Removal of chromium and toxic ions present in mine drainage by *Ectodermis* of *Opuntia*

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Abstract

This work presents conditions for hexavalent and trivalent chromium removal from aqueous solutions using natural, protonated and thermally treated *Ectodermis* of *Opuntia*. A removal of 77% of Cr(VI) and 99% of Cr(III) can be achieved. The sorbent material is characterized using scanning electron microscopy, energy dispersive X-ray spectroscopy, infrared spectroscopy, thermogravimetric analysis, before and after the contact with the chromium containing aqueous media. The results obtained from the characterization techniques indicate that the metal ion remains on the surface of the sorbent material. The percentage removal is found to depend on the initial chromium concentration and pH. The Cr(VI) and Cr(III) uptake process is maximum at pH 4, using 0.1 g of sorbent per liter of aqueous solution. The natural *Ectodermis* of *Opuntia* showed a chromium adsorption capacity that was adequately described by the Langmuir adsorption isotherm. Finally, an actual mine drainage sample that contained Cd, Cr, Cu, Fe Zn, Ni and Pb was tested under optimal conditions for chromium removal and *Ectodermis* of *Opuntia* was found to be a suitable sorbent material. The use of this waste material for the treatment of metal-containing aqueous solutions as well as mine drainage is effective and economical.
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1. Introduction

The term "heavy metals" refers to metallic elements having a density equal to or greater than $6.0 \, g \, cm^{-3}$. The most common heavy metals are cadmium ($8.65 \, g \, cm^{-3}$), chromium ($7.14 \, g \, cm^{-3}$), copper ($8.95 \, g \, cm^{-3}$), lead ($11.34 \, g \, cm^{-3}$), mercury ($13.53 \, g \, cm^{-3}$), nickel ($8.91 \, g \, cm^{-3}$) and zinc ($7.14 \, g \, cm^{-3}$) [1].

Hexavalent chromium Cr(VI) is a major pollutant present in industrial wastewaters common to the metal and mineral processing, as well as plating industries. Cr(VI) is carcinogenic and mutagenic, as well as being a strong oxidizing agent, which irritates plant and animal tissues even in small quantities. It diffuses rapidly through soils and aquatic environments, as well as readily passing through the skin. Cr(VI) species in aqueous solutions are $Cr_2O_7^{2-}$, CrO_4^{2-} and $HCrO_4^{-}$, the relative distribution of which depends on the solution pH and on the Cr(VI) concentration. However, since these ions do not form insoluble compounds, it is not feasible to separate them from wastewater through a direct precipitation method [2].

Adsorption is a physiochemical wastewater treatment process, which is gaining prominence as a means of producing high quality effluents, which are low in metal ion concentrations [3]. The development of inexpensive adsorbents for the treatment of wastewaters is an important area in environmental sciences [4–5].

The removal of Cr(VI) from wastewater can be achieved via sorption-based processes, including synthetic resin [6,7], activated carbon [8], inorganic sorbent material [9], crab shell [10], thermally treated biomass of the brown seaweed, *ecklonia* sp. [11], polyacrylamide-grafted coconut coir pith [12], lignocellulosic substrate extracted from wheat bran [13], roots of *typha Latifolia* [14], eucalyptus bark [15], carrot residue [16] or the so-called biosorbents derived from dead biomass. Of

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these, biosorbents are considered the cheapest, most abundant and environmental friendly option [17,18].

This paper examines the sorption of Cr(VI) and Cr(III) from aqueous solutions and actual mine drainage containing, Cd, Cr, Cu, Fe, Ni, Pb and Zn. Comparing these reveals the influence of the pH, analyte concentration and presence of competing ions. Moreover, in addition to the elemental analysis, we used infrared spectroscopy, scanning electron microscopy and thermogravimetric analysis to characterize the *Ectodermis* of *Opuntia* before and after contact with the metal solution.

2. Materials and methods

2.1. Conditioning of Ectodermis of Opuntia

Natural *Ectodermis* of *Opuntia*. The *Ectodermis* of *Opuntia* was collected from the municipality of Temascalapa in the northern part of the Estado de México. The raw sample was washed with distilled water; sun-dried for 7 days, then dehydrated at 70 °C for 5 h on a stove. Once the biomass cooled off, it was crushed, milled and sieved through a No. 20 mesh. Thereafter, the material was stored in a desiccator. The resulting dried biomass was designated as the control biomass in this article.

