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Removal of Hexavalent Chromium with a Lignocellulosic Substrate Extracted from Wheat Bran

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In this paper, a new recovery system of the toxic hexavalent chromium Cr(VI) is proposed that uses a lignocellulosic substrate derived from the industrial treatment process of wheat bran. We studied the adsorption mechanism of Cr(VI) onto the lignocellulosic substrate and showed that the adsorption reaction consumes a large amount of protons goes along the reduction of Cr(VI) into Cr(III). The oxidation of lignin moieties takes place concurrently to the chromium reduction and leads to the formation of hydroxyl and carboxyl functions. The latter contribute to an increase in the number of ion-exchange sites for the reduced chromium. The maximum adsorption capacity for hexavalent chromium was found at about 35 mg g⁻¹ in an acidic medium. This is comparable to other natural substrates and ordinary adsorbents.

Introduction

Hexavalent chromium species are strong oxidants that act as carcinogens, mutagens, and teratogens in biological systems. Hexavalent chromium exists in water as oxyanions such as chromate (HCrO₄⁻) and dichromate (Cr₂O₇²⁻). Its speciation is dependent on the pH. It causes diseases such as epigastric pain nausea, vomiting, severe diarrhea, and hemorrhage by ingestion. The maximum allowed contaminant drinking level for the drinking water is 0.05 mg L⁻¹ (1).

Chromium(VI) is used in various industries including metallurgy, leather tanning, and electroplating. It is also used as a control agent for corrosion. Therefore, such ions can be a major pollutant of the wastewaters rejected by these industries. Because of this extensive use of chromium, the contamination of groundwaters is unfortunately unavoidable. Among available conventional processes used to remove hexavalent chromium, the most commonly used are reduction and precipitation as chromium hydroxide (2) or ion exchange (3). However, these methods suffer from some disadvantages due to their relatively high operational costs. There is therefore a need for the developments of cheaper alternative technologies that can be used as complement to the usual methods mentioned above.

Adsorption processes were studied and emerged as one of the most promising techniques (4). This process can be a potential alternative to the usual treatments of waters and wastewaters in order to reduce the metal content to the levels established by the legislation. Nevertheless, the sorbent must also be cheap and have a high biodegradability to render the cleanup process suitable and competitive. Several inexpensive sorbents have been tested in the removal of hexavalent

chromium. These sorbents can be biomaterials from agriculture such as condensed tannin gel (5), grape stalk (6), sphagnum moss peat (7), coconut-shell-based activated carbon (8); natural material such as sawdust (9); or industrial waste materials such as red mud (10) and steel wool (11). All these materials showed interesting capacity for hexavalent chromium recovery. In our local context, which can be widely extended, we studied the retention properties of a lignocellulosic substrate (LCS) toward hexavalent chromium. This material constitutes a byproduct of the industrial process of the wheat bran treatment, which leads to the extraction of cosmetic biomolecules. This process generates the LCS compound in very high quantities. Nowadays, LCS has no real potential application, which constitutes a serious handicap for the profitability of the industrial wheat bran treatment. Previous characterizations (12) have revealed that the lignocellulosic substrate is constituted by lignin and cellulose as its major constituents and a nonnegligible proportion (although not quantified) of fatty acid. Lignin and fatty acids bear functional groups such as alcohol, ketone, and carboxylic groups that can be involved in complexation reactions with metallic cations. In a previous work, we reported the study of the retention properties of this material toward copper and lead ions (13, 14).

This paper examines the adsorption of hexavalent chromium from aqueous solutions by a LCS in order to understand the mechanisms that govern hexavalent chromium removal by natural materials. We report here the influence of the pH and analytical concentration of hexavalent chromium on the adsorption. Moreover, in addition to the macroscopic Cr(VI) sorption studies, we used extended X-ray absorption fine structure (EXAFS) spectroscopy to characterize the structure of the sorption complex formed on LCS.

Materials and Methods

Materials. All the reagents used were of the highest available purity (Aldrich and Fluka). Standard solutions of hexavalent chromium were prepared using potassium dichromate (K₂Cr₂O₇).

Sample Preparation. Agro Industrie Recherche Développement (ARD) provided the wheat bran used in this study. The air-dried, coarsely powdered wheat bran (30 g) was subjected to two successive treatments without light protection: (i) acid hydrolysis by 2 mol L⁻¹ H₂SO₄ (1:1 w/w dry matter, at 100 °C for 30 min) to remove starch, proteins, and sugars; and (ii) alkali treatment by 0.5 mol L⁻¹ NaOH (5:1 ratio of bran/sodium hydroxide, stirring for 24 h at room temperature) to remove the low molecular weight lignin compounds after filtration. The solid was then stirred with 0.04 mol L⁻¹ HNO₃ during 4 h in order to protonate all acid sites and was washed with deionized water until the pH reached a constant value close to neutrality. The protonation of all acid sites was checked by potentiometric titrations (13). After these treatments, the material was dried under vacuum, ground to a powder, and sieved at 400 μm.

