REMOVAL OF CHROMIUM (VI) IN AQUEOUS ENVIRONMENTS USING CORK AND HEAT-TREATED CORK SAMPLES FROM *QUERCUS CERRIS* AND *QUERCUS SUBER*

Ali Şen,[a] M. Àngels Olivella,[b] Nuria Fiol,[b] Isabel Miranda,[a] Isabel Villaescusa,[b] and Helena Pereira [a,]*

Chromium (VI) removal and its reduction to chromium (III) from aqueous solution by untreated and heat-treated *Quercus cerris* and heat-treated *Quercus suber* black agglomerate cork granules was investigated. Initial screening studies revealed that among the sorbents tested, untreated *Q. cerris* and *Q. suber* black agglomerate are the most efficient in the removal of Cr(VI) ions and were selected for adsorption essays. Heat treatment adversely affected chromium adsorption and chromium (VI) reduction in *Q. cerris* cork. The highest metal uptake was found at pH 3.0 for *Q. cerris* and pH 2.0 for black agglomerate. The experimental data fitted the Langmuir model and the calculated q_{max} was 22.98 mg/g in black agglomerate and 21.69 mg/g in untreated *Q. cerris* cork. The FTIR results indicated that while in black agglomerate, lignin is the sole component responsible for Cr(VI) sorption, and in untreated *Q. cerris* cork, suberin and polysaccharides also play a significant role on the sorption. The SEM-EDX results imply that chromium has a homogenous distribution within both cork granules. Also, phloemic residues in *Q. cerris* granules showed higher chromium concentration. The results obtained in this study show that untreated *Q. cerris* and black agglomerate cork granules can be an effective and economical alternative to more costly materials for the treatment of liquid wastes containing chromium.

Keywords: Cork; Quercus cerris; Quercus suber; Black Agglomerate; Biosorbent; Chromium; Heat treatment

*Contact information: a: Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade Técnica de Lisboa, Tapada da Ajuda, 1349-017, Lisbon, Portugal; b: Department of Chemical Engineering, Escola Politècnica Superior, University of Girona, Avda Lluis Santaló , s/n 17071, Girona, Spain. *Corresponding author: hpereira@isa.utl.pt*

INTRODUCTION

Chromium-polluted wastewaters include those from industries of dyes and pigments, film and photography, galvanometry, metal cleaning, plating and electroplating, leather, and mining. Chromium is found in hexavalent and trivalent forms in the industrial wastewaters. The hexavalent form is of particular concern because of its greater toxicity. Unlike other toxic pollutants, metals are not biodegradable and can accumulate in living tissues, causing various diseases and disorders in a variety of living species.

Conventional methods for removing metals from industrial effluents are chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange, and adsorption (Villaescusa *et al.* 2004). The industrial practices for chromium removal such as stabilization ponds are only slightly efficient (Üstün 2009). For the adsorption methods, mostly activated carbon and different types of ion-exchange resins are applied. However, the high capital and regeneration costs of these materials limit their large-scale use for the removal of metals. In recent years, studies have focused on finding new low-cost sorbing materials, including many of lignocellulosic nature. A recent review has been made on the cellulosic substrates that have been researched for the removal of metals in aqueous systems (Hubbe *et al.* 2011).

Tree barks have been considered for this purpose, such as pine, Douglas fir, eucalypts, teak (Sarin and Pant 2006; Oh and Tshabalala 2007; Kehinde *et al.* 2009; Jauberty *et al.* 2011), as well as cork (Villaescusa *et al.*, 2002). Cork is one important bark component in some species, namely in cork oak (*Quercus suber*). Because of its unique anatomical and chemical properties, cork is a polyvalent material and a valuable industrial raw material with numerous usage possibilities, the most important being cork stoppers production.

Cork was tested for adsorption of heavy metals in aqueous solutions such as Cu(II), Ni(II), and Zn(II), but the adsorption capacity was found to be lower than that of other lignocellulosic materials (Chubar *et al.* 2004a). However, cork has properties that may be interesting for wastewater treatments, *i.e.* low density and floatability. The important metal binding sites are carboxylic groups, and the adsorption capacity can be increased by pre-treatments such as thermal activation (Chubar *et al.* 2004b).

Heating treatments can significantly change the chemical and anatomical composition of cork. Extractives and hemicelluloses degrade in early phases of heating, while the heat-treated samples increase their suberin and lignin ratios in relation to untreated cork (Pereira 2007). One commercial example of heat-treated cork is the expanded or black cork agglomerates that are used for insulation purposes.