Protonated *Ectodermis* of *Opuntia*. In order to prepare the protonated biomass, the control was treated with a 1 M H_2SO_4 solution (145 mL/10 g) for 24 h, which replaced the natural mix of ionic species with protons and sulfates. The acid-treated biomaterial was washed with deionized distilled water several times and thereafter dried at room temperature for 3 days. The resulting biomass was designated as the protonated biomass.

Thermally treated *Ectodermis* of *Opuntia*. Control samples were kept in ovens at 60 and 100 °C for 24 h. Both thermally treated biomasses were stored in a desiccator. The resulting biomasses were designated as the thermally treated biomasses.

In this article, the comparison of the efficiencies for Cr(VI) and Cr(III) removal is presented in Section 3.3. Everywhere else, the results presented correspond to the control biomass.

2.2. Metal detection in aqueous solution

The colorimetric method was used to measure the concentrations of the chromium species. A solution of 1–5 diphenylcarbazide in acid forms a pink complex with Cr(VI), which can be spectrophotometrically analyzed at 540 nm (Perkin-Elmer Lamba 25). To estimate the total Cr concentration, Cr(III) was oxidized to Cr(VI) at high temperature (130 °C) by the addition of excess of potassium permanganate prior to using the 1–5 diphenylcarbazide method. Cr(III) concentration was calculated as the difference between total Cr and Cr(VI) concentrations [19]. Since the mine drainage contains Cd, Cr, Cu, Fe, Ni, Pb and Zn, the methods described in AWWA were used [20].

2.3. Batch experiments

Adsorption studies were carried out by batch technique to obtain rate and equilibrium data. For these investigations a series of test tubes containing equal volumes (10 mL in each case) of adsorbate solutions of varying concentration were employed, at selected pH (2 or 4). A known amount of adsorbent (0.1 g or 0.05 g) of particle size 20 mesh was then added into each test tube and agitated intermittently from 5 min to 24 h. Equilibrium was attained in 1 h. Shaking for anytime between 1 and 24 h gave practically the same uptake. Adsorbate initial concentration ranged from 50 mg L^{-1} to 500 mg L^{-1}. This methodology has been previously proposed [20a,24].

To optimize the adsorbent concentration for the Cr removal from the aqueous solution, the adsorption studies were carried out at two different adsorbent doses. The effect of the pH was determined by studying the adsorption of metal ions at fixed concentrations at different pH values (2 and 4). At specific time intervals, the test solutions were centrifuged to separate the adsorbent material and the supernatant. The adsorbent material was dried and characterized using SEM, while the supernatant was analyzed for aqueous metal concentration using the 1–5 dyphenilcarbacide method. All experiments were conducted in duplicate.

2.4. Adsorption models

The results obtained by the adsorption experiments were analyzed by the models of Langmuir and Freundlich. The Langmuir isotherm model assumes uniform energies of adsorption onto the surface with no transmigration of adsorbate in the plane of the surface. The linear form of the Langmuir isotherm is given by Eq. (1), where q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), and Q^0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ^0}\right) + \left(\frac{C_e}{Q^0}\right) \tag{1}$$

The adsorption data was also analyzed by the Freundlich model. The logarithmic form of the Freundlich model is given by Eq. (2), where q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), and K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively [21,22]

$$\log q_e = \log K_F + (1/n) \log C_e \tag{2}$$

2.5. Bromatological analysis

The *Ectodermis* of *Opuntia* before and after the contact with the chromium was analyzed for cellulose, hemicellulose, fiber content and humidity in accordance with food legislation [23].

2.6. Fourier transform infrared analysis (FTIR)

Infrared spectra of the biomass were obtained using a Fourier transform infrared spectrometer (FTIR Nicollet AVATAR 360). For the FTIR study, 30 mg of finely ground biomass was encapsulated in 300 mg of KBr (Sigma) in order to prepare translucent sample disks.

