



ORIGINAL ARTICLE

# Effect of chromium speciation on its sorption mechanism onto grape stalks entrapped into alginate beads



Carlos Escudero <sup>a,\*</sup>, Núria Fiol <sup>a</sup>, Isabel Villaescusa <sup>a</sup>, Jean-Claude Bollinger <sup>b,1</sup>

<sup>a</sup> Chemical Engineering Department, Universitat de Girona, Avda. Lluís Santaló, s/n, 17075 Girona, Spain

<sup>b</sup> Université de Limoges, Groupement de Recherche Eau Sol Environnement (GRESE), Faculté des Sciences, 123 Avenue Albert Thomas, 87060 Limoges, France

Received 3 October 2012; accepted 18 March 2013

Available online 26 March 2013

## KEYWORDS

Sorption;  
Chromium;  
Speciation;  
Mechanism;  
Alginate;  
Grape stalks

**Abstract** Sorption of Cr(III) and Cr(VI) ions onto 2% grape stalk (GS) powder entrapped in a biopolymeric gel matrix of calcium alginate (CA) has been investigated and a mechanism for the retention of both, Cr(VI) and Cr(III) is proposed. Protons were found to be consumed in Cr(VI) sorption/reduction and to compete with Cr(III) for the sorbent active sites. Isotherm equilibrium was modelled according to Langmuir equation: maximum capacity was found to be 6.4 and 3.6 mg g<sup>-1</sup> for Cr(III) and Cr(VI), respectively. The important Ca<sup>2+</sup> release observed when Cr(III) is sorbed indicates that ion exchange is the main mechanism involved at concentrations lower than 200 mg L<sup>-1</sup> while other mechanisms such as microprecipitation or coordination might take place for higher initial concentrations. In the case of Cr(VI), the sorption mechanism is based on the reduction to Cr(III) promoted by both protons and the functional groups on the GS surface; this reduction-formed Cr(III) is retained by the alginate gel matrix and by microprecipitation onto the surface of GS particles. ESR and SEM-EDX were used to identify chromium species sorbed on the solid phase. Results from this study suggest that GS entrapped in CA gel beads is an effective sorbent for both, Cr(III) and Cr(VI) removal from aqueous solutions.

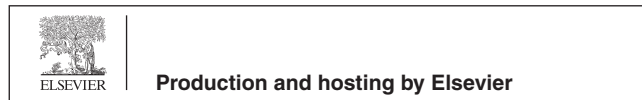
© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

\* Corresponding author. Tel.: +34 972 418 416; fax: +34 972 418 399.

E-mail addresses: [carlos.escudero.o@gmail.com](mailto:carlos.escudero.o@gmail.com) (C. Escudero), [nuria.fiol@udg.edu](mailto:nuria.fiol@udg.edu) (N. Fiol), [isabel.villaescusa@udg.edu](mailto:isabel.villaescusa@udg.edu) (I. Villaescusa), [jean-claude.bollinger@unilim.fr](mailto:jean-claude.bollinger@unilim.fr) (J.-C. Bollinger).

<sup>1</sup> Tel.: +33 555 457 469.

Peer review under responsibility of King Saud University.



## 1. Introduction

During the last 15 years, the processes for the treatment of aqueous effluents to remove metal ions and organic compounds using low-cost sorbents have been in continuous development and improvement. In addition, reusing waste biomaterials is considered an environmentally-friendly practice and is supported by government policies.

Chromium occurs in wastewaters in both trivalent and hexavalent forms as a result of its use in many industries such

as electroplating, leather tanning, paints and pigments. Due to the high toxicity of Cr(VI) (Zhitkovich, 2011), numerous studies have been devoted to its removal by biosorption from wastewater while studies on Cr(III) are scarce (Mohan and Pittman, 2006; Saha and Orvig, 2010; Miretzky and Cirelli, 2010). In spite of not being particularly toxic, Cr(III) must be also of a special concern as its environmental oxidation to Cr(VI) represents a potential source of toxicity. Therefore, it is of great importance in any treatment process to ensure the removal of both Cr(VI) and Cr(III) from wastewater. In this context, some authors have investigated their removal using composite alginate-goethite beads (Lazaridis and Charalambous, 2005), seaweed biosorbent (Kratochvil et al., 1998) and humic acids encapsulated in calcium alginate beads (Pandey et al., 2003).

We recently studied Cr(VI) uptake by grape stalks (GS) encapsulated in calcium alginate (CA) beads (Fiol et al., 2005, 2004). The entrapment of GS into CA beads enhanced Cr(VI) sorption yield and provided the sorbent with an appropriate shape and a greater mechanic strength for its possible use in continuous (column) sorption processes.

Our objective was to investigate Cr(VI) and Cr(III) sorption mechanism onto GS-CA beads. To ascertain the role of protons and the possible ion-exchange mechanism, pH evolution and calcium release as a consequence of chromium sorption were evaluated. Moreover, Electron Spin Resonance (ESR) and Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM-EDX) were used to identify chromium species on the solid phase.

## 2. Experimental

### 2.1. Materials

Unless otherwise stated, all reagents are of analytical grade and purchased from Panreac (Barcelona, Spain).

The beads contained 2% (w/v) grape stalks entrapped into the calcium alginate gel. This optimal GS percentage and the methodology to prepare the beads were reported previously (Fiol et al., 2005, 2004). Sodium alginate salt from brown algae (Fluka, St. Louis, USA) was used as the hydrocolloidal gelling material using 0.1 M CaCl<sub>2</sub> as fixing solution. GS, kindly supplied by a wine producer from Castilla la Mancha region (Spain), was rinsed three times with boiling water and then, three times with distilled water. The material was then dried, cut and sieved to obtain a fine powder (< 500 μm). Cr(VI) and Cr(III) solutions were prepared by dissolving appropriate amounts of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, respectively in MilliQ water; NaOH and HCl were used for pH adjustment. Chromium standard solutions of 1000 mg L<sup>-1</sup> were used for Flame Atomic Absorption calibrations.

In order to assess the mechanisms governing Cr(VI) and Cr(III) sorption and to understand the role of calcium alginate, the same experiments were performed by using pure CA gel beads as blank.

### 2.2. Metal uptake procedure

Batch experiments were carried out at 20 ± 2 °C in stoppered glass tubes. The experiments consisted of shaking in a rotary stirrer (Rotator Drive STR 4, Stuart Scientific) 40 beads of

either CA or 2% GS-CA, with 15 mL of either Cr(VI) or Cr(III) solutions. After agitation, the solid was removed by filtration through a 0.45 μm cellulose filter paper (Millipore). After filtration, pH of the remaining solution was measured using a Crison Model Digilab 517 pH meter. The initial and final metal concentration in the filtrates, previously acidified, were determined by Flame Atomic Absorption Spectrometry (FAAS) (Varian Absorption Spectrometer SpectrAA 220FS). Each experiment was performed in triplicate for quality control and statistical purposes.

Metal concentration in the sorbent,  $q_e$  (mg g<sup>-1</sup>) was calculated from the difference between the initial,  $C_i$ , and equilibrium,  $C_e$ , metal concentration in solution (mg L<sup>-1</sup>):

$$q_e = (C_i - C_e) \frac{V}{m} \quad (1)$$

where  $V$  (expressed in L) is the solution volume and  $m$  is the wet mass of the beads.