One important aspect of economical and ecological relevance in the use of biological materials is to make a close-to-source material selection. This is the approach taken here regarding chromium contamination that was found at high concentrations in industrial wastewaters in Turkey (Yılmaz *et al.* 2010) by studying the adsorption potential of a local bark source, that of the Turkey oak (*Quercus cerris*).

Turkey oak grows naturally in central and south-eastern Europe and Asia Minor, and its thick bark contains substantial, albeit not continuous, regions of cork. The investigations on *Q. cerris* cork showed that it has similar chemical and anatomical characteristics with those of *Q. suber*, including the response to heating treatments (Şen *et al.* 2012a). These findings triggered the interest to find application areas, including adsorption (Olivella *et al.*, 2011) to *Q. cerris* cork, which is currently unused in Turkey

In the present study, chromium (VI) adsorption was investigated for the first time on heat-treated and untreated cork granules obtained from *Q. cerris* bark and on commercial black agglomerate produced from *Q. suber* cork. The study involved: a) chemical characterisation of the adsorbents *i.e.* elemental analysis and atomic ratios; b) screening of adsorption through a selected pH range; c) determination of adsorption kinetics and adsorption isotherms; d) determination of Cr(VI) reduction capacity of selected granules; e) analysis of functional groups involved in adsorption through FT-IR spectroscopy; and f) microscopic characterization by SEM.

EXPERIMENTAL PROCEDURE

Preparation of Adsorbents

Cork granules were extracted from the bark of mature, 70- to 80-year-old *Q. cerris* trees from southeastern Turkey. The bark samples were granulated with an industry-type hammer and sieved with a Retsch Analytical Sieve Shaker AS 200. The granulometric fraction over 2 mm was fractionated by suspending cork granules (floating layer) from the phloem (sedimenting material) in water for a short time. Cork samples were dried at 60°C for 3 days and inspected visually to separate any conspicuous residual phloem particles. Then, samples were submitted to different thermal treatments.

The heat-treated samples of *Q. cerris* cork were prepared by submitting 2 g samples to four different isothermal heating treatments (200°C, 250°C, 300°C, and 350°C) in a temperature controlled furnace (Heraeus MR 170 E) for 20 min. An untreated sample (coded UN) was also used.

A cork black granulate (BA) was obtained by granulating a commercial insulation cork board (ICB) sample. This board is produced from cork granulates of *Quercus suber* that are treated in an autoclave with 300ºC superheated steam during 20 min (Pereira, 2007). The resulting granules were sieved to a 40-60 mesh size to be used in adsorption tests. Cork samples used in this study are detailed in Table 1.

Table 1. Treatments and Codification of the Sorbents

Sample	Treatment type	Code
Q. cerris cork (QC)	Untreated	UN
	200°C treated	200°C
	250°C treated	250°C
	300°C treated	300°C
	350°C treated	350°C
Q. suber cork from commercial black agglomerate (QS)	Over 300°C steam-heated	BA

Elemental Characterization of the Adsorbents

The C, H, N, and S contents of the cork samples were determined using a Perkin Elmer EA2400 series II Elemental Analyzer. Limits of detection for N and S were 1.20% and 0.44%, respectively. Oxygen content was calculated by the difference. The H/C, O/C, C/N, and (O + N)/C atomic ratios were also calculated.

Batch Equilibrium Studies

Hexavalent chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate ($K_2Cr_2O_7$) in distilled water. A 0.1 M HCl solution was used for initial pH adjustment. All reagents were analytical grade and were purchased from Panreac (Barcelona, Spain). Chromium standard 1.000 mg/L solutions from Merck (Damstadt, Germany) were used for flame atomic absorption (FAAS) calibrations.

Adsorption screening

Adsorption screening was applied to compare chromium (VI) adsorption features of untreated and heat-treated *Quercus cerris* cork (QC) granules and black agglomerate (BA) granules (*Quercus suber*, QS). Experiments within a selected 1.0 to 5.0 initial pH range were carried out to determine the influence of initial pH on performance of the six sorbents. In these experiments, 15 mL of 25 mg/L Cr(VI) solutions were put into contact with 0.1 g of sorbents (particle size 0.25 to 0.42 mm) in glass tapered tubes and agitated at 30 rpm on a rotary shaker for 24 hours (Rotator STR4, Stuart Scientific Bibby) at room temperature (20 ± 2 °C).