2.7. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

After the metal–biomass contact experiments, the samples were characterized by SEM. The samples mounted directly onto metal studs were analyzed in a JEOL JSM-5900 LV microscope to obtain information regarding the surface morphology. The secondary electron images of the material depict approximate sizes in the range of a few microns. A DX-4 analyser was coupled to the microscope to perform the energy dispersive X-ray spectroscopy, which offers in situ elemental analysis.

2.8. Thermal analysis (TGA)

The thermogravimetric analysis was carried out using a TA instruments TGA 51 thermogravimetric analyser, which was operated in a nitrogen atmosphere at a heating rate of $10\,°C\,min^{-1}$ from 25 to $600\,°C$.

3. Results

3.1. Kinetic studies

Preliminary studies on the rate of removal of Cr(VI) and Cr(III) by the control *Ectodermis* of *Opuntia* indicated the sorption process to be quite rapid. The amount of *Ectodermis* of *Opuntia* is related to the amount of chromium removed. With 50 mg, about 55% of the adsorption capacity for Cr(VI) was attained within the first hour of contact, and 77% for Cr(III). When 100 mg is used, the maximum Cr(III) and Cr(VI) removal occurs. The initial rapid adsorption gives way to a very slow approach to equilibrium, and saturation is reached beyond 1 h (Fig. 1).

It is also evident from Fig. 1 that at low concentration ($50\,mg\,L^{-1}$) 99% of Cr(III) is removed. It was also found that at fixed concentration the rate of removal of Cr(VI) and Cr(III) increases with an increase in the amount of biomass. Thus, 100 mg of biomass has been used in all subsequent studies.

The above observations can be explained on the basis of the following two consecutive steps, which may be involved in the adsorption of metal ions by an adsorbent: (a) transport of the ion from the bulk solution to the external surface of the adsorbent, and (b) adsorption of the metal ions on the exterior surface of the adsorbent [24]. Further discussion is provided in Section 3.6.

3.2. pH dependence of chromium removal

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption processes. Its role on the chromium binding was studied by varying the initial concentration of nitric acid in the solution; we use the control biomass to do this test. Fig. 2 shows the removal of Cr mainly depends on the proton concentration. The lower the proton concentration, the higher the efficiency of the Cr removal. In the case of Cr(VI), this effect has been explained by: a surface exchange reaction between chromate and hydroxyl ions, which favors chromate adsorption in acidic media, and by the reduction process of hexavalent to trivalent chromium, which requires a large amount of proton. At pH values below 4, the concentration of soluble trivalent chromium increases when pH decreases, which can be attributed to an increasing competition between protons and trivalent chromium toward surface sites. The effect of pH on the uptake of Cr(VI) and Cr(III) is shown in Fig. 2. This figure shows a greater sorption at pH 4, compared to that at pH 2. The increase in the removal could be related to the surface charges that are strongly dependent on the pH of the solution [25,26].

3.3. Adsorption isotherms

To determine the mechanistic parameters associated with Cr(VI) and Cr(III) adsorption, the results of the experiments were analyzed according to the Langmuir and Freundlich models. The adsorption isotherm studies are of fundamental importance in determining the adsorption capacity of Cr(VI) and Cr(III) onto the biomasses. Table 1 shows the absorption parameters for all the biomasses. The values of Q^0 and the r^2 using the
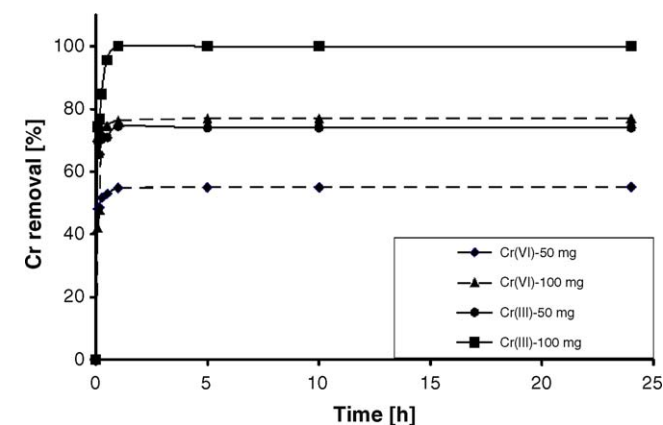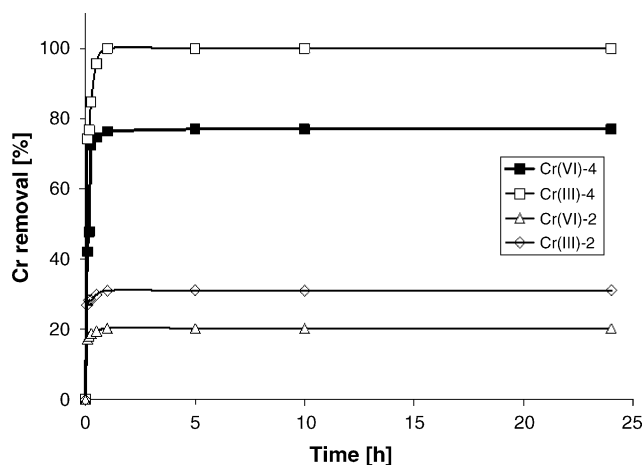