IR, ¹³C-CP/MAS NMR spectroscopies and XPS led us to identify carboxylic and phenolic moieties as the main functional groups (12, 13). The content of acidic surface sites was estimated using ion-exchange reactions and potentiometric titrations in aqueous and nonaqueous media. We determined a concentration of 0.6 and 0.4 mmol g⁻¹ for carboxylic and phenolic moieties, respectively.

Experimental Procedure of Cr(VI) Removal. The adsorption equilibrium experiments of chromium were conducted to determine the adsorption capacity of Cr(VI) under a given set of conditions. Chromium sorption experiments

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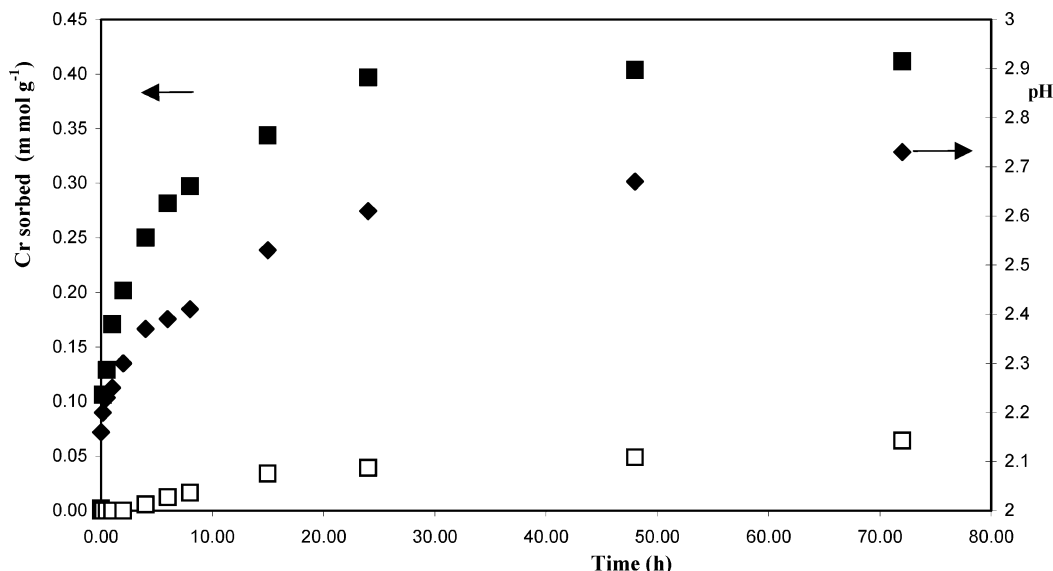


FIGURE 1. Effect of time on the adsorption of hexavalent chromium. $[LS] = 8 \text{ g L}^{-1}$; $[Cr(VI)] = 4 \times 10^{-4} \text{ mol L}^{-1}$; (■) sorbed chromium; (□) soluble trivalent chromium; (◆) pH variation.

were performed according to the batch method. The solid was equilibrated during at least 3 h in NaNO_3 solution (0.1 mol L^{-1}) to achieve a complete hydration of the surface groups. The suspensions were then adjusted to the required pH and chromium concentration values and magnetically stirred at room temperature for 24 h (except for kinetic experiments). The LCS particles were separated from the solutions by filtration with a $0.2\text{-}\mu\text{m}$ Millipore filter. The solution pH was continuously monitored during the experiments.

The solutions were analyzed for hexavalent and total chromium. Hexavalent chromium (Cr(VI)) was detected by the diphenyl carbazide method (15): 1,5-diphenyl carbazide forms a pink complex in the presence of Cr(VI) ions in acidic solutions. The concentration of Cr(VI) was calculated from the absorbance at 542 nm using a UV-visible spectrophotometer. Total chromium (Cr(III) and Cr(VI)) was determined by an inductively coupled plasma spectrometer (ICP-AES, Varian Liberty II). The difference in concentration between total and hexavalent chromium was taken as the concentration of trivalent chromium. The ICP-AES measurements were compared to the measurements made with the Cr(VI) -diphenylcarbrazide method on Etalon samples. Analytical measurements made by the two techniques were always comparable within 5%.

Spectroscopic Characterizations. *IR Spectroscopy.* Infrared spectra were recorded on KBr pellets on a FTIR Spectrometer System from MIDAC Corporation.