### 2.3. Effect of pH

To study the effect of pH on sorption, 15 mg L<sup>-1</sup> solutions of Cr(III) or Cr(VI) at different pH values in the range of 1–6 were contacted with either CA or 2% GS-CA beads for 48 h, following the procedure described above.

### 2.4. Kinetics and equilibrium studies

Batch kinetic experiments were conducted to obtain information about Cr(III) and Cr(VI) removal rate. Experiments were carried out by contacting CA and 2% GS-CA beads with either Cr(III) or Cr(VI) solutions for different contact times. Initial pH was adjusted at 3.0 and allowed to evolve during metal sorption for three different initial chromium concentrations.

Equilibrium isotherms at 20 ± 2 °C were obtained by contacting the beads with solutions of different initial Cr(III) and Cr(VI) concentrations within the range of 25–1500 mg L<sup>-1</sup>. An initial pH of 3.0 and an agitation time of 48 h were chosen according to the results obtained from the experiments of pH effect and kinetics, respectively. Each experiment was performed in triplicate for quality control and statistical purposes. Metal removal data from the equilibrium batch sorption experiments were fitted by the non-competitive Langmuir model:

$$q_e = \frac{K_L q_{\max} C_e}{(1 + K_L C_e)} \quad (2)$$

whose parameters,  $q_{\max}$  (mg g<sup>-1</sup>) and  $K_L$  (L mg<sup>-1</sup>), were calculated by Non-Linear Least Square (NLLS) treatment of experimental data.

### 2.5. Sorption mechanism investigation

In recent studies, the mechanism of Cr(VI) sorption on pure grape stalks has been proved to take place in three steps: Cr(VI) sorption, Cr(VI) reduction to Cr(III) and sorption of the formed Cr(III) onto the solid or its release into the aqueous phase (Escudero et al., 2009; Fiol et al., 2008). Therefore, Cr(VI) reduction by 2% GS-CA beads was investigated here in order to assess the contribution of GS to the overall Cr(VI) removal process. To do this, total chromium and Cr(VI) were analysed in the remaining solutions by FAAS and the 1,5-diphenylcar-

bazide colorimetric method (Clesceri et al., 1998), respectively. The difference between total and Cr(VI) concentrations would correspond to the Cr(III) formed by reduction and released into the solution. Besides, the pH-change with time during the sorption process has been checked to account for this proton-consuming reaction.

Furthermore, it has been reported that Cr(III) sorption onto pure CA beads takes place via ion exchange between positively charged Cr(III) species and calcium cations from the beads (Araujo and Teixeira, 1997). Therefore, the concentration of  $\text{Ca}^{2+}$  released into solution during Cr(III) sorption was measured by Flame Emission Photometry (Sherwood Model 410).

Blank experiments were also performed to check the change of pH and the natural release of calcium when beads were contacted with water adjusted to pH 3.0.

Chromium-laden sorbent surface was analysed by ESR: Cr(III), containing unpaired electrons ( $d^3$  configuration) is ESR positive, while Cr(VI) ( $d^0$  configuration) would provide no ESR signal. Experiments were performed at room temperature using an ESR Spectrometer Bruker ELEXSYS E580 (microwave frequency Q-band = 34.082 GHz, modulation frequency = 100 kHz, modulation amplitude = 3 Gauss, central field = 12000 Gauss, field sweep = 4000 Gauss, power = 1.968 mW, power attenuation = 20 dB). After being contacted with a  $100 \text{ mg L}^{-1}$  Cr(VI) solution for 48 h, CA or 2% GS-CA beads were analysed by ESR. As water strongly absorbs microwave energy, samples were dried in an oven for about 24 h, crushed and loaded in a quartz sample tube.

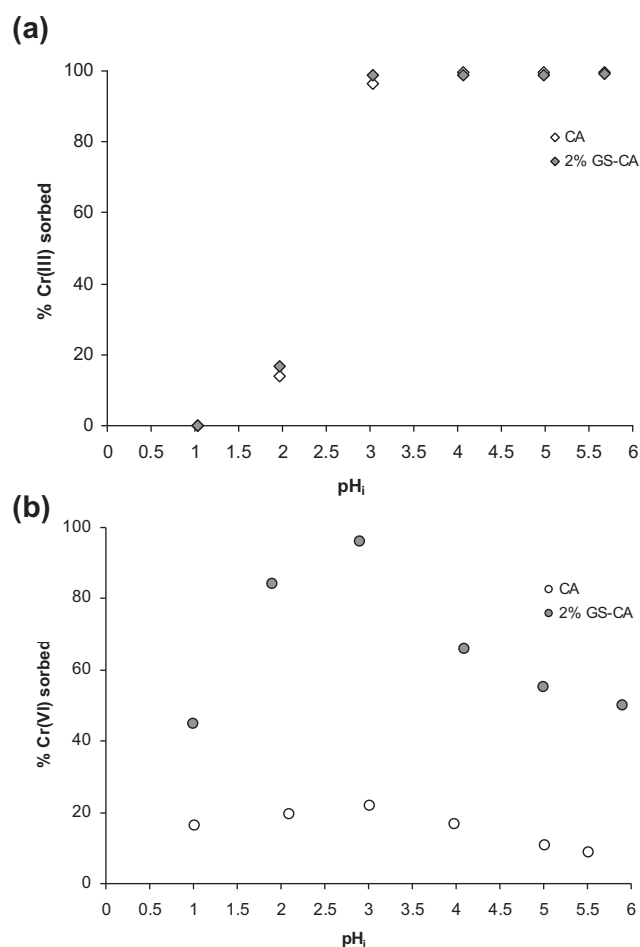
In order to obtain morphologic and local chemical information of the gel beads before and after Cr(III) or Cr(VI) sorption, SEM and EDX analyses were carried out. Furthermore, micrographs in the Backscattered Electron mode (BSE) were also taken in an attempt to detect the presence of metallic nodules on the solid surfaces under study. An Electron Microscope Zeiss DSM 960 A equipped with Energy Dispersive X-ray analyser Link Isis Pentafet (Oxford) was employed for the topological and chemical analysis of the sorbent surfaces. The treatment of the electronic images was performed with Quartz PCI and Picture Gear software. Chromium loading of the samples was carried out according to the procedure described before, with an initial metal concentration at  $800 \text{ mg L}^{-1}$  and initial pH adjusted to 3.0. Prior to the microscopic analysis, samples were dried for 3 days at  $40^\circ\text{C}$  and coated with a thin layer of graphite to improve their electrical conductivity.

### 3. Results and discussion

#### 3.1. Effect of pH

The pH of metal solutions has been identified as one of the most important parameters affecting biosorption: protons can compete with positively charged sorbates for active sites, and influence both chemical speciation of the metal in solution and the charge of the sorbent surface. Moreover, the concentration of protons can modify the redox potential of sorbates and sorbents.

Fig. 1 shows the percentage of Cr(III) and Cr(VI) removed by CA and 2% GS-CA beads as a function of initial pH. In the case of Cr(III) (Fig. 1a), GS shows almost no contribution to sorption as both sorbents exhibit the same pH dependence profile, indicating that CA is mainly responsible for sorption.



**Figure 1** Cr(III) and Cr(VI) sorption onto CA and 2% GS-CA beads as a function of initial pH. Initial metal concentration:  $15.0 \text{ mg L}^{-1}$ ; sorbent dose:  $42 \text{ mg mL}^{-1}$ .