Chromium (VI) adsorption experiments

Untreated (UN) and black agglomerate (BA) samples were selected after adsorption screening, since maximum chromium adsorption was obtained with these samples. Batch experiments were conducted on UN and BA samples at 20 ± 2 °C in stoppered glass tubes by agitating a 0.1 g sample with 15 mL of 25 mg/L chromium(VI) solution in a rotary mixer at 30 rpm. After agitation, the sorbents were removed by filtration through a 0.45 µm cellulose paper (Millipore Corporation). The total chromium concentration, *i.e.*, Cr(VI) + Cr(III), in filtrates was determined by flame atomic absorption spectrometry using a Varian Spectrometer (Model 220FS). Control experiments (blank) were conducted under the same experimental conditions using deionized water. In all sets of experiments, each test was carried out in duplicate and the average results are presented.

The initial solution pH was 2.0 and 3.0 when BA and UN samples were used respectively. No efforts were made to maintain the solution pH during the adsorption process. The adsorbed metal concentration was obtained from the difference between initial and final metal concentration in solution. The pH variation during the sorption process was monitored using a pH meter (Crison Model Digilab 517).

In order to obtain the sorption isotherms, the time necessary for the system to reach equilibrium was determined. For this purpose, kinetics experiments were performed by putting each of the two sorbents into contact with a 25 mg/L Cr(VI) solution for different times within the range 0 to 96 hours.

For isotherm experiments initial Cr(VI) concentrations were 25, 50, 100, 200, 300, 500, 750, and 1000 mg/L, respectively, and the agitation time was 48 h. The following equation was used to compute the specific uptake by the sorbent, q (mg/g of dry solid):

$$q = (Ci - Cf) \times V \div w \tag{1}$$

where Ci and Cf are initial and final (equilibrium) concentration, V (L) is the solution volume, and w (g) is the mass of dry sorbent used.

Point of Zero Charge (PZC) test

The point of zero charge (pH_{pzc}) was determined in UN and BA samples by mass titration following the procedure described by Fiol and Villaescusa (2009). Different masses of sorbent materials within the concentration range 20 to 90 g/L were put into contact with a 0.03 M KNO_3 solution. The aqueous suspensions were shaken for 24 h in a shaker at 200 rpm until pH equilibrium was reached. The pH_{pzc} is the pH at which a plateau is achieved when plotting equilibrium pH versus sorbent mass concentration.

Cr(VI) Reduction Assay

It is well demonstrated that, at acidic pH, Cr(VI) can be reduced to Cr(III) after contact with lignocellulosic materials, and the converted Cr(III) could be totally or partially released into the solution (Fiol *et al.* 2008; Park *et al.* 2008). Therefore, it is important to determine if reduction of Cr(VI) takes place when in contact with QC and BA sorbents to understand the mechanism of Cr(VI) removal when using these natural sorbents.

Total chromium and Cr(VI) in the liquid phase were quantified by using two different techniques: total chromium was analyzed by Flame Atomic Absorption Spectroscopy (FAAS) and Cr(VI) by the standard colorimetric 1,5-diphenylcarbazide method, in a spectrophotometer (Cecil, CE2021) (Clesceri *et al.* 1998). Cr(III) was calculated as the difference between total chromium and Cr(VI). The Cr(VI) standard solution used for obtaining the calibration curve in the diphenylcarbazide method was analysed by FAAS. Analytical measurements made by the two techniques were comparable within 5%.

Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared spectra (FTIR) were used to investigate changes in the functional groups of the adsorbents due to Cr(VI) adsorption. Elucidating the functional group involved in a sorption process is one of the key factors to understand the mechanism of metal binding by natural adsorbents. Each initial and each Cr(VI)-loaded adsorbent was mixed separately with spectroscopic grade KBr (Acros, New Jersey, U.S.A.) and made in the form of pellets. FTIR spectra were recorded on a Galaxy 5000 FTIR spectrometer (Mattson Instrument Co., Madison, WI). All FTIR spectra were measured in the 4000 to 400 cm^{-1} range by co-addition of 32 scans with a resolution of 4 cm^{-1}.

For FTIR analysis, UN and BA cork granules were loaded with 1000 mg/L of Cr(VI) solutions following the batch procedure described above. As a blank, the same procedure was made using Milli-Q water adjusted at pH 2.0 and pH 3.0 for BA and UN cork, respectively. The blank and the chromium loaded samples were dried until constant weight and kept in a desiccator until the moment of analysis.

