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Removal of Chromium(VI) and Chromium(III) from Aqueous Solution by Grainless Stalk of Corn

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Abstract: Grainless stalk of corn (GLSC) was tested for removal of Cr(VI) and Cr(III) from aqueous solution at different pH, contact time, temperature, and chromium/adsorbent ratio. The results show that the optimum pH for removal of Cr(VI) is 0.84, while the optimum pH for removal of Cr(III) is 4.6. The adsorption processes of both Cr(VI) and Cr(III) onto GLSC were found to follow first-order kinetics. Values of k_{ads} of 0.037 and 0.018 min^{-1} were obtained for Cr(VI) and Cr(III), respectively. The adsorption capacity of GLSC was calculated from the Langmuir isotherm as 7.1 mg g^{-1} at pH 0.84 for Cr(VI), and as 7.3 mg g^{-1} at pH 4.6 for Cr(III), at 20°C. At the optimum pH for Cr(VI) removal, Cr(VI) reduces to Cr(III). EPR spectroscopy shows the presence of Cr(V) + Cr(III)-bound-GLSC at short contact times and adsorbed Cr(III) as the final oxidation state of Cr(VI)-treated GLSC. The results indicate that, at pH $\approx$ 1, GLSC can completely remove Cr(VI) from aqueous solution through an adsorption-coupled reduction mechanism to yield adsorbed Cr(III) and the less toxic aqueous Cr(III), which can be further removed at pH 4.6.

Keywords: Adsorption-coupled reduction, agricultural waste biomass, chromium removal, waste water treatment

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INTRODUCTION

In recent years, contamination of the environment by chromium, especially hexavalent chromium, has become a major area of concern. The hexavalent form is 500 times more toxic than the trivalent form (1) and is toxic to microorganisms, plants, animals, and humans (2,3). Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation, chromium chemicals production, pulp and paper production. Tanning industry is an especially large contributor of chromium pollution to water resources. In our country, chromium concentrations 1000 times up to the permitted limit have been detected near tanning industries.

In view of the pollution hazard caused by hexavalent chromium, several methods of removal have been reported, including filtration, chemical precipitation, adsorption, electrodeposition, and membrane systems (4), or even ion exchange process (5). Adsorption is an effective and versatile method for removing chromium that solves the problems of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used (6–8). Remediation using biomaterials, such as sugar cane bagasse, degraded cellulosic materials, fern, etc., is gaining importance as a low-cost alternative for the treatment of Cr-contaminated waters (9–16). Grainless stalk of corn (GLSC) is one of the harvests' by-product of maize, a crop that is widely cultivated throughout the world, with close to 33 millon hectares planted worldwide. Therefore, GLSC could be a potential source of biomaterial for the removal of Cr from wastewaters in a cost-effective manner. The objective of this work was to evaluate the efficiency of GLSC in removing chromium(VI) and (III) from aqueous solutions, at different pH, contact time, temperature and chromium/adsorbent ratio. A low Cr(VI) adsorption capacity by pre-boiled and dried (120°C, 24 h) GLSC has been reported (17). The pH explored in that work was outside the optimum pH range for Cr(VI) removal by GLSC (*vide infra*). Besides, the authors did not check the reduction of Cr(VI) to Cr(III) by GLSC (that certainly takes place as shown by the results presented here). Therefore, the adsorption capacity of GLSC was calculated on the basis of Cr(VI) ions concentration in solution, without taking into account the concentration of Cr(III) ions released to the solution. In the present work, we have

(i) found that the Cr(VI) uptake by untreated GLSC is considerably higher than reported for pre-boiled GLSC;
(ii) checked the reduction of Cr(VI) to Cr(III) by GLSC, upon analysis of both Cr(VI) and total Cr(Cr(VI) + Cr(III)) in the aqueous phase as well as total Cr in the solid phase;

(iii) verified the oxidation state of chromium bound to the biomaterial by EPR spectroscopy;
(iv) determined the optimum pH for the removal of Cr(VI) by GLSC from the aqueous phase; and
(v) evaluated the uptake capacity of GLSC on the basis of total Cr, at the optimum pH.

Separately, we studied the adsorption of Cr(III) onto GLSC and determined the Cr(III) uptake capacity, sorption kinetics and the optimal pH for Cr(III) removal, with the intention to find the conditions to remove residual Cr(III) from water.

MATERIALS AND METHODS

Materials

GLSC used in this study was obtained from commercial variety "Ruby 306" maize, collected from Alvarez, Santa Fe, Argentina. GLSC was dried at 40°C for 12 h, powdered and sieved to retain the fraction of particles in the range of 0.12–0.5 mm size. The sieved material was stored at room temperature in sealed polyethylene bags.

All the chemicals used were of analytical grade. Pure water, first deionized and then doubly distilled, was used for each experiment. The aqueous solutions of Cr(VI) and Cr(III) were prepared by dissolving potassium dichromate and chromium(III) nitrate in pure water. The pH of the reaction mixtures was adjusted with perchloric acid.