Fig. 1. Hexavalent and trivalent chromium removal from aqueous solution as a function of time. The chromium concentration (Cr(VI) or Cr(III)) in the aqueous solution was $50\,mg\,L^{-1}$, the amount of the control biomass is indicated in the figure for each case, the pH of the solution was 4 and the temperature $18 \pm 1\,°C$.

Fig. 2. Sorption of Cr(VI) and Cr(III) in time at pH 2 and 4. The concentration of the aqueous solution was $50\,mg\,L^{-1}$ in each case. The amount of control biomass used was 100 mg.

Table 1
Langmuir and Freundlich constants for the removal of Cr(VI) and Cr(III)

Pollutant-biomass/ parameters	Langmuir		Freundlich	
	Q^0 (mg g^{-1})	r^2	K_F (mg g^{-1})	r^2
Cr(VI)-control	6.22	0.971	1.27	0.957
Cr(III)-control	11.72	0.920	2.69	0.823
Cr(VI)-protonated	3.47	0.991	2.79	0.982
Cr(III)-protonated	13.12	0.792	1.492	0.901
Cr(VI)-thermally treated (60 °C)	2.91	0.716	0.448	0.632
Cr(III)-thermally treated (60 °C)	15.38	0.772	1.01	0.923
Cr(VI)-thermally treated (100 °C)	2.38	0.951	1.06	0.443
Cr(III)-thermally treated (100 °C)	10.64	0.547	1.12	0.706

Langmuir model are higher for the control biomass with Cr(VI) and Cr(III). On the other hand, the protonated, thermally treated (60 and 100 °C) for Cr(VI) the best correlation are obtained using the Langmuir model, however, Cr(III) shows better correlation values with the Freundlich model using biomass protonated, thermally treated (60 and 100 °C). The variation in the fitted values using the Langmuir and Freundlich models have been also been found in recent reports which indicate that Cr(VI) can be described by the Freundlich isotherm, however, the Langmuir values fit well to experimental results only for a limited range of concentrations. The authors conclude that these phenomena can be due to the heterogeneity of the adsorbent material [12,30].