Scanning Electronic Microscopic (SEM-EDX) Analysis

The same samples used for FTIR were used for SEM analysis. The granules were deposited on a double-sided carbon tape, and a layer of Au/Pd with approximately 450° A thickness was deposited using a Quorum Technologies E5100 (former Polaron) sputter coater. The samples were observed with a Hitachi S-2400 scanning electron microscope with a Bruker EDX (Energy Dispersive X-Ray Spectroscopy) detector attached using an acceleration voltage of 20 kV at magnifications of 50 to 1000x. The images were recorded in digital format.

RESULTS AND DISCUSSION

Elemental Composition of the Sorbents

The elemental composition of the sorbents is important to clarify the affinity of cork components to chromium. The results indicate that with heat treatment, the carbon ratio increases rapidly in QC samples from 48% (UN) to 64% (200°C) and reaches a limit of 68% (350°C). The BA shows the same carbon ratio as the 350°C treatment, probably because of the similarity of the heating temperatures. As a consequence of this, the oxygen ratio decreases rapidly with heating (UN 45%, 200°C 26%) until 23% (350°C and BA). Heating also modifies the elemental H/C ratio (1.49 in UN, 1.67 in 200°C and 1.38 in 350°C treatments). It is interesting to note that UN and BA exhibited similar H/C ratios (UN 1.49 and BA 1.48). The O/C and (N+O)/C ratios also showed similar pattern, but UN and BA values were quite different (0.70 to 0.26 O/C and (N+O)/C ratios for UN and BA, respectively) (Table 2.).

Table 2. Elemental Composition, Atomic Ratios (H/C and O/C) and Polarity Index ((N+O)/C) of the Cork Samples

Samples	C (%)	H (%)	O (%)	H/C	O/C	(N+O)/C
200°C	64.28	8.96	26.76	1.67	0.31	0.31
250°C	68.12	9.02	22.87	1.59	0.25	0.25
300°C	67.20	7.97	24.83	1.42	0.28	0.28
350°C	68.98	7.94	23.08	1.38	0.25	0.25
BA	68.28	8.45	23.28	1.48	0.26	0.26
UN	48.64	6.05	45.32	1.49	0.70	0.70
UNCr	43.38	5.47	51.16	1.51	0.88	0.88
BACr	64.05	6.97	28.98	1.31	0.34	0.34

Chromium Sorption and Mechanism

It is well recognised that metal biosorption processes are pH-dependent, as the proton concentration influences the sorbent ionization and the chemical speciation of metal in solution. Additionally, in the case of Cr(VI) sorption, the knowledge of the protons role in the sorption process is of great importance to assess the mechanism involved.

Figure 2 shows the amount of chromium sorbed for an initial 25 mg/L Cr(VI) concentration within the pH range 1.0 to 5.0 and a contact time of 24 h. The results show that the highest sorption was found at pH 3.0 for UN and 200°C treated and at pH 2.0 for BA. These results are consistent with those obtained previously in which it was described that the acidic conditions are more favourable to the sorption of chromium (Seng *et al.* 2001; Fiol *et al.* 2003).

There was almost no difference in the chromium(VI) sorption between these sorbents at pH 4.0 and pH 5.0 for 350°C and BA sample, respectively. The maximum Cr(VI) removal for 350°C was 26.2 % at pH 3.0, while for BA it was 69.4% at pH 2.0.

Because the net charge on the sorbent surface determines the protonation or deprotonation of the sorbent in aqueous media, the zero point charge (pHpzc) was determined. The pHpzc values, 4.40 (UN) and 5.54 (BA), show that sorbent surfaces were positively charged in interaction with chromium solutions.

At the optimal sorption pH, Cr(VI) is present as the negative species $Cr_2O_7^{2-}$ and $HCrO_4^-$. Therefore, the adsorption observed at pH lower than the pH_{pzc} of UN (pH 4.40) and BA (pH 5.54) must be due to the electrostatic attraction between these negative ionic species and the positive surface charge.

As shown in Fig. 2, the increase of temperature treatment had an adverse effect on Cr(VI) sorption onto *Q. cerris*. Thus, it seems that the heat treatment may modify some surface functional groups that are involved in chromium sorption. Indeed, both H/C and

O/C ratios decreased with the increase of temperature (Table 2), confirming that the temperature affects the nature of binding sites (*e.g*. dehydroxylation of –OH groups of lignin) with the subsequent Cr(VI) sorption decrease.