Chromium Analysis

The Cr(VI) concentration was determined spectrophotometrically at 540 nm by using a double-beam UV-vis spectrophotometer (JASCO V-550 model) after complexation with 1,5-diphenylcarbazide (18). Total Cr concentration (Cr(VI) + Cr(III)) was determined by oxidizing Cr(III) to Cr(VI) using saturated solution of potassium persulfate and silver nitrate as catalyst (19), prior to the 1,5-diphenylcarbazide reaction. The Cr(III) concentration was calculated as the difference between the total and Cr(VI) concentrations. The amount of Cr adsorbed by the GLSC mass treated with Cr(VI) was calculated from the difference between the Cr(VI) concentration of the control solutions and the final total Cr concentration in the respective supernatant solutions. The amount of Cr in the solid phase was verified on samples calcined with Na_2CO_3/K_2CO_3 (1:1), then treated with sulphuric acid and reacted with

1,5-diphenylcarbazide. The removal (%) of Cr(VI) and total Cr by GLSC, and the amount of initial Cr(VI) present in solution as Cr(III) (%) were calculated as shown below:

$$\textit{total Cr removal}\ (\%) = 100 \times ([\mathrm{Cr(VI)}]_{\mathrm{initial}} - [\mathrm{Cr(total)}]_{\mathrm{final}})/[\mathrm{Cr(VI)}]_{\mathrm{initial}}$$

$$\textit{Cr(VI) removal}\ (\%) = 100 \times ([\mathrm{Cr(VI)}]_{\mathrm{initial}} - [\mathrm{Cr(VI)}]_{\mathrm{final}})/[\mathrm{Cr(VI)}]_{\mathrm{initial}}$$

$$\textit{Cr(III) in solution}\ (\%) = 100 \times ([\mathrm{Cr(total)}]_{\mathrm{final}} - [\mathrm{Cr(VI)}]_{\mathrm{final}})/[\mathrm{Cr(VI)}]_{\mathrm{initial}}$$

EPR and FT-IR Analysis

GLSC and Cr-containing GLSC solid samples were examined by EPR and IR spectroscopy. FT-IR spectra of GLSC and Cr-loaded GLSC were recorded on Perkin Elmer FT-IR Spectrum One spectrophotometer, employing the KBr dilution technique (1.5%, w/w). The IR spectra clearly showed the presence of hydroxyl and carboxylate as the main surface functional groups in GLSC. Shift of the OH stretching modes could be observed comparing the IR spectra of untreated and Cr-treated GLSC. Moreover, band intensity changes in the carboxylate stretching frequency region were clearly indicative of Cr binding to this functional group in GLSC.

The EPR spectra were performed on a Bruker ESP 300 E spectrometer at room temperature. The microwave frequency was generated with a Bruker 04 ER (9–10 GHz) and measured with a Racal-Dana frequency meter. The magnetic field was measured with a Bruker NMR-probe gaussmeter. *g*-Values were determined by reference to diphenylpicrylhydrazyl (DPPH) ($g = 2.0036$) as an external standard. Typical sharp Cr(V) and broad Cr(III) EPR signals could be observed in Cr(VI)-treated GLSC samples taken at different contact times. At the end of the reaction, only the Cr(III) signal appeared. The broad Cr(III) signal was the only observed in the EPR spectra of Cr(III)-treated GLSC samples.

Samples for EPR and FT-IR analysis were prepared using 0.5 g of GLSC suspended in 25 mL of

(i) water,
(ii) solutions with a varying amount of Cr(VI) at pH 0.86 or
(iii) solutions with a varying amount of Cr(III) at pH 4.6.

The mixtures were stirred during different time-intervals and then centrifuged. The supernatants were separated and the solids were dried under vacuum and analyzed by EPR and FT-IR spectroscopy.

FT-IR spectra of GLSC treated with water or acid were essentially identical, thus revealing that the acid treatment does not modify the composition of the material surface.

Effect of pH

Batch studies were conducted at 20°C using 0.5 g of GLSC suspended in 23 mL of a solution with a varying amount of perchloric acid. Separate solutions of 0.0282 mol L^{-1} Cr(VI) or 0.0375 mol L^{-1} Cr(III) were prepared from the corresponding salts: $K_2Cr_2O_7$ and $Cr(NO_3)_3$. A 2 mL aliquot of the chromium solution (either Cr(VI) or Cr(III)) was added to the GLSC suspension and the mixtures were magnetically stirred during 3 h (Cr(VI)) or 4 h (Cr(III)). The final mixtures were centrifuged and the supernatants were analyzed for the Cr content.

Effect of Contact Time

Kinetic studies were carried out at 20 ± 0.1°C, using a series of 50 mL Erlenmeyer flasks. In each flask, 0.5 g of GLSC were suspended in 23 mL of a solution of perchloric acid adjusted to the appropriate optimal pH; pH 0.84 for Cr(VI) and 4.6 for Cr(III). In two typical experiments, two milliliters of 0.0282 mol L^{-1} Cr(VI) solution (at pH 0.84) or 0.0375 mol L^{-1} Cr(III) solution (at pH 4.6) were added to the flask containing the GLSC suspension. The mixtures were magnetically stirred during different time-intervals and then centrifuged. The supernatants were analyzed for their Cr content. Separate controls were maintained for each time period.

Adsorption Isotherms

Equilibrium adsorption experiments were performed with 0.5 g of GLSC, in Erlenmeyer flasks containing 25 mL of solution with a varying amount of Cr(VI), and pH adjusted to 0.84. The Cr(VI) adsorption experiments were performed at 20 ± 0.1, 30 ± 0.1 and 40 ± 0.1°C. The adsorption isotherms for Cr(III) were obtained at 20 ± 0.1°C, suspending 0.2, 0.5 or 1.0 g of GLSC in 25 mL of solution with a varying amount of Cr(III), and pH adjusted to 4.6. The mixtures were magnetically stirred for 3 (Cr(VI)) or 4 h (Cr(III)) to reach equilibrium and then centrifuged. The supernatants were analyzed for their Cr content. All experiments were performed in triplicate for statistical purposes.