3.4. Bromatological analysis

A bromatological test provides information regarding the fiber and moisture content, as well as the nature of food. In these cases, we look for the principal components of the *Ectodermis* of *Opuntia*, namely the amount of cellulose and hemicellulose. These components contain functional groups such as carbonyl, methyl, and hydroxyl groups that interact with the metal ions present in aqueous solutions as shown in the IR characterization. The components of the control material are shown in Table 2. The cellulose amount decreased after the Cr(III) sorption because the sorption takes place in an acid medium. As explained by Nevell, "the glycosidic linkage in cellulose is susceptible to acid-catalyzed hydrolysis. The mechanism of the reaction comprises three stages: rapid protonation of the glycosidic oxygen atom, slow transfer of the positive charge with consequent formation of a carbonium ion and fission of the glycosidic bond, and attack
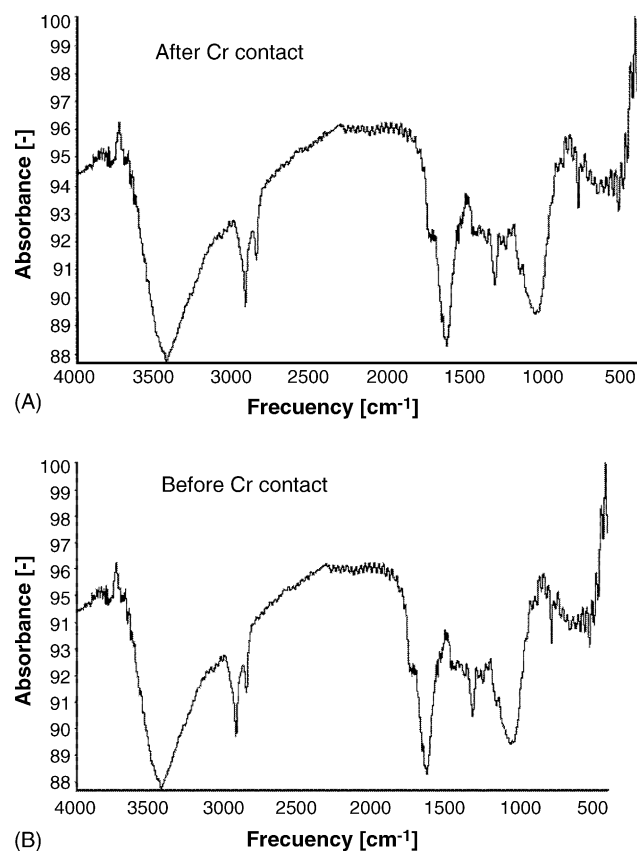

Fig. 3. FTIR spectra of the control biomass (A) after and (B) before the contact with a 50 mg L^{-1} chromium (III) solution, at pH 4.

on the carbonium ion by water to give the free sugar residue and to re-form the hydroxinum ion" [27].

3.5. Infrared spectroscopy analysis

Fig. 3, show the FTIR spectra of the control biomass. These spectra display a number of absorption peaks, indicating the complex nature of the examined biomass.

Table 3 shows the infrared absorption frequencies of each peak and the corresponding functional group. The broad absorption peak around 3428 cm^{-1} is indicative of the presence of the –OH groups of cellulose. The strong absorption peak at 2850 cm^{-1} is assigned to –CH stretching, and those at 1623 cm^{-1} to C=O stretching and C=O chelate stretching of carboxyl groups. The absorption peak at 1414 cm^{-1} is assigned to the symmetric bending of the CH$_3$. The bands at 1317 and 1050 cm^{-1} are indications of carbohydrate units [28–30]. Although slight changes in the absorption peak frequencies can

Table 2
Bromatological analysis of the control biomass before and after the contact with a 100 mg L^{-1} Cr(III) aqueous solution, the pH of the solution was 4.0

Material	% Cellulose	% Hemicellulose	% Lignin	% Humidity
Ectodermis of *Opuntia* before the Cr-contact	28.2	14.4	14.5	7.22
Ectodermis of *Opuntia* after the Cr-contact	23.8	12.3	13.82	7.14

Table 3
Functional groups of the *Ectodermis* of *Opuntia* and the corresponding Infrared absorption frequencies

Frequency (cm^{-1})	Assignment
3428	Hydroxyl group
2850	C–H stretching
1623	C=O stretching of COOH
1414	Symmetric bending of CH_3
1317	Carbohydrate groups
1050	Carbohydrate groups

be observed in Fig. 3B, it was difficult to interpret how these shifts were related with Cr biosorption. However, the position of the peaks indicates that after the biosorption process the biomass contains the same functional groups.

3.6. Cr sorption mechanism

The surface sorbent properties determine the sorption mechanisms. The most commonly reported mechanisms for metal ion sorption are ion exchange, electrostatic interaction, chelation, precipitation and complexation. However, for anions, electrostatic interaction plays an important role in allowing the approach of the ions to the sorbent surfaces [31]. To understand the Cr(VI) sorption mechanism is important to consider the Cr(VI) speciation in the actual aqueous solution, in this study $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions account for about 80 and 20%, respectively. At pH 4, the sorbent surface is positively charged due to protonation, while the sorbate, dichromate ion, exists mostly as an anion leading to the electrostatic attraction between sorbent and sorbate. Fig. 4 shows the possible way this interaction occurs. Similar results have been reported recently [32].