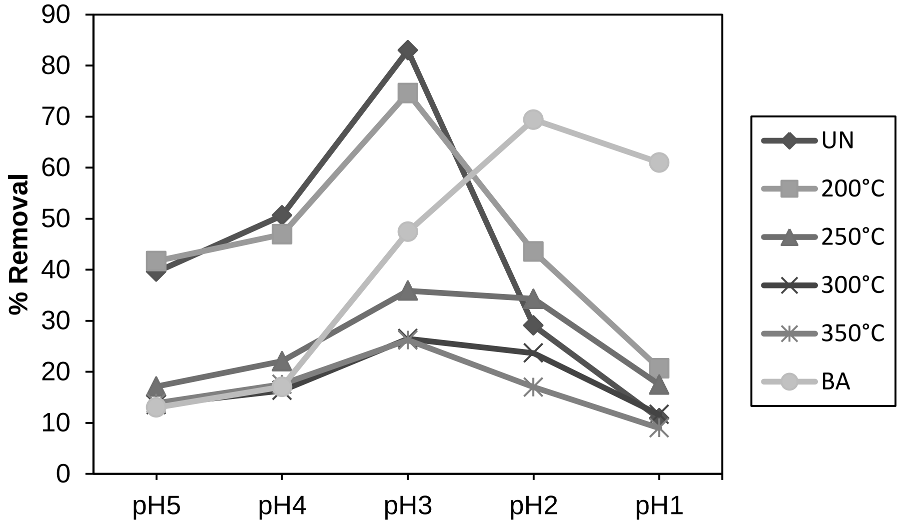

Fig. 2. Chromium removal (%) in the pH range (1.0 to 5.0). Initial Cr(VI) concentration: 25 mg/L, sorbent particle size: 0.25 to 0.42 mm, contact time: 24 hours

Though BA was also subjected to heat treatment (over 300°C), results shown in Fig. 2 indicate that this sorbent presents quite high sorption yields at the lowest pH values. This could be due to the fact that BA heat treatment was performed under steam in autoclave (Pereira and Ferreira 1989; Pereira 1992), and the possible modification of the binding sites favours chromium sorption. It seems that sorption is more related to binding sites containing hydrogen than oxygen (Table 2).

Reduction of Cr(VI) by the sorbents was observed by analysing the residual chromium in solution. Cr(VI) and Cr(III) concentrations of the residual solutions from experiments performed at initial pH 3.0 are presented in Fig. 3. As reduction is a proton-consuming reaction, the final pH of these solutions was measured and is also shown in the same figure.

As can be seen in Fig. 3, UN was the only sample able to render the residual chromium in its trivalent form. Conversely, in the case of BA, the remaining chromium in solution was almost exclusively as Cr(VI), indicating that at pH 3.0, this sorbent has almost null capacity to reduce Cr(VI).

Temperature treatment higher than 200°C negatively affected the Cr(VI) reduction, as observed in Fig. 3. The variation of pH (ΔpH 1.0 to 2.5) observed in Fig. 3 must be due to proton consumption as a consequence of chromium reduction because the corresponding sorbent blanks did not present any change in the pH. Indeed the highest pH variation was found for UN and 200°C samples and the lowest for the samples that suffered the highest heat treatments. These pH variations (ΔpH) correlate very well with Cr(III) concentration in the residual solutions. The results presented in Fig. 3 confirm that the heat treatment of QC provokes a modification on the surface functional groups involved in Cr(VI) reduction, which seems to play an important role in chromium elimination and explains the differences observed on chromium removal between QC sorbents. Also in the QS sample BA the heating treatment has a high adverse effect on chromium reduction.

