)
E	[kJ/mol]	free sorption energy (Eq. 9)
CEC	[meq/100 g]	cation-exchange capacity

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