X-ray Photoelectron Spectroscopy. XPS was used to characterize the surface chemistry of the LCS. Information was thus obtained on the elemental composition and the functional groups of the surface to a depth of about 0.1–1 nm. XPS spectra were recorded on a VSM-hemispheric spectrometer with a $\text{Mg K}\alpha$ incident X-ray beam. The X-ray source was run at 100 W, and the spectra were recorded at 15 kV. The analyzer chamber pressure was in the 1×10^{-7} – 1×10^{-10} Torr range. The powdered samples were mounted on double-sided carbon tapes. Binding energies were calibrated by assuming 284.6 eV for the C–C component of the C_{1s} line. The elemental composition was estimated using the area of C_{1s} and O_{1s} peaks corrected with their sensitivity factors given in Scofield table. Analysis of sorbed chromium oxidation state was deduced by comparing experimental spectra with those of trivalent (Cr_2O_3) and hexavalent (CrO_3) chromium references.

EXAFS Spectroscopy. (a) *Data Collection.* The EXAFS spectra were collected at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE), Paris-Sud University, on the storage ring DCI with an energy of 1.85 GeV and a mean intensity of 300–200 mA. The measurements were carried out at chromium K-edge (5989 eV) in the fluorescence mode at the XAS-4 station. The monochromator used was a Si(111) channel cut, which was detuned to 50% of the maximal intensity to remove the higher-order harmonics. The detectors were low-pressure ($\approx 0.2 \text{ atm}$) air-filled ionization chambers. The spectra were the sum of 10 recordings in the 5840–7000 eV range, including the chromium K-edge ($\approx 5989 \text{ eV}$). The photon energy was calibrated from the spectrum of a chromium foil, assigning 5989 eV to the preedge peak. Spectra were recorded using sampling steps of 2 eV (EXAFS), and an integration time of 2.0 s per point was used.

EXAFS Spectra Analysis. The EXAFS data analysis was performed with the “EXAFS pour le Mac” and EXAFS98 programs (16). This standard EXAFS analysis (17) includes merging of scans, linear preedge background removal, polynomial atomic absorption calculation (of 5th order), Lengeler–Eisenberger EXAFS spectra normalization (18), and reduction from the absorption data $\mu(E)$ to the EXAFS spectrum $X(k)$. Radial distribution functions $F(R)$ were calculated by Fourier transforms of $k^3 w(k) \mu(k)$ in the range of 2–13 \AA^{-1} ; $w(k)$ is a Kaiser–Bessel apodization window with a smoothness coefficient $\tau = 2.5$. Interatomic distances (R), number of coordinated atoms (N), and Debye–Waller factor (σ) were evaluated by least-squares fitting Fourier-filtered EXAFS spectra using the standard EXAFS formula without multiple scattering:

$$\chi(k) = S_0^2 \sum_i \left[\frac{N_i}{R_i^2} A_i(k) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)} \sin(2kR_i + \Phi_i(k)) \right]$$

Experimental phase, $\Phi_i(k)$, and amplitude, $A_i(k)$, functions for Cr–O atomic pairs have been extracted from the model compounds $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and $\text{Cr}(\text{acac})_3$.

Results and Discussion

Kinetic Studies. The effect of time on adsorption of Cr(VI) was first investigated and is shown in Figure 1, which indicates that the process is rather quick. Nearly 50% of the adsorption

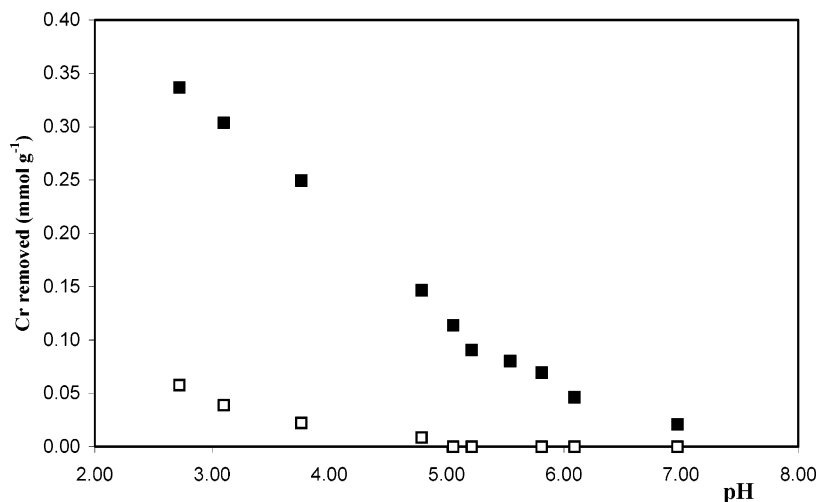


FIGURE 2. pH effect on the sorption and reduction of hexavalent chromium. $[LS] = 8 \text{ g L}^{-1}$; $[Cr(VI)] = 4 \times 10^{-4} \text{ mol L}^{-1}$; (■) sorbed chromium; (□) soluble trivalent chromium.