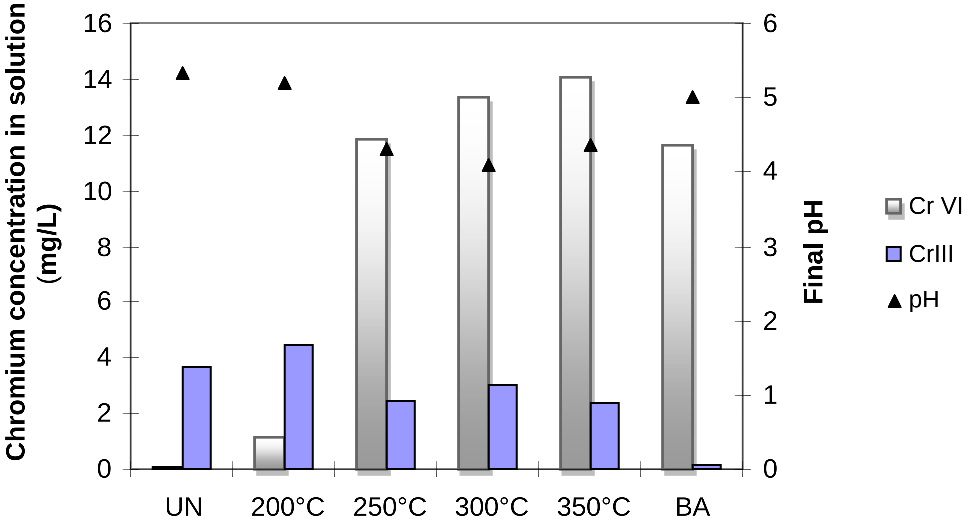

Fig. 3. Concentrations of Cr(VI) and Cr(III) and final pH in the remaining solutions after contact with the sorbents. Cr(VI) initial concentration: 25 mg/ L; Initial pH: 3.

FTIR spectroscopy was applied to identify the functional groups responsible for Cr(VI) sorption. FTIR spectra were obtained with the optimal sorbents UN and BA for chromium removal (Fig. 4). By comparing the spectra before and after adsorption, it was observed that the strong bands at 3426.36 cm^{-1} and 3431.76 cm^{-1} indicating the presence of hydroxyl groups in QC (UN) and black agglomerate (BA) were shifted to 3441.22 cm^{-1} and 3443.73 cm^{-1}, respectively and decreased after the adsorption of chromium. This indicates that surface aliphatic hydroxyl groups are involved in the adsorption of chromium.

Infrared absorption spectra of both samples show that the aromatic skeletal vibrations derived from C=C vibration of aromatic lignin moieties at around 1600 cm^{-1} were affected by chromium sorption. This is confirmed by the shift of the peaks from 1600.8 cm^{-1} to 1585.3 cm^{-1} in the case of BA and from 1516.14 cm^{-1} to 1506 cm^{-1} in UN. The decrease in wave number could be due to the higher steric hindrance for the formation of hexavalent chromium complexes on positively charged groups of the lignin moieties (*e.g.* hydroxyl). The functional groups of the lignin moieties seem to play a significant role on sorption of chromium. This is shown by a decrease in the intensities of the peaks at 1271 cm^{-1} in the case of UN and 1261 cm^{-1} in BA, attributed to C-O-CH_3 (methoxyl deformation). This could indicate the oxidation of lignin in these sorbents upon addition of Cr(VI). Then the adsorbed Cr(VI) might be partially reduced to Cr(III) with the oxidation of neighboring electron-donor functional groups (*e.g.* the O-CH_3 group) (Albadarin *et al.* 2011).

Therefore, these results indicate that lignin plays a significant role in the sorption of Cr(VI) and its reduction to Cr(III).