In the case of Cr(III), at pH values below 4, the main specie is Cr^{3+} [2]. As presented in the infrared spectroscopy analysis section, there is a broad absorption peak around 3428 cm^{-1}
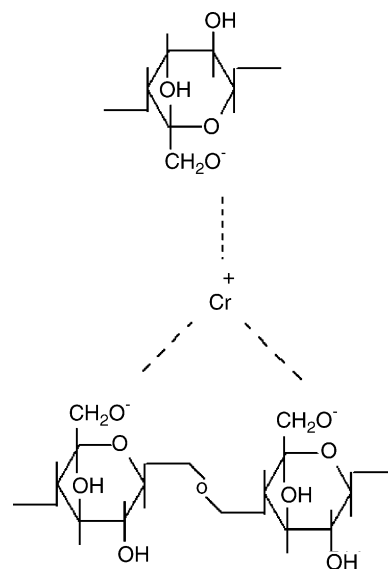
Fig. 5. Scheme of the possible Cr(III) interaction with the cellulose of the control biomass.

indicating of the presence of the –OH groups of cellulose. This functional group is responsible for Cr(III) sorption, a schematic representation of the phenomena is shown in Fig. 5. This result agrees with recent research, which indicates that metal binding is due to the interaction with the vicinal hydroxyl groups [33].

Another mechanism that is implicated in the removal of Cr(VI) under acidic conditions is the reduction of Cr(VI) to Cr(III). This implies that there is proton consumption in the Cr(VI) reduction. Recent research indicates that the participation of protons in the reduction can be explained as: (a) protons can be released from, or bound to, various functional groups of the biomass depending on the solution pH, and (b) protons are consumed during the reduction of Cr(VI) according to reactions
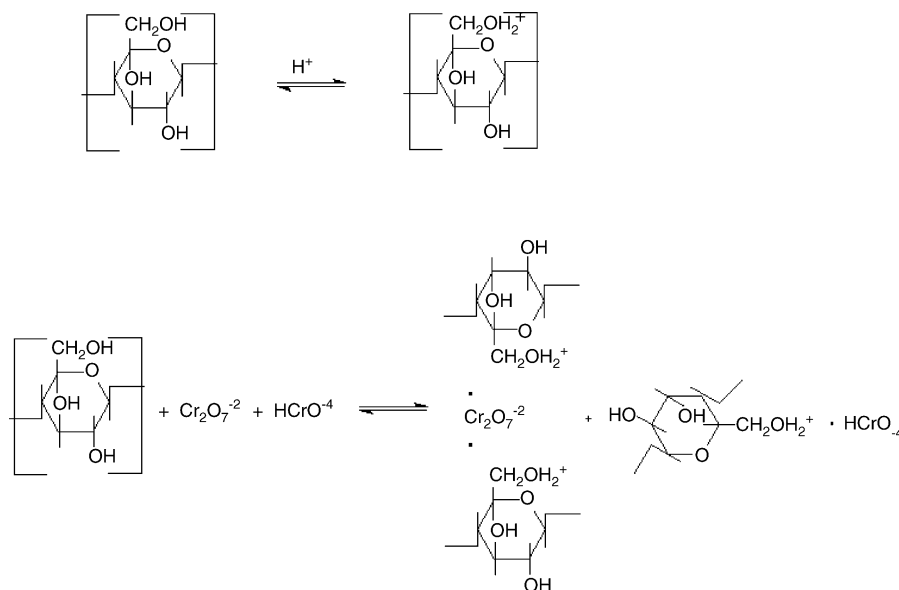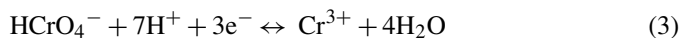
Fig. 4. Scheme of the possible Cr(VI) interaction with the cellulose of the control biomass.

(3) and (4) [19,29]:

$$HCrO_4{}^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \tag{3}$$

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O \tag{4}$$

In order to investigate the contribution of each mechanisms for Cr(VI) removal from aqueous solution, future research should use a larger working volume in order to measure pH changes during the contact tests or maintain a constant pH using a buffer or additions of NaOH or H$_2$SO$_4$ solutions during the metal biosorption.