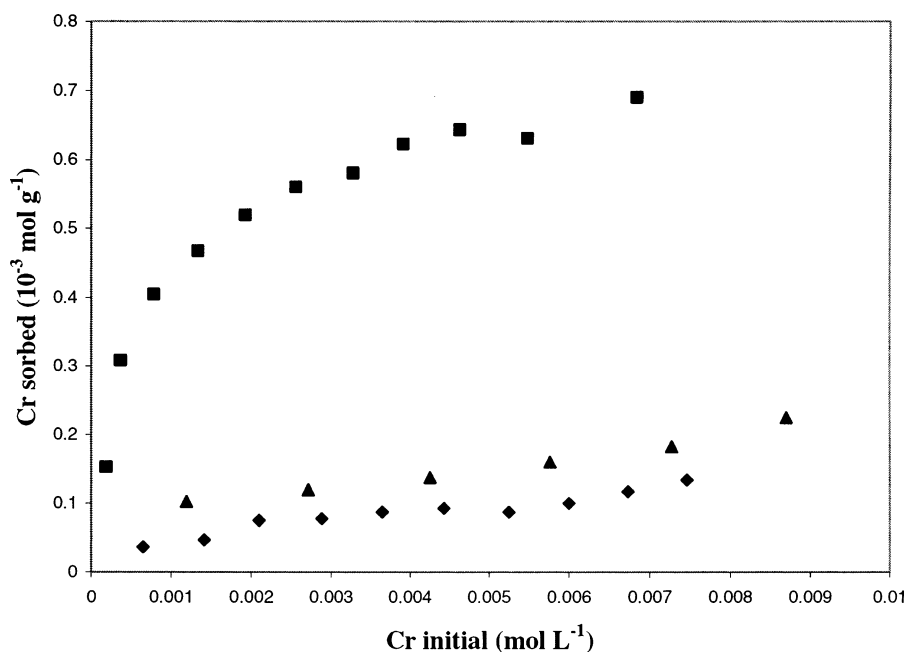


FIGURE 3. Cr(VI) adsorption isotherms on LCS at two HNO_3 concentrations. $[LS] = 4 \text{ g L}^{-1}$; (■) $C_{HNO_3} = 8 \times 10^{-3} \text{ mol L}^{-1}$ (pH 2.1); (▲) $C_{HNO_3} = 8 \times 10^{-4} \text{ mol L}^{-1}$ (pH 3.1); (◆) without HNO_3 .

capacity was reached within 4 h. The initial rapid adsorption gives way to a very slow rate of approach to the equilibrium, and saturation is reached only after 24 h. Beyond 15 h, the concentration of trivalent chromium increases in the solution, which indicates that the removal of hexavalent chromium proceeds according to a redox process. The pH variations reported in Figure 1 also show that the adsorption reaction of hexavalent chromium consumes protons.

pH Dependence of Chromium Removal. The pH of the aqueous solutions is an important controlling parameter in the heavy metal adsorption processes. Its role on the removal of hexavalent chromium was studied by varying the initial concentration of nitric acid in the suspension. Figure 2 demonstrates that the conversion of Cr(VI) mainly depends on the proton concentration. The higher the proton concentration, the higher the efficiency of the Cr(VI) conversion. Such a dependence was already observed with anionic materials (5,7) as well as on the amphoteric substrate (19), such as ferrous oxide. It has been explained both 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 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.

Influence of Analytical Chromium Concentration. Figure 3 shows typical adsorption isotherms for the chromium LCS system. It is generally observed that the adsorption density, which corresponds to the concentration of chromium removed ($10^{-3} \text{ mol g}^{-1}$) increases when the pH of the solution decreases. Isotherm data have been used to calculate the maximal sorption capacity of the lignocellulosic substrate by substituting the required equilibrium concentration in the Langmuir equation. The Langmuir isotherm is expressed by

$$\frac{C_e}{C_s} = \frac{C_e}{C_s^{\max}} + \frac{1}{C_s^{\max}b} \quad \text{with } C_s = K_d C_e$$