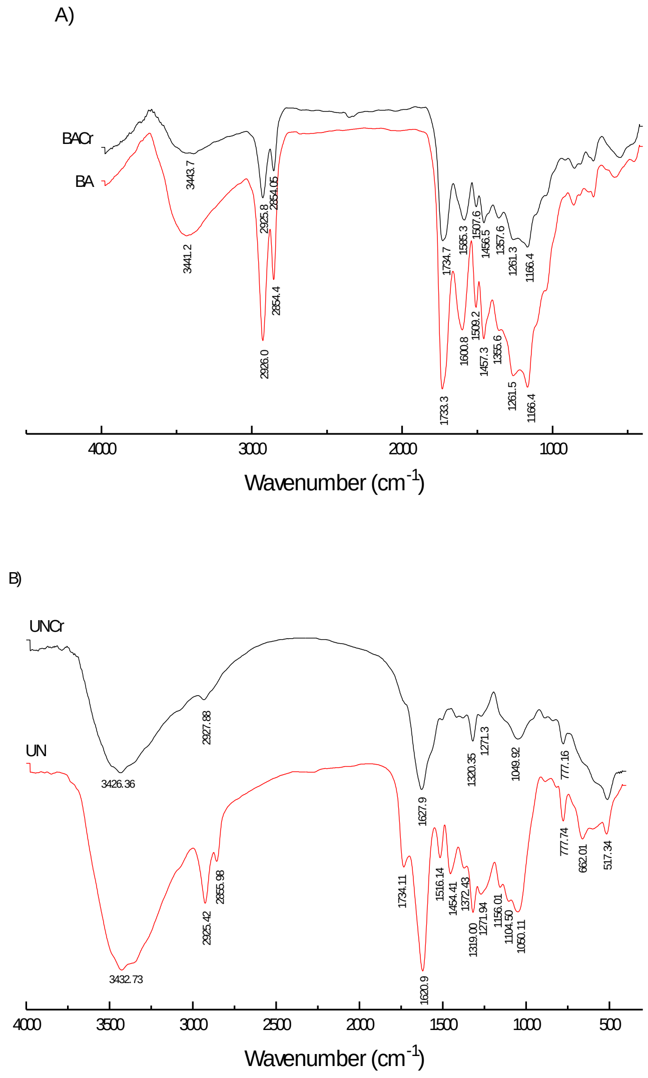

Fig. 4. FTIR spectra of the A) BA and BA treated with 1000 mg/L Cr(VI) solution (BACr) at pH 2 for 24 h. and B) UN and UN treated with 1000 mg/L Cr(VI) solution (UNCr) at pH 3 for 24 h

In the case of the UN sample, other compounds were also involved in the chromium sorption process. The UN sample interaction of carbonyl oxygen (C=O) of suberin with chromium was reflected by the disappearance of the peak at 1734.11 cm^{-1} (Marques *et al.* 1994). According to Shen *et al.* (2010), carbonyl groups may provide binding sites for Cr(III) resulting from Cr(VI) reduction. The carbonyl groups were not affected by chromium sorption on BA. It is also shown that while the intensities of the peaks contributed by cellulose and hemicelluloses in BA were insignificantly affected (*e.g.* 1166 cm^{-1} corresponding to C-O bond), the intensity of the peak at 1052 cm^{-1} in UN characteristic to polysaccharides (cellulose and hemicelluloses) is clearly affected by Cr(VI), indicating it could play an important role of the adsorption. A strong band at around 1627.88 cm^{-1} is assigned to calcium oxalate ions present in phloem residues in the QC cork (Şen *et al.* 2012b).

The two bands in the 2800 to 2900 cm^{-1} region can be associated with the presence of suberin corresponding to the asymmetric and symmetric vibration, respectively, of C-H in the olephinic chains. In BA, a minor shift of these bands was observed, and a clear decrease of these bands was shown in UN, indicating that these groups were involved in the sorption. This is also consistent with the variations of C-H stretching in UN with a shift from 1454.41 cm^{-1} and 1372.43 cm^{-1} to 1418.09 cm^{-1} and 1383 cm^{-1}, respectively.

Therefore, while in the case of BA, lignin is taken to be the main component responsible for Cr(VI) sorption, in the case of UN, suberin and polysaccharides play significant roles in the sorption. The O-H groups, C=O groups, and C-O groups (as evidenced by the stretching absorption band) seem to contribute to the chromium adsorption (Vinodhini and Das 2009).

A complementary SEM-EDX analysis was applied to analyze the distribution of the chromium adsorption on the cork granules (Hossain *et al.* 2010). The spectra obtained show the presence of chromium in the UN and BA samples. The scanning along the surface of the samples indicated that chromium had a homogenous distribution within the cork granule (Fig. 5).