RESULTS AND DISCUSSION

The treatment of GLSC with Cr(VI) in acid aqueous solution showed that the adsorption of chromium by the material occurs together with its reduction to Cr(III). It is known that in solution a number low-molecular-weight organic molecules reduce Cr(VI) and this reaction strongly depends on pH (20,21). Therefore, to evaluate the experimental results it was important to know if Cr(III) observed in the supernatant was produced by redox reaction of Cr(VI) with organic matters leached out from the material. GLSC was washed several times with 0.1 mol L^{-1} $HClO_4$ and the solid and washing solutions were treated separately with Cr(VI). The GLSC soluble fractions showed to be unreactive toward Cr(VI) while, for a number of evaluations, the solid fraction and the unwashed material yielded the same amount of adsorbed chromium and Cr(III) in solution, and identical kinetic parameters. Thus, it can be stated that organic matter leached out by the material does not cause the reduction of Cr(VI).

Since the pH, time, and temperature affect the portion of Cr(III) present in the aqueous solution, the Cr(VI) adsorption capacity of the material was evaluated on the basis of Cr(VI) removal considering the reduction effects. For this reason, Cr(VI) and total chromium (Cr(VI) + Cr(III)) were traced during the standardized adsorption tests.

Effect of pH

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the adsorbent. Hence, metal adsorption is critically linked with pH. Results of Cr(VI) adsorption experiments by GLSC are given in Fig. 1(a). Maximum total-chromium removal yield was obtained at pH 0.4 and the removal efficiency decreased by increasing pH. It must be noted that, although the removal of Cr(VI) was 100% at pH 0.4, the adsorbed chromium was 44%, and 56% remained in solution as reduced Cr(III). In the 0.5–1.5 pH range, the reduction is the process more affected by the increasing pH. In this pH range, Cr(VI) removal decreases from 56 to 28% while total chromium removed is not much affected (from 44 to 40%). Besides, the difference between Cr(VI) and total-chromium removal yield decreases by increasing pH showing that the reduction of Cr(VI) is favored in the strongly acid solutions. At $pH > 3$ there was neither adsorption nor reduction of Cr(VI) by GLSC.

The effect of pH on the removal of Cr(III) by GLSC is shown in Fig. 1(b). It is clear that adsorption of Cr(III) species increases with increasing pH. At $pH < 3$, there was no adsorption of Cr(III), and the

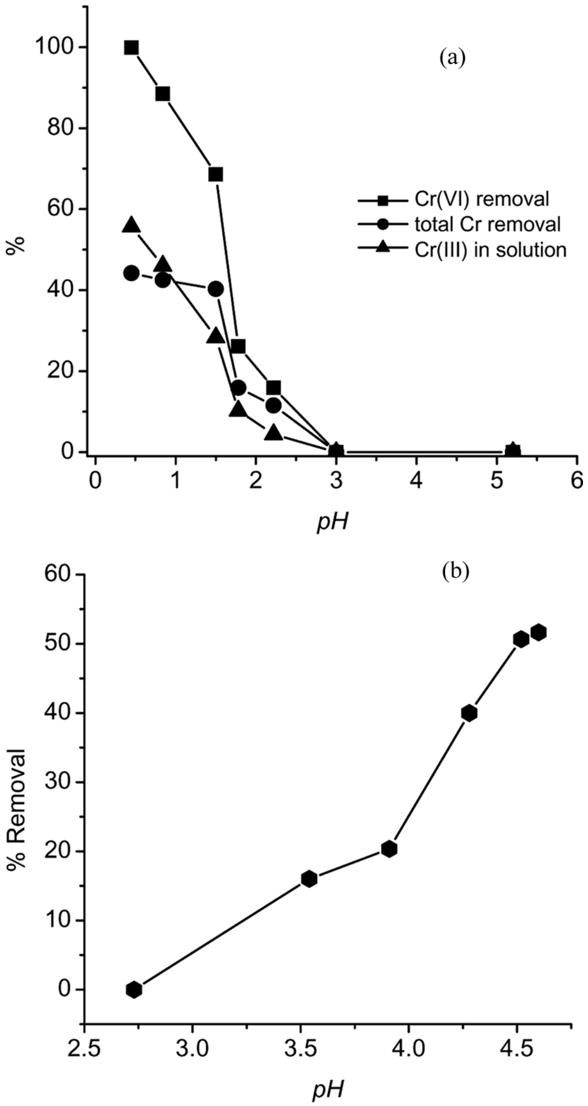

Figure 1. Effect of pH on the removal of Cr(VI) (a) and Cr(III) (b) by GLSC. Conditions: mass of GLSC = 0.5 g, T = 20°C, V = 25 mL. (a) $[\mathrm{Cr(VI)}]_{\mathrm{initial}} = 0.0023\,\mathrm{mol\ L^{-1}}$, contact time = 3 h. (b) $[\mathrm{Cr(III)}]_{\mathrm{initial}} = 0.003\,\mathrm{mol\ L^{-1}}$, contact time = 4 h.

Cr(III) removal yield increased up to 52% at pH 4.6. Experiments beyond pH 5.0 were not performed due to the precipitation of chromium(III) hydroxide.