These results are in agreement with previous literature data (Araujo and Teixeira, 1997). One should point out that for the initial Cr(III) concentration of these experiments ( $15 \text{ mg L}^{-1}$ ), almost all chromium was removed ( $>96\%$ ) by both types of beads, presumably because the metal concentration is low and there are still unbound active sites in both CA and 2% GS-CA beads. Thus, taking into account the results presented in Fig. 1a, the role of GS in metal sorption is not clear: this aspect will be clarified below.

It can also be observed (Fig. 1a) that Cr(III) sorption is very low at initial pHs 1 and 2 ( $<20\%$  of metal removal) while almost 100% removal is achieved for both types of gel beads at  $\text{pH} \geq 3$ . A similar sorption trend as a function of pH for Cr(III) was previously reported for different sorbents of both, raw and modified lignocellulosic bases (Miretzky and Cirelli, 2010).

In the case of Cr(VI) (Fig. 1b), 2% GS-CA beads show higher efficiency (almost 100% removal at initial concentration  $15 \text{ mg L}^{-1}$ ) than CA beads (20% removal), indicating that GS plays an important role. Concerning the effect of initial pH on metal sorption, a similar trend was observed for both CA and 2% GS-CA beads: the percentage of metal removal increases until a maximum at pH 3 and then decreases for higher pH values in both cases. Optimal pH values of ca. 2.0–3.0 for Cr(VI)

removal on biomass sorbents have been found by other authors (Saha and Orvig, 2010; Miretzky and Cirelli, 2010; Dakiky et al., 2002).

The different sorption behaviour observed for both Cr(III) and Cr(VI) can be discussed taking into account the pH effect on both the metal speciation and the ionization of the functional groups at the sorbent surface.

In aqueous solutions, Cr(III) and Cr(VI) show different speciation patterns as a function of pH. The species distribution diagram as a function of pH, calculated by MEDUSA computer program (Puigdomènech, 2010), indicates that at the working pH (3.0), Cr(III) species distribution percentage is around 70%  $\text{Cr}^{3+}$  and 30%  $\text{CrOH}^{2+}$  ( $\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$ ,  $\log K = -3.56$ ).

Due to the cation exchange capacity of the CA hydrogel, these two species could be sorbed on both, CA and 2% GS-CA beads. However, under conditions of strong acidity, a low Cr(III) uptake is observed as  $\text{H}^+$  strongly competes with both cationic species for the sorbent basic active sites.

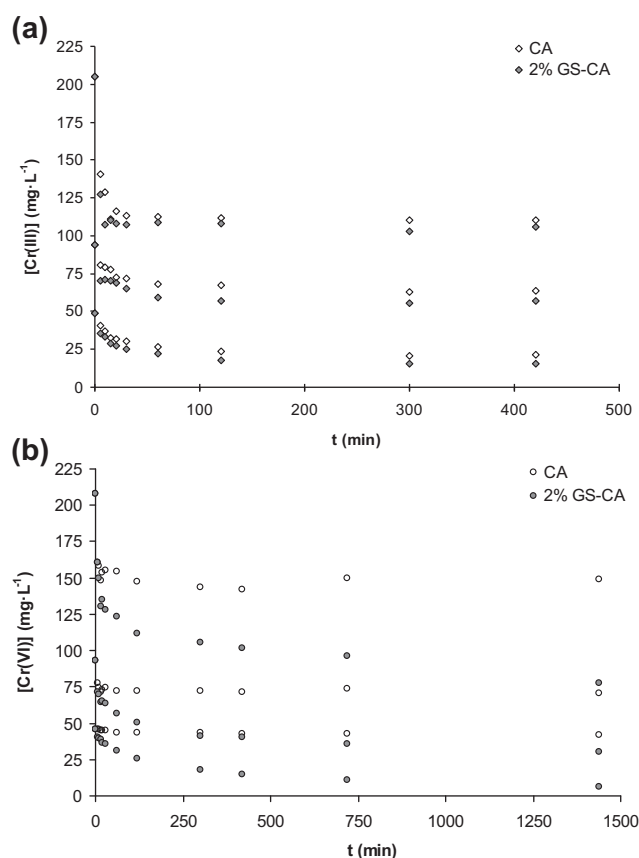
In the case of Cr(VI), in the same experimental conditions (15  $\text{mg L}^{-1}$  metal concentration and pH 3.0),  $\text{HCrO}_4^-$  is the predominant species (98%) ( $2\text{H}^+ + 2\text{CrO}_4^{2-} = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ ,  $\log K = 14.69$ ;  $\text{H}^+ + \text{CrO}_4^{2-} = \text{HCrO}_4^-$ ;  $\log K = 6.55$ ).

As described previously, the pH of the solution may also influence on the ionization of the surface functional groups and consequently on the net surface charge of the sorbent. The  $\text{pK}_a$  values for guluronic and mannuronic acids, monomers of the formation of alginate structure, have been reported to be 3.65 and 3.38, respectively (Percival and McDowell, 1967). Taking into account these data, alginate gel is charged positively at  $\text{pH} < 2.5$ , neutral at  $\text{pH} \approx 3.0$ –3.5 and negatively charged at  $\text{pH} > 4.0$ . Therefore, Cr(III) ion uptake cannot be explained by electrostatic sorbent-sorbate interactions as CA is positively or neutrally charged at pH around 3.0. Thus, another mechanism different from electrostatic attraction must be involved in Cr(III) uptake. Conversely, electrostatic interactions could be responsible for the low Cr(VI) sorption (as the  $\text{HCrO}_4^-$  species) observed for CA gel beads in the pH range of 1–3. The decrease of Cr(VI) uptake when increasing the pH above 3.0 can also be explained by the electrostatic repulsion between  $\text{HCrO}_4^-$  and the negatively charged sorbent surface.

The point of zero charge of GS was previously determined to be  $\text{pH}_{\text{pzc}} = 5.0$  (Fiol and Villaescusa, 2009). Thus, at pH 3.0 the net charge at the GS surface is positive. Taking into account the ionization state of the functional groups of both CA and GS, the anionic Cr(VI) species  $\text{HCrO}_4^-$  is expected to be mainly sorbed by electrostatic interactions onto GS entrapped in 2% GS-CA beads.

### 3.2. Sorption kinetics and isotherms

Cr(III) sorption on both types of beads is quite fast and seems to occur in two steps (Fig. 2a). The first step involves rapid metal uptake within the first 15 min of contact time followed by the subsequent removal until a plateau is reached after approximately 200 min. The fast kinetics observed at the beginning of the process strongly suggests that ionic exchange can be a possible sorption mechanism (Mohan and Pittman, 2006; Saha and Orvig, 2010; Miretzky and Cirelli, 2010; Araujo and Teixeira, 1997). This mechanism is further investigated by measuring the calcium release related to Cr(III) sorption.



**Figure 2** Effect of contact time on the removal of (a) Cr(III) and (b) Cr(VI) by CA and 2% GS-CA for three different initial metal concentrations.  $\text{pH}_0 = 3.0$ ; sorbent dose,  $42 \text{ mg mL}^{-1}$ .  $[\text{Cr(III)}]_0$  48.85, 93.95 and  $204.77 \text{ mg L}^{-1}$ ;  $[\text{Cr(VI)}]_0$  45.70, 93.21 and  $207.86 \text{ mg L}^{-1}$ .