3.7. Scanning electron microscopy (SEM)

The scanning electron micrographs (Fig. 6) clearly reveal the surface texture and porosity of the sample. These micrographs give clues to the sorption process. In Fig. 6a, the surface of the biomass is a continuous structure with features around 100 μm, while in Fig. 6b, new shiny, bulky, spherical particles containing chromium have formed. This result agrees with the adsorption model described by Langmuir as previously discussed above. The presence of Cr over the surface of the control biomass was confirmed by EDX analysis, as shown in Fig. 7.
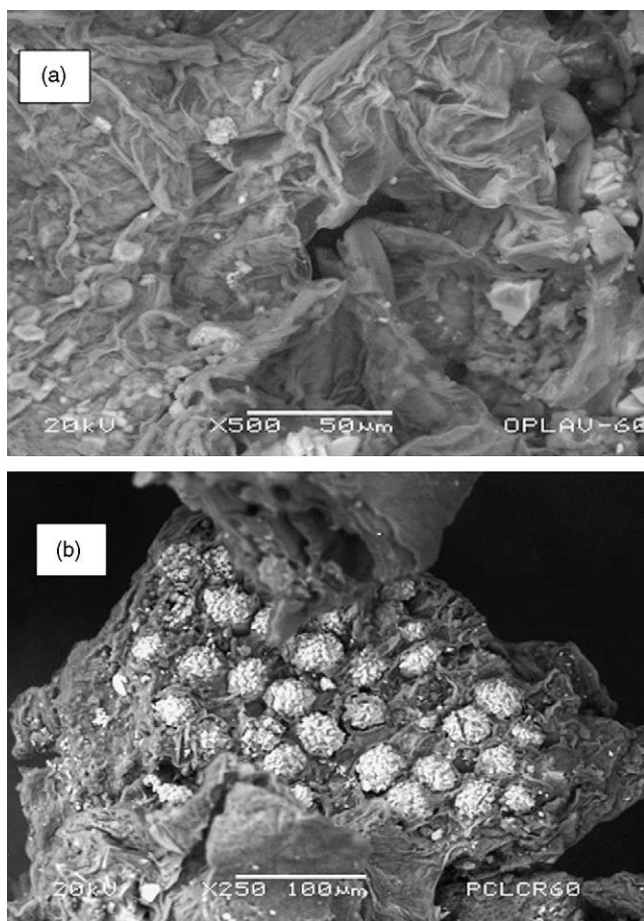

Fig. 6. Scanning electron microphotographs of the control biomass (a) before and (b) after the contact with a Cr(III) aqueous solution. The pH of the aqueous media was 4, the amount of *Ectodermis* of *Opuntia* was 100 mg and the contact time was 1 h.
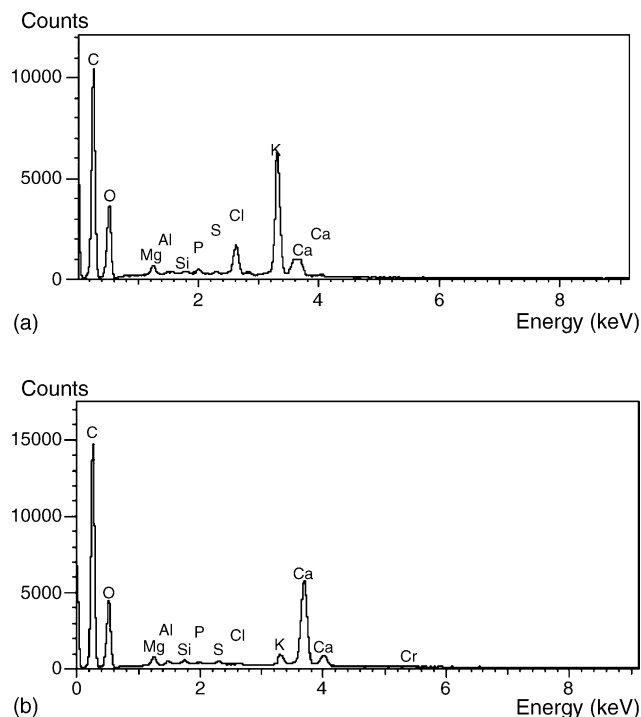

Fig. 7. Elemental composition of the control biomass (a) before and (b) after the contact with a Cr(III) aqueous solution. The pH of the aqueous media was 4, the amount of *Ectodermis* of *Opuntia* was 100 mg and the contact time was 1 h.