where K_d is the distribution coefficient that characterizes the

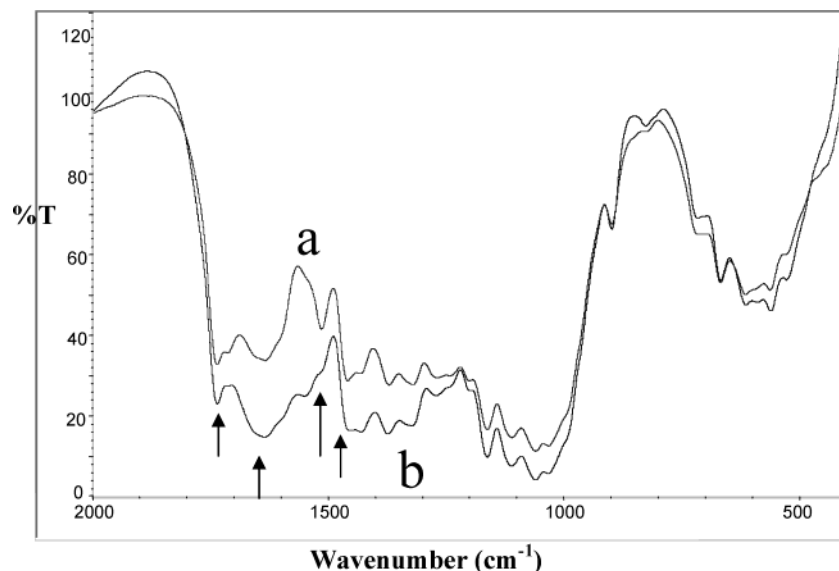


FIGURE 4. IR spectra of untreated LCS (a) and LCS contacted 24 h with acidic containing Cr(VI) solution (b). The arrows indicate the main modifications induced by the adsorption of hexavalent chromium.

TABLE 1. Isotherm Parameters for Hexavalent Chromium Sorbed onto LCS

C_{HNO_3}	C_s^{max} (mmol g ⁻¹)	b (g L ⁻¹)	r^2
8×10^{-3}	0.72	6.7	0.99
8×10^{-4}	0.19	3.2	0.97
	0.16	2.6	0.99

affinity of the metal for the sorbent, C_s^{max} is the maximum adsorption capacity of the solid, C_e is the concentration in the equilibrium solution, C_s is the measured sorption per unit weight of solid, and b represents the Langmuir bonding term related to the energy of adsorption. Table 1 summarizes the Langmuir parameters of hexavalent chromium adsorption for different nitric acid concentrations. The retention capacity (about 0.72 mmol g⁻¹, i.e., 35 mg g⁻¹) of LCS toward hexavalent chromium in acidic medium compares well with those reported onto various natural substrates, which range from 15 to 60 mg of Cr/g, and commonly used adsorbent such as activated carbon and resin (about 50 mg of Cr/g of dry resin) (20). The very low cost of lignocellulosic materials is a real advantage that renders it a suitable alternative for the cleanup of industrial effluents.

The retention capacity of hexavalent chromium in acidic media is unexpectedly high if we compare this result with those obtained previously in the case of copper and lead ions on the same materials (14). This is a strong piece of evidence in supporting that the adsorption of hexavalent chromium yields to the creation of new ion-exchange sites through a redox process.

Adsorption isotherms have been monitored onto pure cellulose and pure lignin under similar conditions of pH and analytical chromium concentrations. No significant sorption has been observed onto cellulose even in acidic medium. For lignin, an extensive conversion of hexavalent Cr was observed although not quantified because of the high solubility of this substrate in our conditions. These observations clearly demonstrate that the adsorption reaction of hexavalent chromium onto lignocellulosic substrate involves lignin moieties.

Infrared Spectroscopy. Figure 4 shows the infrared spectra of the virgin lignocellulosic substrate and the lignocellulosic particles contacted with the acidic Cr(VI) solutions. The most prominent peaks in the untreated material were attributed

to lignin components: guaiacyl (1030, 1160, 1230, and 1270 cm⁻¹) and syringyl units (1110 and 1320 cm⁻¹). The bands at 1460 and 1510 cm⁻¹ were attributed to methoxy deformation and to vibration of aromatic skeleton, respectively (21). The bands at 900, 1060, and 1380 cm⁻¹ were characteristics of carbohydrate units (22). The band at 1740 cm⁻¹ was attributed to the stretching vibration of free carbonyl from carboxylic groups, whereas the shoulder at 1710 cm⁻¹ suggests the possibility of intermolecular associations of carboxylic functions (23). The relatively large bands at 1637 cm⁻¹ can be confidently attributed to the stretching vibration of carboxylate anion.