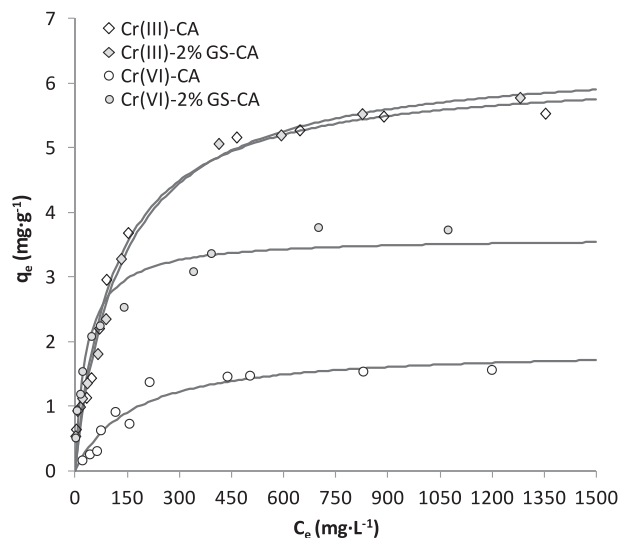
A similar trend was found for Cr(VI) sorption onto both types of beads: a quite rapid short phase followed by a relatively slow and long phase until the achievement of a constant concentration in solution (Fig. 2b). When results are compared for both types of beads, it is worth noting that for an initial metal concentration ca.  $50 \text{ mg L}^{-1}$ : (i) the residual metal concentrations in solution at equilibrium are 17.1 and  $11.1 \text{ mg L}^{-1}$  when Cr(III) solution was contacted with CA and 2% GS-CA beads, respectively; (ii) the residual metal concentrations are 41.2 and  $3.5 \text{ mg L}^{-1}$ , respectively when the sorbents are contacted with Cr(VI). The slight sorption differences found for Cr(III) and the large differences found for Cr(VI) allow to hypothesize that Cr(III) is mainly sorbed on CA and Cr(VI) on GS.

Experimental equilibrium data were fitted to the Langmuir sorption isotherm model (Eq. (2)), which provided good correlation coefficients. The values of maximum capacity obtained in Table 1 indicate that, for both oxidation states, beads containing GS are the most effective. These results confirm that the main active material for Cr(III) sorption at low concentration is CA, and it is only at high metal concentrations when GS plays an important role. Fig. 3 also puts into evidence the good correlation between experimental and predicted sorption behaviour and confirms that Cr(VI) is mainly sorbed on the



**Table 1** Langmuir model parameters for Cr(III) and Cr(VI) sorption onto CA and 2% GS-CA.

Cr(III)	$q_{\max}(\text{mg g}^{-1})$	$K_L 10^3 (\text{L mg}^{-1})$	$R^2$
CA	$6.2 \pm 0.2$	$9 \pm 1$	0.985
2% GS-CA	$6.4 \pm 0.3$	$8 \pm 1$	0.978
Cr(VI)			
CA	$1.9 \pm 0.2$	$6 \pm 2$	0.925
2% GS-CA	$3.6 \pm 0.2$	$31 \pm 7$	0.931

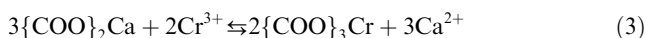
**Figure 3** Cr(III) and Cr(VI) sorption isotherms onto CA and 2% GS-CA beads. Solid lines represent Langmuir model prediction and symbols, the experimental data. Initial pH 3.0; sorbent dose: 42 mg mL<sup>-1</sup>.

GS entrapped into the bead and there is only a slight sorption onto pure CA.

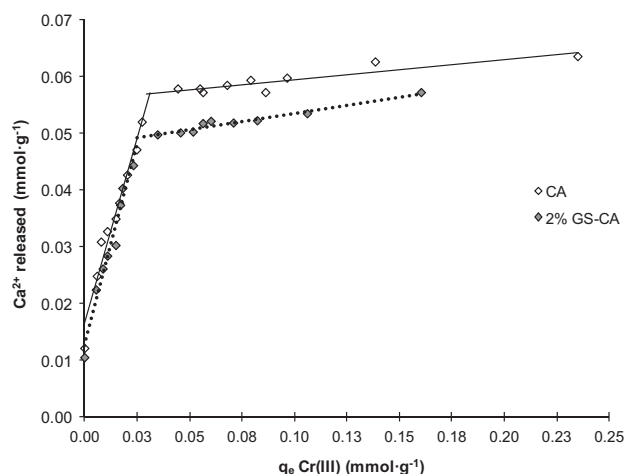
### 3.3. Sorption mechanism

CA has been reported to be a useful sorbent for the removal of divalent metals such as copper, lead, cadmium (Papageorgiou et al., 2009; Pandey et al., 2007) and Cr(III) (Nayak et al., 2007). In these works, it was found that metal sorption mechanism by CA beads takes place via ion exchange: Ca<sup>2+</sup> bound to the carboxyl groups of the biopolymer are replaced by metal cations from the solution.

Taking into account that at pH 3, both Cr<sup>3+</sup> and Cr(OH)<sup>2+</sup> are present in solution, the reactions involved in Cr(III) sorption by CA might be summarized as:



If ion exchange is responsible of Cr(III) species sorption onto CA and 2% GS-CA gel beads, the molar ratio [Ca<sup>2+</sup> released]/[Cr(III) sorbed] should lie between 1.5 and 1.0,

**Figure 4** Calcium released (mmol g<sup>-1</sup>) as a function of chromium(III) sorbed (mmol g<sup>-1</sup>) at equilibrium.

corresponding to the stoichiometric ratio for 3Ca<sup>2+</sup>/2Cr<sup>3+</sup> and 1Ca<sup>2+</sup>/1Cr(OH)<sup>2+</sup>, respectively. This ratio can be calculated as:

$$R = \frac{C_{\text{Ca}^{2+}}}{(C_{\text{Cr(III)}i} - C_{\text{Cr(III)}e})} \quad (5)$$

where  $C_{\text{Ca}^{2+}}$  (mmol L<sup>-1</sup>) is the concentration of calcium released and  $C_{\text{Cr(III)}i}$ ,  $C_{\text{Cr(III)}e}$  are the initial and equilibrium Cr(III) concentrations in solution, respectively.

According to Fig. 4, the amount of calcium released linearly increases with the amount of Cr(III) sorbed (slope around 1.3) for both types of beads, until a capacity around 0.03 and 0.04 mmol g<sup>-1</sup> is achieved for 2% GS-CA and CA beads, respectively. This slope lies in the stoichiometric ratio range indicated previously, confirming that at low and medium Cr(III) concentrations, ion exchange is the predominant sorption mechanism. For higher Cr(III) concentrations, other sorption mechanisms might occur, for there is no further release of calcium though the amount of chromium sorbed by the alginate still increases. Results suggest that for high metal concentrations, Cr(III) ions might diffuse deeper into the 2% GS-CA bead and other mechanisms such as microprecipitation, physical interactions or sorption onto GS might take place. These results are in agreement with those reported by other authors that studied Cr(III) sorption onto dry protonated alginate beads (Araujo and Teixeira, 1997; Nayak et al., 2007).