3.8. Thermal analyses (TGA)

Fig. 8 shows the thermogravimetric behavior of the *Ectodermis* of *Opuntia*. The maximum weight loss due to degradation is 60%. By 250 °C all of the moisture is gone and the change in the thermogravimetric slope indicates significant material loss. Once the temperature reaches 450 °C, the amount of material remains constant indicating the inorganic fraction of the *Ectodermis* of *Opuntia*. This analysis provides information regarding the mass reduction of the material with temperature. From the environmental point of view, once the metal ions are sequestered from the aqueous solution a significant reduction of the sorbent mass can be achieved, if the sorbent containing the metal ions is
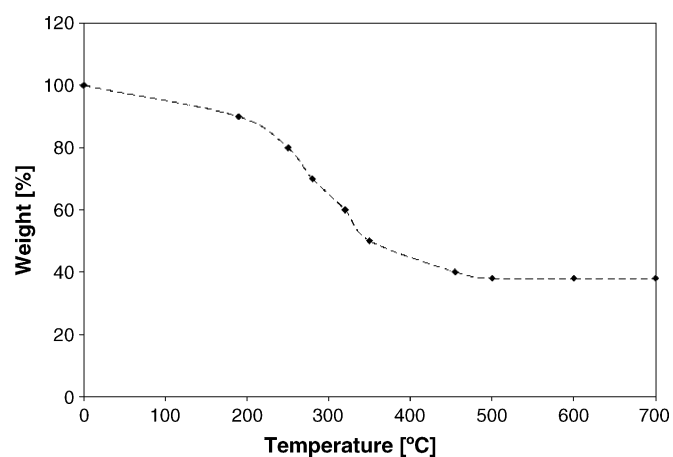

Fig. 8. Thermal behavior of the *Ectodermis* of *Opuntia* containg Cr(III).

Table 4
Metal removal of mine drainage using the control *Ectodermis* of *Opuntia*

Pollutant	Initial concentration ($mg\,L^{-1}$)	Final concentration ($mg\,L^{-1}$)
Cd	1.14	BDL
Cr	2.86	BDL
Cu	0.19	BDL
Fe	679.16	36.53
Zn	76.2	19.28
Ni	1.06	BDL
Pb	0.5	BDL

BDL: Below detectable limit.

heated. This could result in a reduction in the by-products and disposal cost of the wastewater treatment. As recently stated, the removal of toxic substances from wastewater using low-cost alternatives to activated carbon is an important area in environmental sciences [23].

3.9. Mine drainage sorption experiments

To test the applicability of the sorption process, actual mine drainage samples containing Cd, Cr, Cu, Fe Zn, Ni and Pb were evaluated. Control adsorbent was added to these samples and the change in metal ion content was measured. The pH of the solution was 4, the contact time was 1 h and the amount of control adsorbent was 100 mg. The results of the removal of the metal ions from the solution are shown in Table 4. All of the metal ions were detected in the original mine drainage by means of atomic absorption spectroscopy. The biomass adsorbent effectively sequestered all of the metals in the mine samples.

4. Conclusions

Ectodermis of *Opuntia* is a sorbent material capable of removing Cr(VI) and Cr(III) from aqueous solutions. The naturally occurring control biosorbent removes Cr(VI) and Cr(III) from aqueous solutions in a greater amount than the treated biomass. The equilibrium of the metal ion sorption is reached within 1 h. The sorption capacity at pH 4 is higher than at pH 2. The bromatologycal analysis indicates the presence of cellulose and hemicellulose in the biomass, while infrared spectroscopy identifies the functional groups. Experimental sorption data adequately correlated with the Langmuir model. SEM analysis indicates that the chromium sorption takes place on the surface of the control biomass. EDX analysis confirms the metal presence in the sorbent material after contact with the solutions. The thermogravimetric analysis indicates that at a temperature of 400 °C there is a large mass consolidation.

These results demonstrate the great potential of plant biomaterial residues, as low-cost heavy metal adsorbents. The heavy metal removal technique using such biomaterials would be an effective method for the economic treatment of wastewater.

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