The adsorption of Cr(VI) induces some substantial modifications of the IR spectrum. The suppression of the peaks located at 1460, 1510, and 1710 cm⁻¹ and the decrease of the ratio of the COOH and COO⁻ groups intensities can be observed. This decrease was already observed in the case of copper ions, and the coordination of the latter with carboxylate moieties was underlined by XAS spectroscopy (24). Our results obtained by IR spectroscopy suggest that hexavalent chromium induces an oxidation of only lignin components and that the retention of Cr ions occurs through a complexation reaction involving carboxylate moieties (lignin and fatty acids). Moreover, the bands at 900, 1060, and 1380 cm⁻¹ that are characteristic of carbohydrate units remain unaltered by the adsorption of hexavalent chromium. Fatty acids are characterized in the IR spectrum (not shown here) by two aliphatic vibrations at 2920 and 2850 cm⁻¹. These two bands are not affected by the sorption of hexavalent chromium.

X-ray Photoelectron Spectroscopy. The XPS survey spectrum of LCS consists of two major elements: carbon and oxygen. The presence of sorbed chromium has been detected on LCS after chromium sorption, and the Cr_{2p} peaks have been analyzed. It consists of two contributions corresponding respectively to 2p^{1/2} and 2p^{3/2} energy levels. Quantification of chromium sorbed was possible only with the sample containing a high level of sorbed metal, and the error was estimated within 10%. The C_{1s} peak has been deconvoluted considering three components and a constant half-width peak at 2.0 eV. Due to similarities of the O_{1s} chemical shifts, which brought up difficulties in estimating their relative intensities, the discussion in this section will focus on the relative intensities of C_{1s} peak components as well as on the O/C ratio (Table 2).

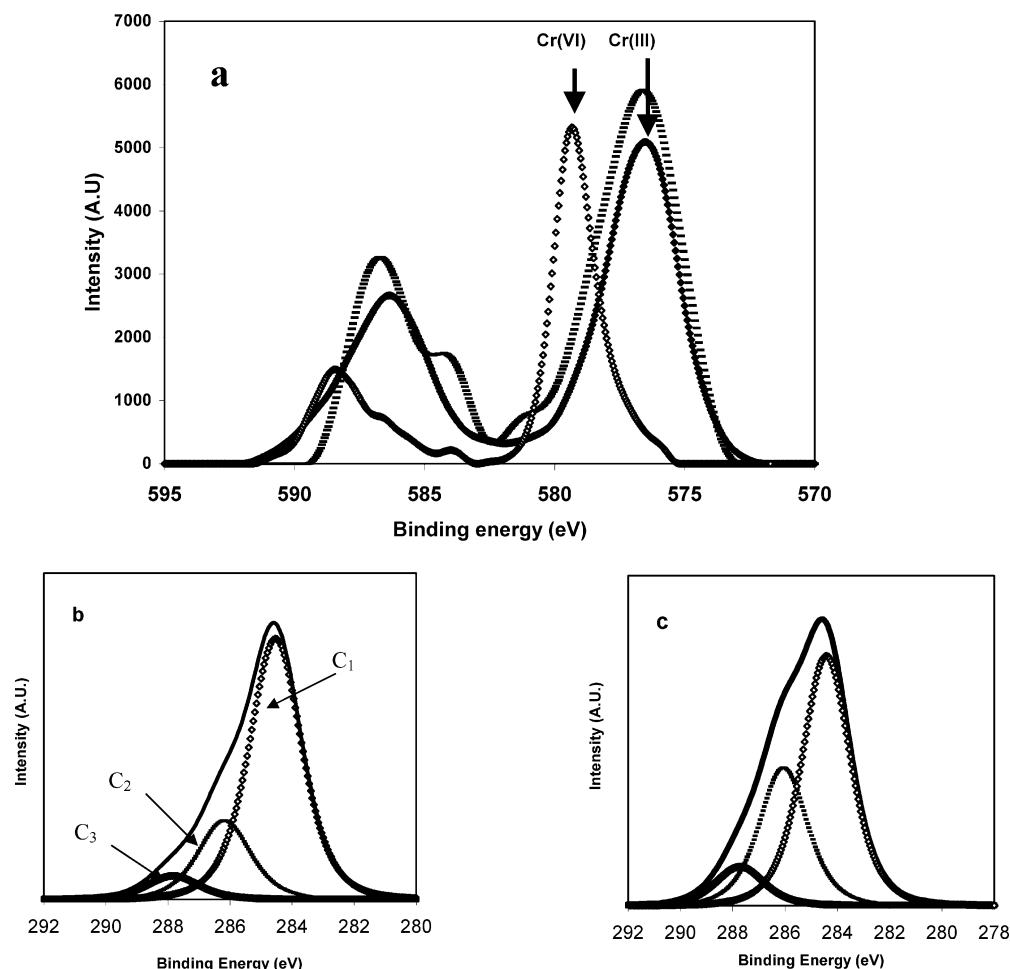


FIGURE 5. XPS spectra of LCS: (a) Cr_{2p} signals of Cr–LCS system (—), Cr^{III}O₃ (◆), Cr^{VI}O₃ (◇); (b) C_{1s} signal of untreated LCS; (c) C_{1s} signal of LCS contacted 24 h with acidic-containing Cr(VI) solution. The continuous line represents the superimposition of experimental and fitted curve.