During Cr(III) and Cr(VI) sorption an increase in solution pH was noticed. This  $\Delta\text{pH}$ , calculated as the difference between the final pH and its initial value (pH = 3.0), for the sorption experiments at three different initial metal concentrations as well as the  $\Delta\text{pH}$  measured for the blank solutions (MilliQ water adjusted at pH 3 with concentrated HCl) is presented in Table 2. Results put into evidence that the contact of CA and 2% GS-CA beads with the blank solutions provokes an important increase of pH ( $\Delta\text{pH} = 2.9$  for CA and  $\Delta\text{pH} = 3.2$  for 2% GS-CA) indicating that the sorbent beads contain basic surface groups {C<sub>x</sub>OH} that may be protonated, giving place to the development of positive surface charges:



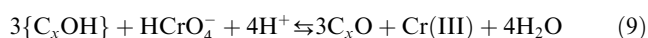
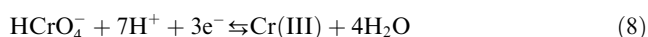
**Table 2** Increase of solution pH ( $\Delta$ pH) after contact of different Cr(III) and Cr(VI) solutions with CA and 2% GS-CA for 48 h. Sorbent concentration: 42 mg mL<sup>-1</sup>.

Cr(III)			Cr(VI)		
C <sub>0</sub> (mg L <sup>-1</sup> )	CA	2% GS-CA	C <sub>0</sub> (mg L <sup>-1</sup> )	CA	2% GS-CA
48.85	0.6	0.9	45.70	2.8	3.4
93.95	0.4	0.5	93.21	2.8	3.4
204.77	0.2	0.4	207.86	2.8	4.1
Blank	2.9	3.2	Blank	2.9	3.2

The  $\Delta$ pH for the blank is higher than for the Cr(III) sorption assays (Table 2). Moreover, the higher the initial Cr(III) concentration is, the lower the  $\Delta$ pH at equilibrium. This fact is indicative of an inhibition of the protonation provoked by Cr<sup>3+</sup> and Cr(OH)<sup>2+</sup> species and corroborates the competition between H<sup>+</sup> and Cr(III) ions for the sorbent active sites. These two effects (inhibition of protonation and competition), seem to be less important in the case of 2% GS-CA beads presumably because of the presence of GS, whose active sites are also available to be protonated and to interact with chromium ions.

Conversely, Cr(VI) sorption provokes a similar  $\Delta$ pH when it is sorbed on CA and a significant increase of  $\Delta$ pH compared to the blank when it is sorbed on 2% GS-CA beads. These results corroborate that Cr(VI) sorption on CA does not imply an additional proton consumption; nevertheless, protons seem to be involved in metal sorption on 2% GS-CA beads, due to the GS-promoted reduction of Cr(VI) to Cr(III).

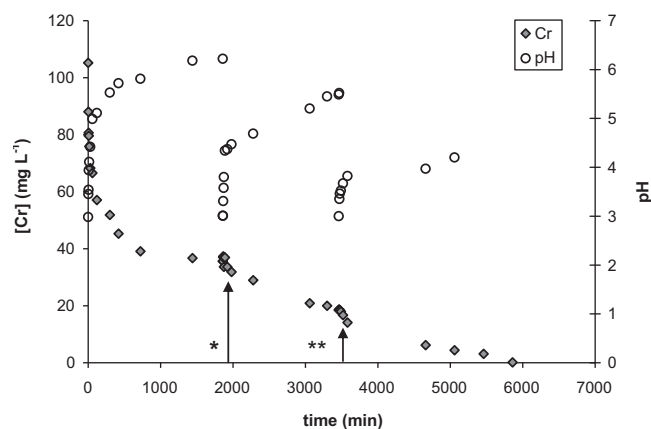
Therefore, if Cr(VI) sorption on 2% GS-CA gel beads involves Cr(VI) reduction to Cr(III), the concentration of protons in the medium should be a limiting factor in the following reaction:



where  $\{C_xOH\}$  and  $\{C_xO\}$  represent the reduced and the oxidized form of reactive sites onto GS, respectively, and Cr(III) is either Cr<sup>3+</sup><sub>(aq)</sub> or Cr(OH)<sup>2+</sup>.

A specific experiment was carried out in order to check whether H<sup>+</sup> acts as a limiting reagent of Cr(VI) sorption onto 2% GS-CA. For this purpose, 4 L of a 92.3 mg L<sup>-1</sup> Cr(VI) solution was contacted in a 5 L stirred tank with 2% GS-CA beads (42 mg mL<sup>-1</sup> sorbent dose). As soon as the pH of the solution achieved almost a constant value, pH was readjusted to the initial value (pH 3.0) by adding negligible amounts of concentrated hydrochloric acid. In this assay, variation of both metal concentration and pH was followed as a function of time. Two readjustments were necessary until chromium was totally removed from solution.

Results plotted in Fig. 5 show that in a first step, after 1500 min, pH increased to a constant value around six and chromium concentration also reached a constant value around 38 mg L<sup>-1</sup>. After the first pH readjustment, chromium sorption reactivated and as a consequence of this, pH increased again and chromium concentration decreased to reach a new equilibrium state: chromium concentration was around 20 mg L<sup>-1</sup> and the pH  $\approx$  5.5. After the second pH readjustment, chromium totally

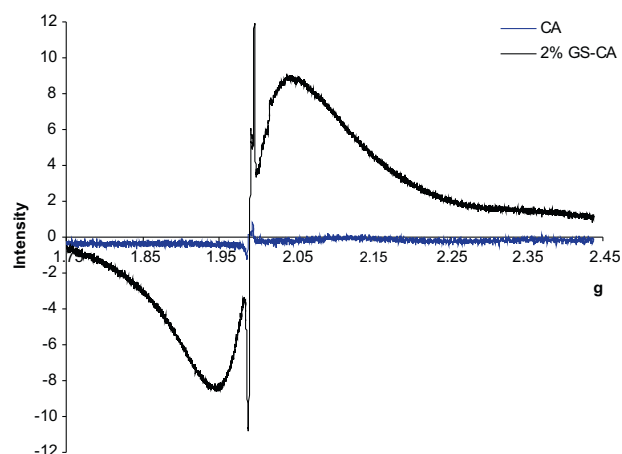


**Figure 5** Chromium concentration in solution and pH variation as a function of contact time of Cr(VI) with 2% GS-CA gel beads. Initial Cr(VI) concentration: 92.3 mg L<sup>-1</sup>, sorbent dose: 42 mg mL<sup>-1</sup>. The arrows indicate the times at which pH readjustment was carried out.

disappeared and the solution pH was stabilized in a value about 4.0. These results corroborate the role of H<sup>+</sup> as a limiting reagent in Cr(VI) sorption onto 2% GS-CA gel beads.

Taking into account both experimental evidences: (i) the contribution of the entrapped GS to Cr(VI) sorption (Fig. 2b) and (ii) the increase of  $\Delta$ pH when Cr(VI) is sorbed on 2% GS-CA (Table 2), it was expected that Cr(VI) reduction takes place to some extent, leading to the presence of Cr(III) in the filtrates. Indeed, several authors who reported Cr(VI) sorption mechanism partially based on its reduction to Cr(III) found that the Cr(III) formed remains fixed to the surface (Nakano et al., 2001) or is partially released to the solution (Fiol et al., 2008; Park et al., 2004, 2008; Gardea-Torresdey et al., 2000; Dupont and Guillon, 2003; Zheng et al., 2011).

Furthermore, we previously reported (Escudero et al., 2009) the presence of Cr(III) in solution after contacting pure GS with Cr(VI) solutions at pH 3.0 as an evidence of Cr(VI)



**Figure 6** ESR spectra of CA and 2% GS-CA beads after Cr(VI) sorption. Initial Cr(VI) concentration: 92.3 mg L<sup>-1</sup>, sorbent dose: 42 mg mL<sup>-1</sup>, initial pH: 3.0.

reduction to Cr(III) and of only partial sorption of the formed Cr(III). The presence of Cr(III) after Cr(VI) sorption onto GS confirmed by X-ray photoelectron spectroscopy analysis was reported in another of our previous works (Fiol et al., 2008). However in this study the analysis of chromium in the filtrates showed that all the chromium present in solution was Cr(VI).