The pH of the solution modifies the behavior of the material surface and, in consequence, modifies its adsorption capacity for Cr(VI) and Cr(III). The high adsorption of Cr(VI) at low pH (<2) could be explained considering that the high proton concentration generates positively charged surfaces, so that the negatively charged hexavalent chromium species (CrO_4^{2-} and $HCrO_4^-$) can be adsorbed to these surfaces (22) easier than at higher pH. However, the observation of reduced Cr(III) as the final oxidation state of chromium bound to the material and in the aqueous phase, should indicate that the mechanism of Cr(VI) adsorption by GLSC is not simply anionic adsorption but adsorption-coupled reduction (see below). This is in agreement with the fact that reduction of Cr(VI) consumes protons and is favored at lower pH. On the other hand, at $pH > 3$, positively Cr(III) species adsorb preferably because the adsorption process is dominated by electrostatic interactions among the ionized acid sites on the material surface and the Cr(III) cations (23).

From these results, pH 0.84 was selected as the most suitable for all subsequent studies on Cr(VI) removal by GLSC, and pH 4.6 was chosen to study the effect of the other parameters on the Cr(III) removal by GLSC.

Effect of Contact Time

The kinetics of metal ion adsorption is an important parameter for designing adsorption systems and is required for selecting optimum operating conditions for full-scale batch processes. The effect of contact time on the chromium removal by GLSC is shown in Fig. 2. The removal of total chromium increases with time up to 120 min and thereafter becomes nearly constant. Therefore, for all the experiments, the contact time was maintained for 3 h to ensure that equilibrium was really achieved. The final adsorbed chromium represents 50% of the initial Cr(VI), the other 50% was reduced to Cr(III) and released to the solution after an induction period (Fig. 2). These facts suggest that the mechanism of Cr(VI) removal by GLSC is adsorption-coupled reduction, such as proposed for other biomaterials (24).

The kinetic evaluation was made on the basis of total-chromium removal. For this purpose, time-dependent adsorption data were fitted to the Lagergren equation, which is one of the most widely used equation for the adsorption of solute from a liquid solution (25). It may be represented as follows:

$$\ln(q_e - q) = \ln q_e - k_{ads} t \qquad (1)$$

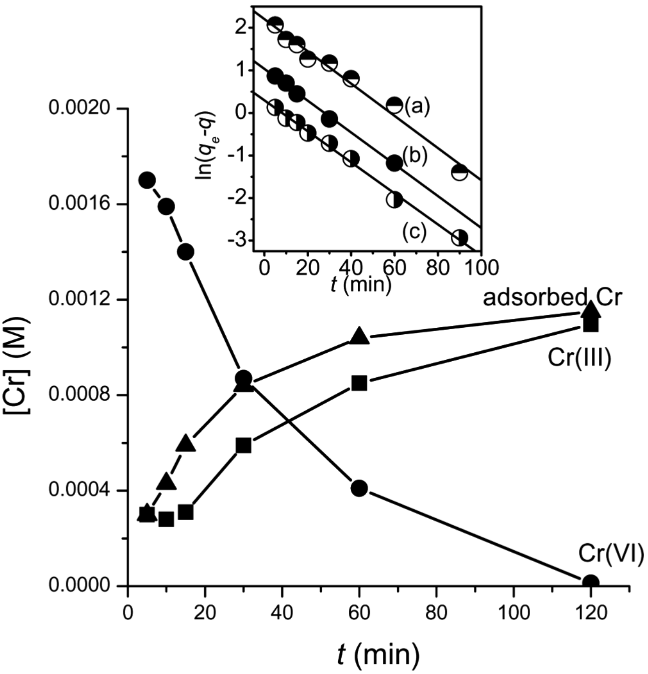

Figure 2. Effect of contact time on chromium removal by GLSC: $[Cr(VI)]_{initial} = 0.0023\,mol\,L^{-1}$, mass of GLSC = 0.5 g, pH = 0.84, T = 20°C, V = 25 mL. Inset: Lagergren plot based on total Cr removal, for three different $[Cr(VI)]_{initial}$: a) $0.0093\,mol\,L^{-1}$, b) $0.0023\,mol\,L^{-1}$ and c) $0.001\,mol\,L^{-1}$.

where q_e and q (mg/g) are the amounts of total Cr adsorbed at equilibrium and at any time t (min), and k_{ads} (min^{-1}) is the first-order adsorption rate constant. The parallel linear plots of $\ln(q_e - q)$ versus t shown in the inset of Fig. 2 for three different $[Cr(VI)]_{initial}$, indicate the applicability of Eq. (1) to the present data. The value of k_{ads} obtained from the slope of these lines is $0.037 \pm 0.002\,min^{-1}$ ($r^2 = 0.9976$).

Figure 3 shows the effect of contact time on the Cr(III) removal by GLSC at pH 4.6. The Cr(III) removal increases with time up to 240 min and then reaches a plateau. Therefore, for all the experiments, the contact time was maintained for 4 h to ensure that equilibrium was really achieved. The kinetic data were fitted to the Lagergren equation, and the value of k_{ads} obtained from the slope of the plots of $\ln(q_e - q)$ versus t (inset in Fig. 3) is $0.018 \pm 0.001\,min^{-1}$ ($r^2 = 0.9819$).

The values of k_{ads} for Cr(VI) and Cr(III) are similar to those reported in previous works for other natural adsorbents (23,26).