TABLE 2. XPS Data for Untreated LCS and Contacted 24 h with Acidic-Containing Cr(VI) Solution at Two Concentrations

peak	BE (eV)	LS		LS–Cr(VI) (6 mmol L ^{–1})		LS–Cr(VI) (10 mmol L ^{–1})	
		elemental composition	area (%)	elemental composition	area (%)	elemental composition	area (%)
C ₁	284.6		71.8		65.6		58.5
C ₂ (1s)	286.4	0.76	21.7	0.70	27.2	0.66	32.3
C ₃	288.2		6.4		7.2		9.1
O (1s)	531.0	0.24		0.29		0.33	
Cr (2p)	580.1			0.30		0.40	
	589.5						
O/C		0.32		0.42		0.50	

The three components of the C_{1s} peak (Figure 5b,c) can be assigned to three different classes of carbon atoms present in cellulose and lignin: the C₁ peak corresponds to a carbon atom bound to an hydrogen atom or to another carbon atom, C–H or C–C bonds; the C₂ peak corresponds to a carbon atom singly bound to an oxygen atom, C–O; and the C₃ peak corresponds to a carbon atom doubly bound to an oxygen atom, C=O, or to two oxygen atoms, O–C–O (13). Comparison of XPS spectra with those of pure lignin and pure cellulose coupled with pyrolysis studies (12) have previously shown that the relatively high content of C₁ carbon type can be confidently attributed to the presence of fatty acid, although no quantification was possible.

Analysis of Chromium Reduction by XPS. To facilitate the XPS spectra intensity comparison of Cr_{2p} peaks of

chromium sorbed onto LCS, they were normalized. The XPS spectrum (Figure 5a) of Cr-treated LCS reveals an extensive reduction of hexavalent chromium sorbed onto LCS to its trivalent form. Indeed, the two contributions of Cr_{2p} peaks of chromium sorbed are at 576.3 and 587 eV. These values compare well with the binding energy of Cr(III) in Cr₂O₃ at 576.3 and 586.2 eV but are significantly distinct from the binding energy of Cr(VI) in CrO₃ that are at 579.3 and 588.3 eV. The slight difference between the Cr 2p_{1/2} peaks (586.2 and 587 eV) is attributed to different chemical environments. Indeed, in Cr₂O₃, the chromium atoms are bound to oxygen atoms by a double bond, whereas in Cr–LCS it is likely that chromium is bound to oxygen with a single bond (25). Only small shoulders, which appear on both Cr_{2p} peaks at 580.8 and 584 eV seem to indicate that it can subsist some trace of hexavalent chromium and that reduction is not still complete. The presence of trivalent chromium onto lignocellulosic substrate was also checked by ESR.

Analysis of Surface Functional Modifications by XPS.

Table 2 shows the chemical modifications of LCS induced by the conversion of hexavalent chromium. The increase of the O/C ratio is attributed to the conversion of C₁ into C₂ and C₃ carbon types. In agreement with IR analysis, this can be explained by the oxidation of lignin aromatic carbons. Indeed, oxidized functions, especially alcoholic and carboxylic sites, have been generated. This interpretation is supported by the studies of Pizzi (26) and Ostmeier and Elder (27), which propose that the preservation of wood components by chromate copper arsenate treatments involves the formation of chromate ester moieties. Chromate ester moieties would