#### 3.4. ESR analysis of the sorbent after Cr(VI) sorption

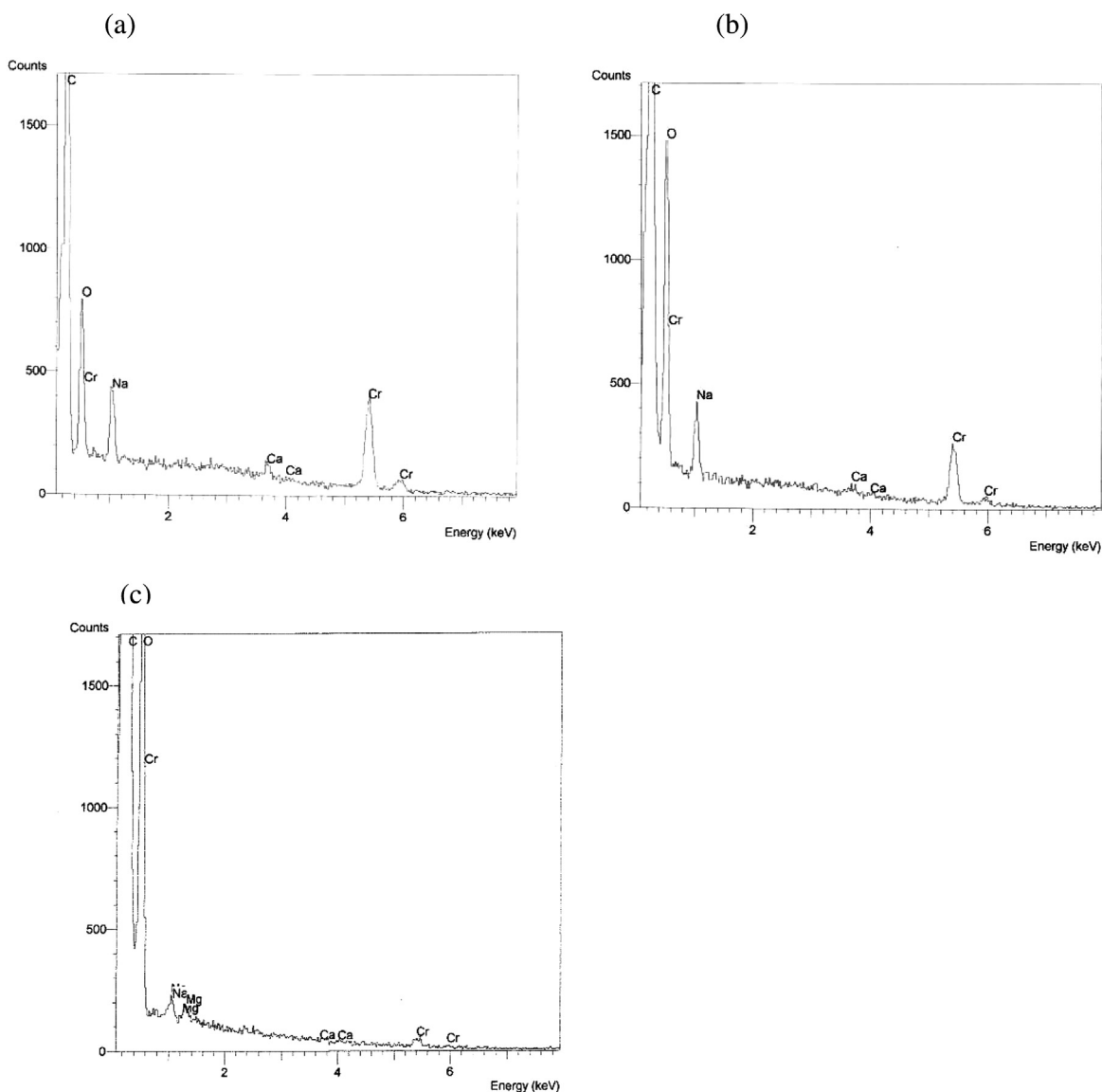
The unexpected absence of Cr(III) in the solution made necessary to check that one of the most important steps of chromium sorption onto GS, i.e. Cr(VI) reduction, was taking place even though GS was entrapped into CA. The analysis of the chromium-laden sorbent surface was carried out from the ESR spectra of both CA and 2% GS-CA beads, after being contacted with a Cr(VI) solution (Fig. 6). A very low ESR signal was observed for CA beads while an intense response was detected in the case of 2% GS-CA, where the broad peak at  $g = 1.989$  corresponds to Cr(III) that possesses

three unpaired electrons and the sharp peak at  $g = 1.998$  is representative of the species Cr(V) with only one unpaired electron. These two signals were also reported by other authors when contacting Cr(VI) solutions with materials such as coir pith (Suksabye et al., 2009) and wood (Humar et al., 2004).

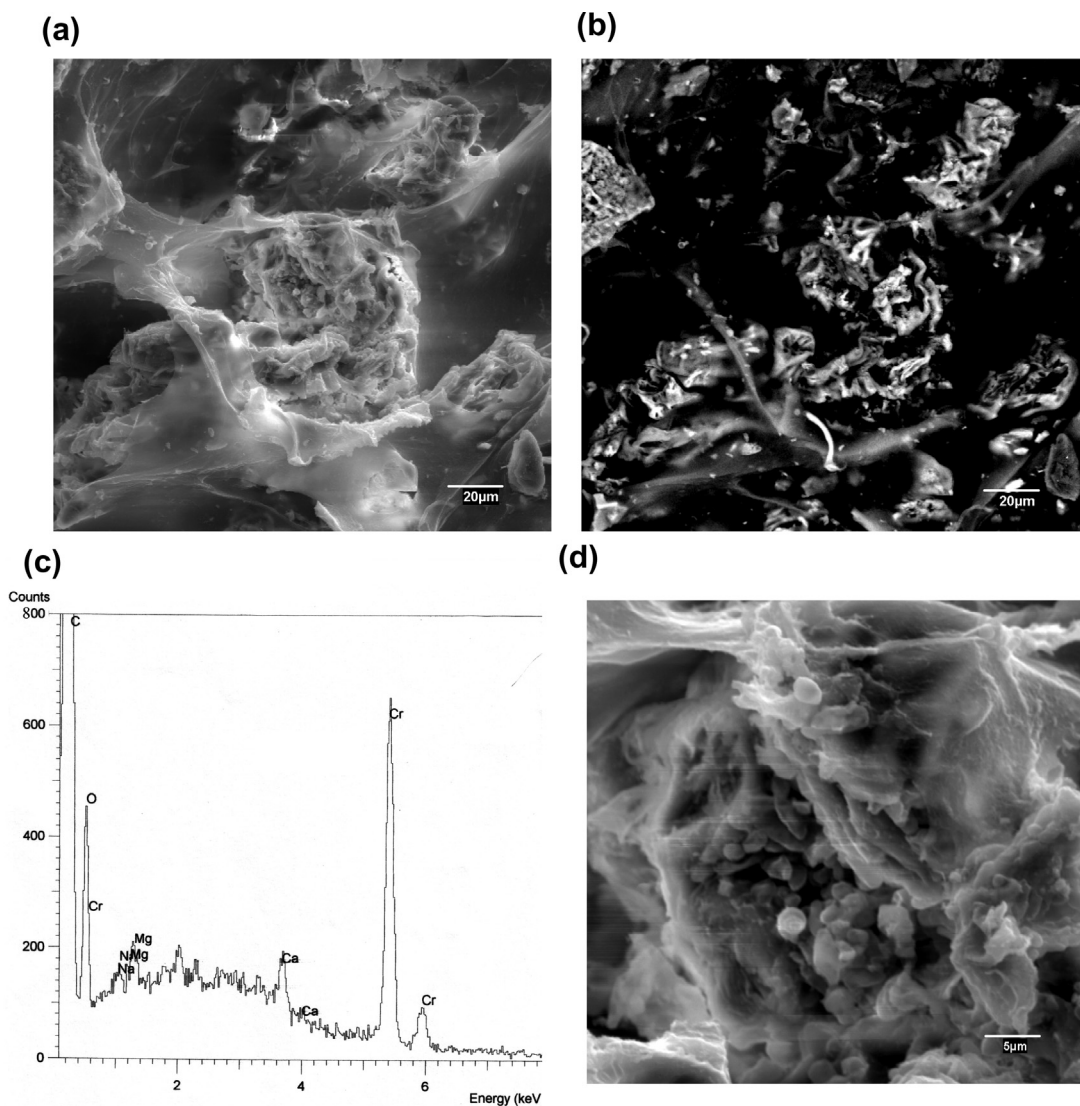
These results indicate the low capacity of CA to reduce Cr(VI) to Cr(III) as compared to the capacity of 2% GS-CA beads and corroborate that: (i) GS are mainly responsible for Cr(VI) reduction, (ii) the reduction takes place with formation of Cr(III) and Cr(V) species and (iii) the formed Cr(III) remains entrapped into the 2% GS-CA beads, therefore being absent in the remaining solution after the sorption process.