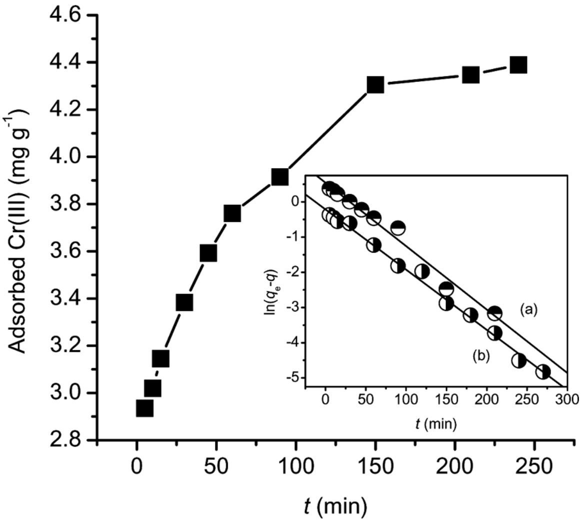

Figure 3. Effect of contact time on Cr(III) removal by GLSC: $[Cr(III)]_{initial} = 0.003\,mol\ L^{-1}$, mass of GLSC = 0.5 g, pH = 4.6, T = 20°C, V = 25 mL. Inset: Lagergren plot for the adsorption of Cr(III) on GLSC, for two different $[Cr(III)]_{initial}$: a) $0.003\,mol\ L^{-1}$, and b) $0.001\,mol\ L^{-1}$.

Adsorption Isotherms

Adsorption isotherms of Cr onto GLSC were obtained at pH 0.84 by varying the initial Cr(VI) concentration in the range of 66 to 1000 mg L^{-1}. The Cr(VI) adsorption capacity of GLSC was evaluated on the basis of Cr(VI) removal considering reduction effects. The adsorption isotherms thus obtained on the basis of total chromium are represented in Fig. 4. As it can be observed, the isotherms exhibit asymptotic behavior. The shape of these curves is typical of low surface coverage but high affinity of the solid particles against adsorbate. Therefore, isotherms data were fitted to Langmuir and Freundlich adsorption models, given by Eq. (2) and (3).

$$q_e = Q^{\circ} b\ C_e/(1 + b\ C_e) \tag{2}$$

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

where C_e and q_e are the equilibrium adsorbate concentrations in the aqueous (mg L^{-1}) and solid phase (mg g^{-1}), respectively. Langmuir equation can be used to calculate the maximum adsorption capacity Q°

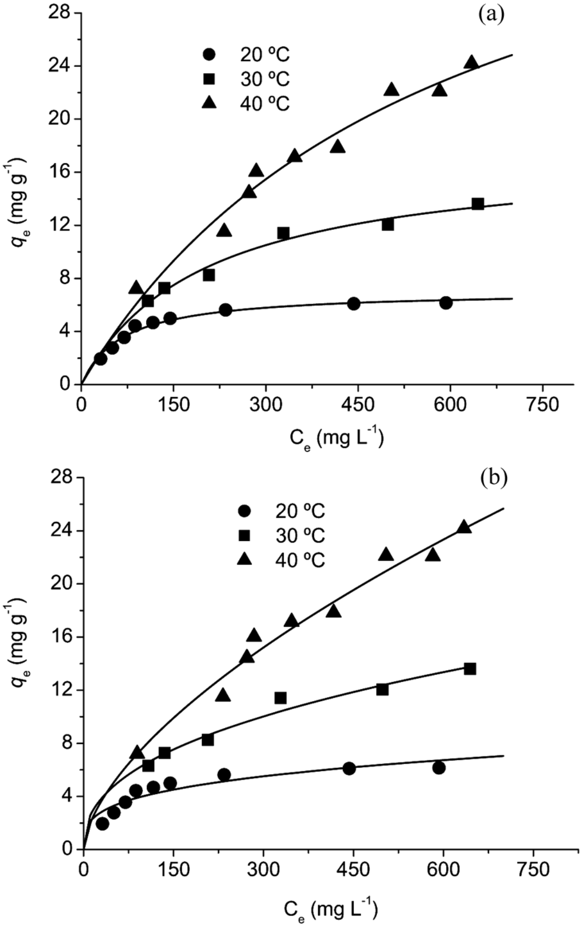

Figure 4. Adsorption isotherms for Cr(VI) removal by GLSC based on total Cr removal: $[Cr(VI)]_{initial} = 66\text{–}1000\,mg\ L^{-1}$, mass of $GLSC = 0.5\,g$, contact $time = 3\,h$, $pH = 0.84, V = 25\,mL$. Solid lines represent the fitting of the data by the (a) Langmuir and (b) Freundlich models.

(mg/g) and the energy parameter of adsorption b (L/mg). In the Freundlich model, K_f (mg/g) and $1/n$ constants are relative indicators of adsorption capacity and adsorption intensity, respectively. For values in the range $0.1 < 1/n < 1$, adsorption is favorable (27). Calculated isotherm parameters and correlation coefficients at the three temperatures are listed in Table 1. Figure 4 and correlation coefficients show that the adsorption data fit both the Langmuir and Freundlich models well

Table 1. Langmuir and Freundlich constants and correlation coefficients for chromium removal by GLSC