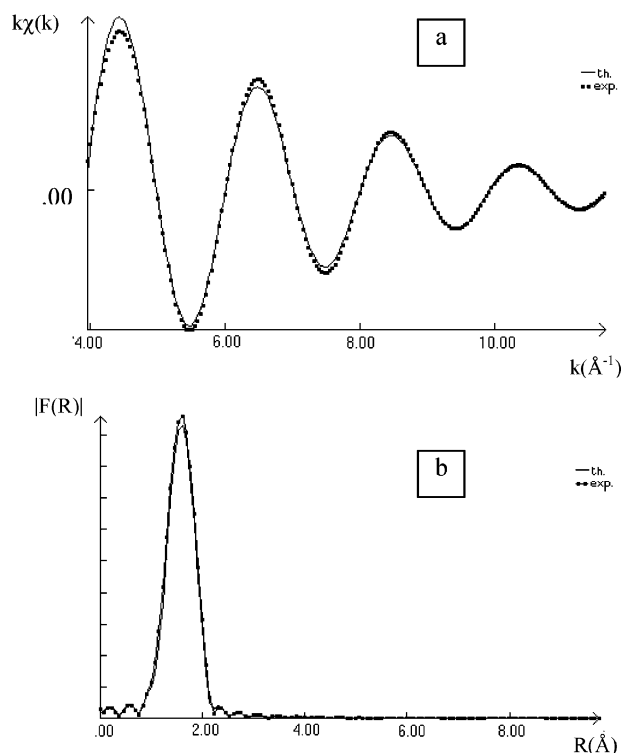


FIGURE 6. (a) First-shell fit of the EXAFS function of Cr(III)-LCS system. Experimental first-shell filtered data in the 1.01–2.11-Å range (dotted line), and best fit (solid curve) modeled as Cr–O contributions. Experimental phase and amplitude functions were extracted from the EXAFS spectrum of the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ reference compound. (b) Radial structure function (RSF) of the first shell and its numerical simulation. RSF is not phase-shift corrected.

be formed by covalent bonding of CrO_4^{2-} ions with carbon or with hydroxy and methoxy groups of lignin fraction phenylpropane units aromatic nuclei.

The increase of carboxylic function content can be easily related to the increase in the retention capacity of LCS. In a previous work (13), we estimated from XPS and potentiometric titrations that 38% of C_3 carbon type (e.g., 2.4% of total carbon) is carboxylic moieties. In this case, the increase of C_3 carbon content from 6.4 to 9.1% corresponds to the formation of 0.7 mmol g^{-1} of carboxylic functions by reaction with hexavalent chromium. We can therefore link together the increase in LCS retention capacity to the increase in carboxylic moieties content (both are multiplied by a factor of 2).

XAS Study of Cr(III)–LS System after Cr(VI) Reduction.

XAS is used in order to obtain information on the local environment of the chromium, with the aim of characterizing the surface sites of LCS involved in the chromium complexation. The dried Cr(III)–LCS compound was obtained after Cr(VI) treatment ($\text{K}_2\text{Cr}_2\text{O}_7$, $6 \times 10^{-3} \text{ mol L}^{-1}$) of LCS (4 g L^{-1}) at pH around 2 (HNO_3 , $8 \times 10^{-3} \text{ mol L}^{-1}$). The amount of trivalent chromium thus sorbed onto LCS was equal to $7 \times 10^{-4} \text{ mol L}^{-1}$. The k^3 -weighted EXAFS, the corresponding Fourier transform, and the fitted curves of the filtered first shell of the Cr(III)–LS system are shown in Figure 6. Adsorption is collected to $k = 11.7 \text{ Å}$, resulting in a good resolution of peaks in the Fourier transform. The k^3 -weighted and phase-corrected Fourier transform function gave a main peak at 1.65 Å , which arises from first-shell oxygen back-scattering. The absence of a significant peak around 2.60 Å allows us to exclude the formation of chromium polynuclear species (28, 29), which indicates that chromium complexes are isolated species. Using the single-scattering approach by fitting the filtered first shell signal, quantitative EXAFS results

were obtained. The chromium ion is surrounded by six oxygen atoms ($N = 6.05$) at an average Cr–O bond distance of $r = 2.04 \pm 0.02 \text{ Å}$, with a relative Debye–Waller factor σ equal to 0.024 Å . These data seem to indicate a coordination through carboxylate functional groups of LS and thus that chromium ions are held in inner-sphere complexes. Indeed, these results are in good agreement with those obtained for chromium complexes through X-ray crystallography with carboxylic ligands (30, 31) in which Cr–O (COOH) distances were equal to 1.99 and 2.00 Å . On the other hand, Cr–O bond distances, which involve phenolic moieties were equal to $1.91\text{--}1.95 \text{ Å}$ (30, 32), are less probable. Previous results obtained by IR and XPS spectroscopies are confirmed by XAS studies about involvement of carboxylic moieties in chromium complexation.

These studies show that the lignocellulosic substrate is an efficient adsorbent for chromium(VI) removal from aqueous solutions, owing to its very low cost and its relatively interesting sorption capacity. The process, which is a function of the pH and the concentration of the analytical hexavalent chromium, is enhanced by redox processes. Sorption capacity of the lignocellulosic substrate could be related to the abundance of lignin and fatty acid moieties, which allow the reduction of hexavalent chromium into trivalent one as well as the fixation of Cr(III) on carboxylic moieties. Further experiments are in progress in order to validate the efficiency of this material in the cleanup of real industrial effluents. These results may be of value in developing sound remediation strategies for water contaminated with toxic first-row transition metals.

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