#### 3.5. SEM-EDX analysis of the loaded sorbent

Local chemical composition of the 2% GS-CA beads was analysed from EDX spectra of: (a) CA matrix, (b) CA/GS interface and (c) GS particle after Cr(III) sorption (Fig. 7). The CA shows the highest intensity in the EDX spectra of the three



**Figure 7** EDX analysis of 2% GS-CA beads after Cr(III) sorption: (a) CA region; (b) CA/GS interface; (c) GS particle.



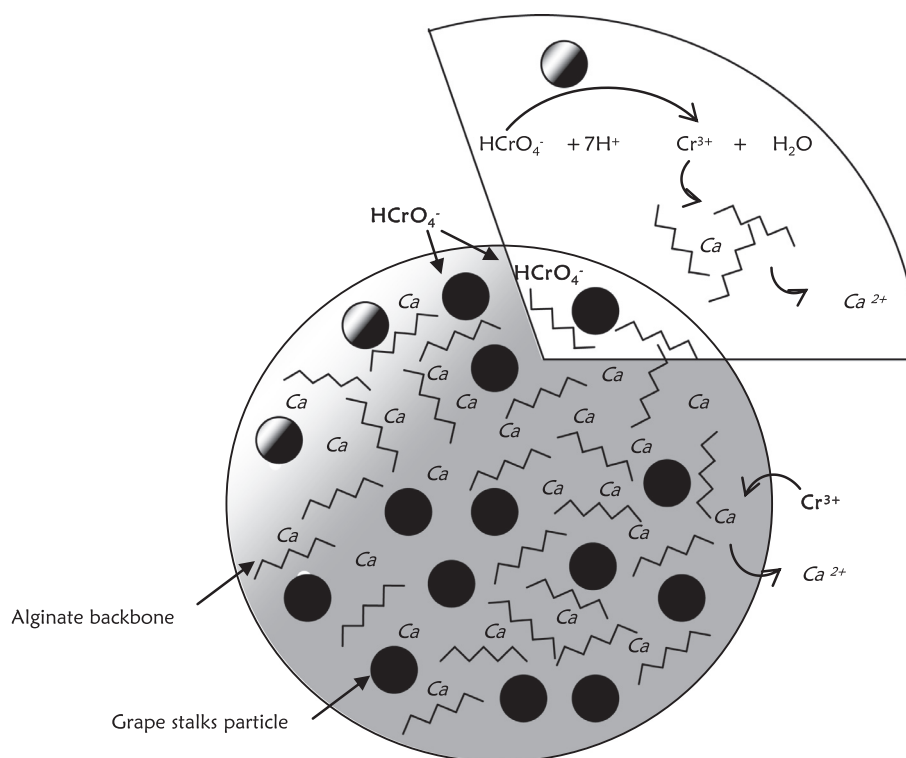
**Figure 8** Electronic micrograph of 2% GS-CA gel beads after treatment with Cr(VI) solution. (a) Scanning mode; (b) Backscattered mode; (c) EDX analysis; (d) focus on the GS region, SEM mode.

regions, corresponding to a chromium concentration about 7.3%. Chromium concentration decreases to about 3.7% when the CA/GS interface is analysed and finally, the lowest concentration was detected in the GS particle (only 0.3%). These results strongly support the role of CA as mainly responsible for Cr(III) sorption, while only a small amount of Cr(III) would be taken up by the GS particles.

The SEM and BSE micrographs before and after Cr(VI) sorption onto CA beads revealed neither topological nor morphological differences (data not shown), pointing out that the alginate structure suffers almost no modification after the contact with Cr(VI). Additionally, when EDX spectra and quantitative chemical analysis of the surface of the CA region were performed, chromium was not detected. These microscopical and spectroscopical data strongly support the low Cr(VI) sorption observed in both, kinetic and equilibrium experiments. However, when Cr(VI) sorption onto 2% GS-CA beads was explored, different modifications were detected. In the SEM

micrograph (Fig. 8a) GS particles are surrounded by the CA matrix; and some pellets on the surface of the GS particle seem to appear after Cr(VI) sorption. BSE picture (Fig. 8b) demonstrated that the GS particles appeared with a particular brightness, indicating thus that it could be a chromium-enriched region. When the same region of the sorbent was further analysed by EDX (Fig. 8c), an intense line related to the presence of chromium appeared, indicating a high chromium content (5.4%) on the GS surface. These results are indicative of a selective concentration of chromium on the surface of the GS particles when the material is treated with Cr(VI). To check this observation, further analysis was carried out, focusing only on the GS surface: SEM analysis shows (Fig. 8d) important nodule coverage of the GS particle, suggesting some kind of surface microprecipitation or deposition of chromium species. However, by means of the ESR technique, it had been previously checked if the presence of Cr(III) sorbed onto 2% GS-CA, coming from Cr(VI) reduction. It is possible then that





**Figure 9** Cr(III) and Cr(VI) sorption/reduction scheme.

after Cr(VI) reduction a certain local basification occurs and Cr(III) precipitates as hydroxide on the surface of the GS particle.

#### 4. Conclusions

GS encapsulated into CA gel beads can be used as an efficient adsorbent for both Cr(III) and Cr(VI) removal from aqueous solutions.

Protons are involved in both Cr(III) and Cr(VI) sorption mechanism: while in the case of Cr(III), protons compete with  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})^{2+}$  species, in the case of Cr(VI), they act as a limiting reagent of the removal process.