				Langmuir constants			Freundlich constants		
	GLSC (g)	pH	T (°C)	Q° (mg/g)	b (L/mg)	r^2	K_f (mg/g)	1/n	r^2
Cr(VI)	0.5	0.84	20	7.1(2)	0.015(2)	0.9722	1.1(3)	0.29(5)	0.8521
	0.5	0.84	30	18(1)	0.0050(7)	0.9763	0.9(2)	0.41(4)	0.9694
	0.5	0.84	40	45(6)	0.0017(4)	0.9679	0.4(1)	0.62(5)	0.9715
Cr(III)	0.5	4.6	20	7.30(5)	0.64(4)	0.9931	4.6(5)	0.10(3)	0.7556
	0.2	4.6	20	7.0(3)	0.24(5)	0.9817	2.5(5)	0.22(5)	0.8599
	1.0	4.6	20	1.9(2)	0.12(7)	0.8964	0.5(3)	0.3(1)	0.6981

at the three chosen temperatures. The magnitudes of K_f and $1/n$ show easy separation of Cr from the aqueous medium and indicate favorable adsorption. The obtained b values imply strong binding of chromium to GLSC. The fact that desorption of Cr from GLSC at 20°C, with either acid or base, affords only 10% recovery may be due to the strong bonding of Cr to the adsorbent. An increase of temperature from 20 to 40°C resulted in enhancing the adsorptive capacity of GLSC from 7.1 to 45 mg g^{-1}, indicating that the chromium-removal process by adsorption onto GLSC has an endothermic nature. The increase in Cr(VI) uptake may be due to creation of some new sorption sites on the adsorbent surface or the increased rate of intraparticle diffusion of adsorbate ions into the pores of adsorbent at higher temperature as diffusion is an endothermic process (28,29).

The Cr(VI) uptake capacity by GLSC is comparable to those reported for other agricultural waste materials presented in Table 2. These results reinforce the feasibility of employing GLSC as biomaterial for Cr(VI) removal from aqueous solution since it presents a good adsorption capacity in comparison to other low-cost materials. Aside of the Cr uptake capacity, the major advantage of GLSC as low-cost material is that it is readily available and does not present an alternative profitable use. It must be noted that in the case of pre-boiled GLSC, rice bran, red pine sawdust, eucalyptus bark, and sugar cane bagasse the authors did not considered the possible reduction of Cr(VI) to Cr(III) by the biomaterial, and the Langmuir constants were calculated on the basis of Cr(VI) ions in solution. Therefore, the Cr(VI) adsorption onto these biomaterials could be lower than reported (38). It is worth noting that pre-boiling of GLSC reduces its adsorption capacity considerably. Furthermore, the adsorption isotherm of Cr(VI) onto pre-boiled GLSC was obtained at pH 2 (17), a pH that is outside of the 0.5–1.5 pH range

Table 2. Adsorption capacities of GLSC compared to other adsorbents

Adsorbents	Adsorption capacity (mg/g)	Reference
Soya cake	0.28	(27)
Pre-boiled GLSC	0.28^a	(17)
Coconut shell powder	1.23	(30)
Rice bran	1.67^a	(31)
Sugar beet pulp	5.12	(32)
Red pine sawdust	5.50^a	(33)
Coffe husks	7.0	(34)
Cactus	7.08	(35)
Grainless stalk of corn	7.1	This paper
Almond shells	10.6	(35)
Sugar cane bagasse	13.4^a	(36)
Lentinus sajor-caju	22.1	(26)
Eucalyptus bark	45.0^a	(37)

[a] Reduction of Cr(VI) to Cr(III) was not considered in the calculation of adsorption capacity.

where Cr(VI) uptake is maximum. This fact should also account for the low value of the Langmuir constant.

The adsorption isotherm of Cr(III) onto GLSC was obtained at pH 4.6 and three adsorbent doses (0.2 to 1.0 g/25 mL), by varying the initial Cr(III) concentration in the range of 8.5 to 255 mg L^{-1}, at 20°C. The adsorption isotherms thus obtained are shown in Fig. 5. The results showed that with increase in the adsorbent dose from 0.2 to 0.5 g/25 mL, the percent adsorption increased, but as the adsorbent dose augmented from 0.5 g/25 mL to 1.0 g/25 mL, the percent adsorption strongly diminished. Therefore, at this pH and temperature, maximal Cr(III) removal was attained with adsorbent dose of 0.5 g/25 mL. The reduction of the adsorption capacity when increasing the adsorbent dose over 0.5 g/25 mL may be due to the aggregation of adsorption sites resulting in decrease in total adsorbent surface area of GLSC particles and an increase in diffusion path length. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are presented in Table 1. The Langmuir model is better correlated to the experimental data than the Freundlich model. The values of the Q° and b determined from Langmuir equation as well as K_{f} and $1/n$ constants from Freundlich model, clearly suggest for a favorable adsorption of Cr(III) onto GLSC at pH 4.6. The magnitude of Q° is comparable to other agricultural waste materials earlier reported in the literature (23).

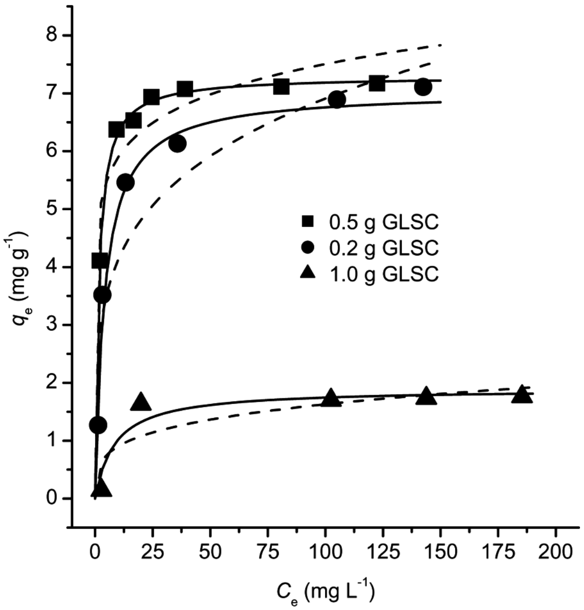

Figure 5. Adsorption isotherms for Cr(III) removal by GLSC: $[\mathrm{Cr(III)}]_{\mathrm{initial}} =$ 8.5–255 mg L^{-1}, mass of GLSC = ● 0.2 g, ■ 0.5 g and ▲ 1.0 g, contact time = 4 h, h, T = 20°C, pH = 4.6, V = 25 mL. Lines represent the fitting of the data by the (—) Langmuir and (—) Freundlich models.

Cr-GLSC Spectroscopic Characterization

EPR and FT-IR spectra of the untreated and Cr-treated GLSC were performed to get more information about the adsorption mechanism of chromium.

The FT-IR is an important tool to identify the functional groups in materials capable of adsorbing metal ions. The GLSC surface is mainly composed of polysaccharides (pectines, uronic acids, cellulose, comprise ≈80% of the dry matter). These biopolymers have hydroxyl and carboxylic functional groups. Figure 6 shows the IR spectra of GLSC and Cr-loaded GLSC. The spectrum of GLSC shows broad absorption bands around 3430 and 3300 cm^{-1} indicative of the existence of bound OH and $-CO_2H$ groups, bands at 2933-2870 cm^{-1} due to CH stretching modes, and strong peaks at 1730 ($\nu_{C=O}$) and 1425 (ν_{C-O} coupled to δ_{OH}) cm^{-1} displayed by the $-CO_2H$ groups. These bands show changes in shape and intensity in the FT-IR spectra of GLSC loaded with Cr(VI) or Cr(III). The similarity of spectra of GLSC contacted with Cr(VI)

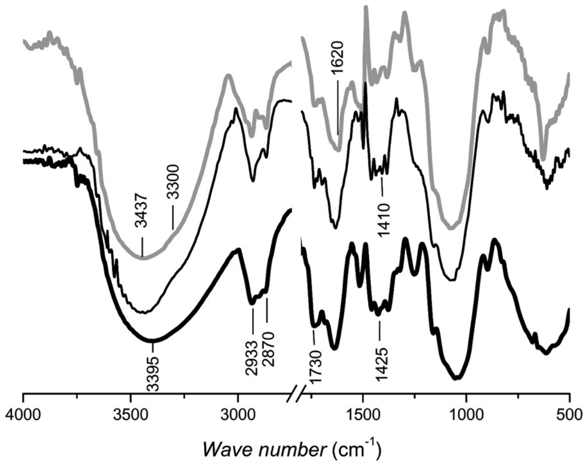

Figure 6. FT-IR spectra of GLSC (▬), Cr(VI)-treated GLSC (—) and Cr(III)-treated GLSC (▬).

and Cr(III), suggests that the same type of binding sites are involved in both cases. In the Cr-treated GLSC spectra the intensity of the two bands at 1620 and 1410 cm^{-1}, corresponding to the asymmetric and symmetric stretching modes of carboxylate, strengthened relative to those of $-CO_2H$, suggesting that Cr is adsorbed on carboxylate sites of GLSC. This fact agrees with previous studies performed with other adsorbents that have shown that the Cr binding may occur via carboxylic ligands on the adsorbent surface (8). Changes in the shape and position of the ν_{OH} bands from 3395 to 3437 cm^{-1} are indicative of additional Cr-binding through the hydroxyl groups of the adsorbent.

EPR is a powerful tool to obtain information on the oxidation state of adsorbed Cr. While Cr(VI) is EPR silent, Cr(III) and Cr(V) afford characteristic bands and can be distinguished by this technique. Typically, room temperature X-band EPR spectra of Cr(V) species exhibit strong narrow signals (1–5 G) centered at $g \sim 1.98$, whereas Cr(III) species, due to the much shorter relaxation time of Cr(III), afford broader signals at $g \sim 2.00$, with 500–1000 G width. Figure 7 shows EPR spectra of GLSC after treatment with Cr(III) and Cr(VI). Before treatment, GLSC is EPR silent. EPR spectra of GLSC treated with Cr(VI) taken at different contact times exhibit a sharp signal at g = 1.9788, characteristic of Cr(V), superimposed to a broad signal (~600 G) at g ~ 2.00, typical of Cr(III). The intensity of this broad signal increased with longer contact times while the sharp Cr(V) signal diminished and finally disappeared, thus indicating that Cr(V) was further reduced to Cr(III) on the