While fast kinetics was observed in the case of Cr(III) sorption onto both types of beads, Cr(VI) sorption onto 2% GS-CA was much slower. Results put into evidence that diffusion limitations appear in the case of Cr(VI). Cr(III) and Cr(VI) sorption equilibrium onto both, CA and 2% GS-CA gel beads showed a Langmuir-type sorption behaviour.

The significant  $\text{Ca}^{2+}$  release related to the sorption of Cr(III) on both types of beads indicates that ion exchange is the most important mechanism involved on Cr(III) sorption at low concentrations while other mechanisms must take place at higher initial Cr(III) concentrations.

ESR results evidence that GS on 2% GS-CA beads are mainly responsible for Cr(VI) to Cr(III) reduction and the process takes place with formation of paramagnetic Cr(V) intermediates. SEM-EDX analysis of sorbent surfaces after chromium sorption demonstrates that Cr(III) is sorbed mainly by CA hydrogel while Cr(VI) is concentrated preferably on the surface of GS particles.

From the data obtained in the present work, a suggested mechanism scheme for Cr(VI) sorption onto 2% GS-CA is

presented in Fig. 9. This scheme is based on a series of steps involving, either sequentially and/or in parallel: (i) diffusion of the Cr(VI) through the alginate hydrogel, (ii) reduction to Cr(III) promoted by the GS and (iii) retention of the formed Cr(III) by the CA or microprecipitation on the GS surface.

#### Acknowledgements

The authors wish to thank Prof. Dr. Carlos J. Gómez-García (University of Valencia, Spain) for his valuable help in the acquisition of ESR spectra. Thanks are also given to Ms. Carme Carulla, from the Technical Research Services of the UdG, for her assistance and technical support in the SEM-BSE-EDX analysis of the materials. This work has been supported by Ministerio de Educación y Cultura, Spain, project, CTM2008-02236-E/TECNO. This research was made possible thanks to a fellowship (Ref. BES-2004-4373) from Ministerio de Educación y Ciencia to Carlos Escudero.

#### References

- Araujo, M.M., Teixeira, J.A., 1997. Trivalent chromium sorption on alginate beads. *Int. Biodeterior. Biodegrad.* 40, 63–74.
- Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Springer, Berlin.
- Dakiky, M., Khamis, M., Manassra, A., Mer'eb, M., 2002. Selective sorption of Chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents. *Adv. Environ. Res.* 6, 533–540.
- Dupont, L., Guillon, E., 2003. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environ. Sci. Technol.* 37, 4235–4241.

- Escudero, C., Fiol, N., Poch, J., Villaescusa, I., 2009. Modelling of kinetics of Cr(VI) sorption onto grape stalk waste in a stirred batch reactor. *J. Hazard. Mater.* 170, 286–291.
- Fiol, N., Villaescusa, I., 2009. Determination of sorbent point of zero charge: usefulness in sorption studies. *Environ. Chem. Lett.* 7, 79–84.
- Fiol, N., Poch, J., Villaescusa, I., 2004. Chromium(VI) uptake by grape stalks wastes encapsulated in calcium alginate beads: equilibrium and kinetic studies. *Chem. Speciation Bioavailability* 16, 25–33.
- Fiol, N., Poch, J., Villaescusa, I., 2005. Grape stalks wastes encapsulated in calcium alginate beads for Cr(VI) removal from aqueous solutions. *Sep. Sci. Technol.* 40, 1013–1028.
- Fiol, N., Escudero, C., Villaescusa, I., 2008. Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark. *Bioresour. Technol.* 99, 5030–5036.
- Gardea-Torresdey, J.L., Tiemann, K.J., Armendariz, V., Bess-Oberto, L., Chianelli, R.R., Rios, J., Parsons, J.G., Gamez, G., 2000. Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultura byproducts of Avena monida (Oat) biomass. *J. Hazard. Mater.* B80, 175–188.
- Humar, M., Bokan, M., Amartej, S.A., Sentjurc, M., Kalan, P., Pohleven, F., 2004. Fungal bioremediation of copper, chromium and boron treated wood as studied by electron paramagnetic resonance. *Int. Biodeterior. Biodegrad.* 53, 25–32.
- Kratochvil, D., Pimentel, P., Volesky, B., 1998. Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environ. Sci. Technol.* 32, 2693–2698.
- Lazaridis, N.K., Charalambous, C., 2005. Sorption removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate-goethite beads. *Water Res.* 39, 4385–4396.
- Miretzky, P., Cirelli, A.F., 2010. Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. *J. Hazard. Mater.* 180, 1–19.
- Mohan, D., Pittman, C.U., 2006. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J. Hazard. Mater.* B137, 762–811.
- Nakano, Y., Takeshita, K., Tsutsumi, T., 2001. Sorption mechanism of hexavalent chromium by redox within condensed-tannin gel. *Water Res.* 35, 496–500.
- Nayak, D., Banerjee, A., Roy, S., Lahiri, S., 2007. Speciation dependent studies on chromium absorption using calcium alginate and iron doped calcium alginate biopolymer. *J. Radioanal. Nucl. Chem.* 274, 219–224.
- Pandey, A.K., Pandey, S.D., Misra, V., Devi, S., 2003. Role of humic acid entrapped calcium alginate beads in removal of heavy metals. *J. Hazard. Mater.* B98, 177–181.
- Pandey, D., Bera, A., Shukla, L., Ray, L., 2007. Studies on Cr(VI), Pb(II) and Cu(II) adsorption-desorption using calcium alginate as biopolymer. *Chem. Speciation Bioavailability* 19, 17–24.
- Papageorgiou, S.K., Katsaros, F.K., Kouvelos, E.P., Kanellopoulos, N.K., 2009. Prediction of binary adsorption isotherms of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on calcium alginate beads from single adsorption data. *J. Hazard. Mater.* 162, 1354–1374.
- Park, D., Yun, Y.S., Park, J.M., 2004. Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass. *Environ. Sci. Technol.* 38, 4860–4864.
- Park, D., Lim, S.R., Yun, Y.S., Park, J.M., 2008. Development of a new Cr(VI)-biosorbent from agricultural biowaste. *Bioresour. Technol.* 99, 8810–8818.
- Percival, E., McDowell, R.H., 1967. *Chemistry and Enzymology of Marine Algal Polysaccharides*. Academic Press, New York.
- Puigdomènech, I., 2010. *Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA)*, software version 18 February 2004. Inorganic Chemistry Department, Royal Institute of Technology, Stockholm, Sweden. Available free from <http://web.telia.com/~u15651596/>.
- Saha, B., Orvig, C., 2010. Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. *Coord. Chem. Rev.* 254, 2959–2972.
- Suksabye, P., Nakajima, A., Thiravetyan, P., Baba, Y., Nakbanpote, W., 2009. Mechanism of Cr(VI) adsorption by coir pith studied by ESR and adsorption kinetic. *J. Hazard. Mater.* 161, 1103–1108.
- Zheng, Y.M., Liu, T., Jiang, J., Yang, L., Fan, Y., Weeb, T.S., Chen, J.P., 2011. Characterization of hexavalent chromium interaction with Sargassum by X-ray absorption fine structure spectroscopy, X-ray photoelectron spectroscopy, and quantum chemistry calculation. *J. Colloid Interface Sci.* 356, 741–748.
- Zhitkovich, A., 2011. Chromium in drinking water: sources, metabolism, and cancer risks. *Chem. Res. Toxicol.* 24, 1617–1629.