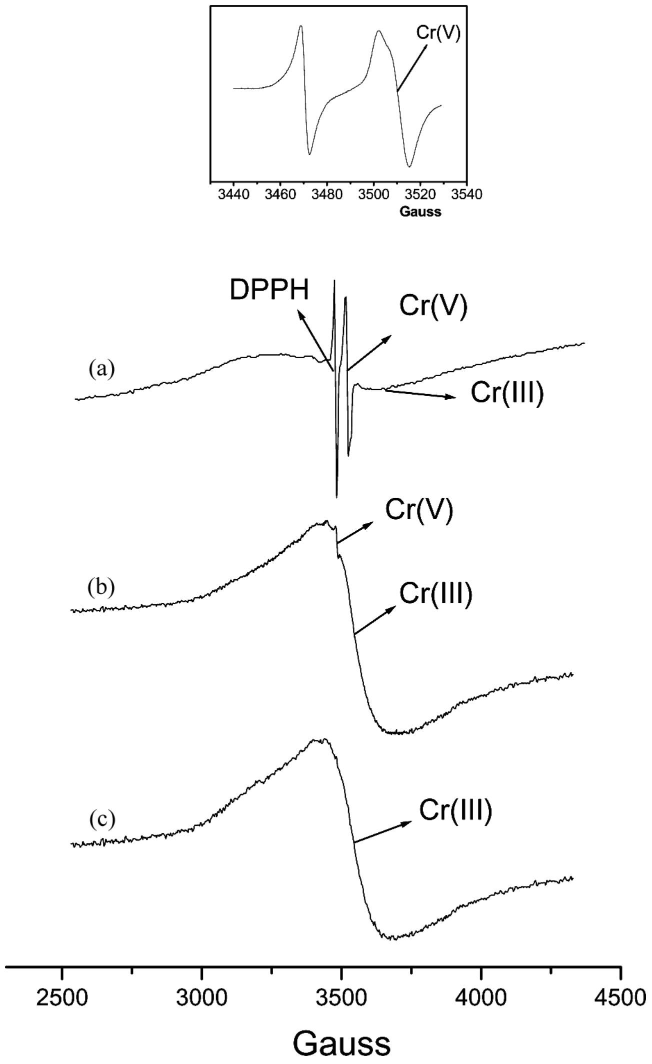

Figure 7. X-band EPR spectra of GLSC treated with Cr(VI) during different time-intervals: (a) 1 h, (b) 4 h, (c) >4 h. $\nu = 9.74572\,\text{GHz}$, $T = 20°\text{C}$, modulation amplitud: 2 G. Inset: $t = 1\,\text{h}$, $\nu = 9.73084\,\text{GHz}$, modulation amplitud = 0.981 G, $T = 20°\text{C}$.

GLSC surface. The superhyperfine (shf) pattern and *g* value of the Cr(V) EPR signal provide useful information on the nature and number of donor groups bound to Cr(V) (39). To improve the spectral resolution, the EPR spectrum was obtained with lower modulation amplitude and the shf coupling pattern of the Cr(V) signal could be observed (Inset in Fig. 7). The *g*-value and the signal shape correspond to oxo-Cr(V) bound to carboxylate and alcohol groups (39). The observation of Cr(V)-bound-GLSC reinforces the adsorption-reduction model for the removal of Cr(VI) by this adsorbent. In aqueous solution, Cr(VI) behaves as an oxoanion, $HCrO_4^-$ or $Cr_2O_7^=$, and cannot bind to a negatively charged functional group, such as carboxylate, because of the repulsion of charges. Therefore, the binding of Cr(VI) at low pH could be occurring *via* protonated ligands followed by reduction of Cr(VI) to Cr(III) subsequently resulting in the binding of Cr(III) to the adsorbent or the release of Cr(III) to the solution.

The spectra of GLSC treated with Cr(III) solution at pH 4.6 only show the growth and stabilization of the broad Cr(III) signal at $g \sim 2.00$. The ionization constants for various carboxylic acids have been reported to be around 3–4 (40). Therefore, at pH higher than 4, the carboxyl groups are deprotonated, making the uptake of Cr(III) cations possible by the surface of the adsorbent.

CONCLUSIONS

On the basis of the data obtained in the present study, the following conclusions can be drawn. The adsorption of both Cr(III) and Cr(VI) by GLSC are pH dependent processes, with a maximum removal of Cr(III) at pH 4.6, while Cr(VI) removed best in the pH range of 0.5–1.5. At low pH, Cr(VI) is reduced to Cr(III) and completely removed from the solution. Reduced Cr(III) is partially retained on the GLSC surface and partially released into the aqueous solution, being this an important issue that must not be neglected. Furthermore, at short contact times EPR spectra are dominated by an intense sharp signal at g 1.9788 indicating the presence of adsorbed Cr(V) on the GLSC surface. The intensity of this signal decreases with time concomitantly with the growth of the broad EPR signal characteristic of Cr(III), indicating that reduced Cr(III) is the final oxidation state of Cr adsorbed on GLSC. Thus, the Cr(VI) removal by GLSC occurs *via* an adsorption-coupled reduction mechanism just as already observed for a number of biomaterials (41,42).

The adsorption capacity of GLSC was calculated from the Langmuir isotherm as $7.1\,mg\,g^{-1}$ at pH 0.84 for Cr(VI), and as $7.3\,mg\,g^{-1}$ at pH 4.6 for Cr(III), at 20°C. These results are comparable with other agricultural waste materials. Temperature dependent studies indicated an increased Cr(VI) removal with increasing temperature.

Time-dependent adsorption data of Cr(VI) and Cr(III) on GLSC were fitted to the Lagergren equation. The kinetic evaluation was made on the basis of total-chromium removal. Values of k_{ads} of 0.037 and 0.018 min^{-1} were obtained for Cr(VI) and Cr(III), respectively, and are comparable or higher than for other biomaterials.

In conclusion, at pH$\approx$1, GLSC have the advantage of converting Cr(VI) to the less toxic Cr(III)-which can be further removed at pH 4.6-, and can potentially be used for the removal of chromium from wastewaters through a cost-effective and environmentally friendly process.

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