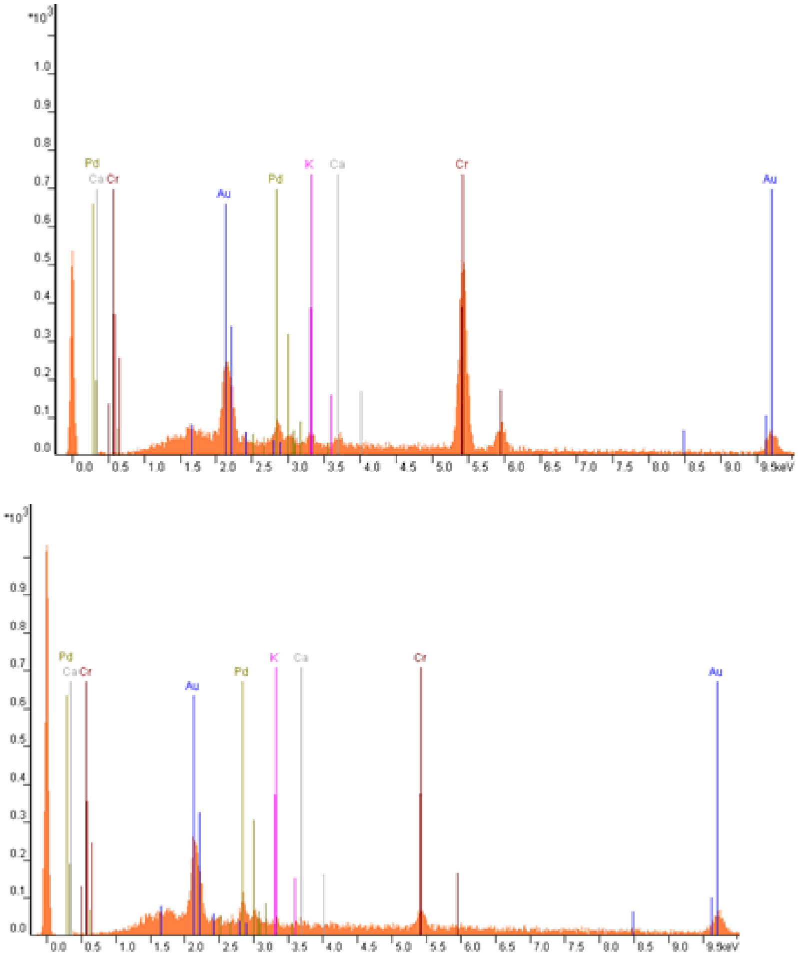

Fig. 5. EDX spectra of *Q. cerris* (above) and *Q. suber* black agglomerate (below) cork samples

No difference in chromium density was observed between the cross-sectioned cell wall and the surface of cell base both in UN and BA samples (Figs. 6 and 7). The UN sample was found to contain phloemic residues (Fig. 8), which also contained a high amount of chromium similar as in cork.

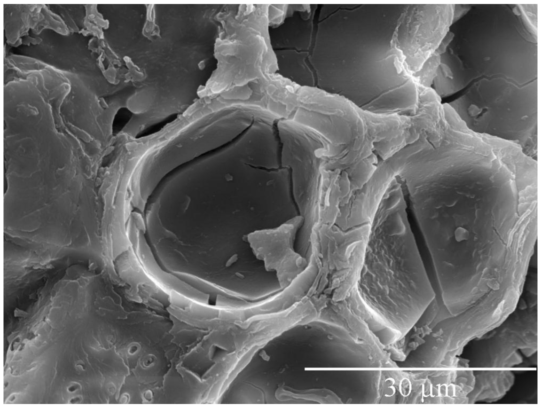

Fig. 6. *Q. cerris* cork cell from UN granule treated with 1000 mg/L chromium solution

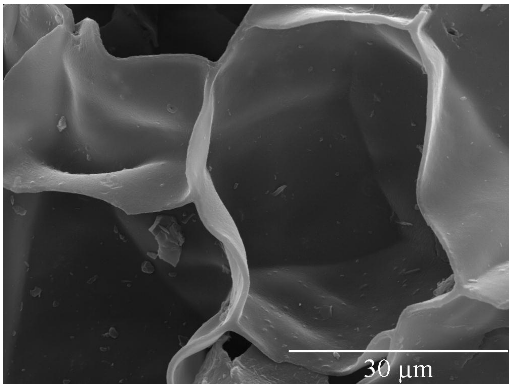

Fig. 7. Cork cell from BA granule treated with 1000 mg/L chromium solution

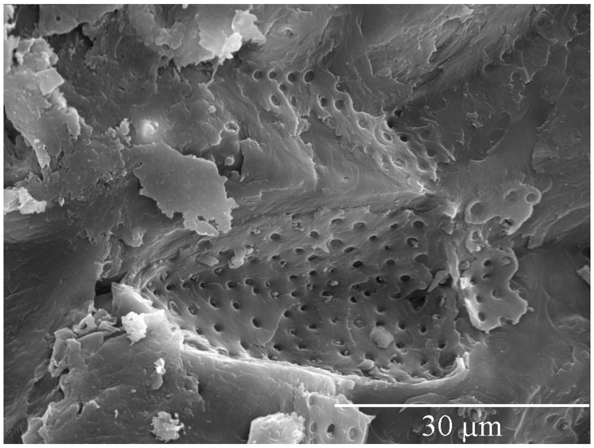

Fig. 8. Phloemic portions in a UN granule

Adsorption Isotherms

The adsorption isotherm tests were conducted based on the equilibrium time found in kinetics experiments (Fig. 9). The equilibrium time was reached at 24 h for BA and 48 h for UN. Thus, an agitation time of 48 h was selected to ensure that equilibrium adsorption had been reached.

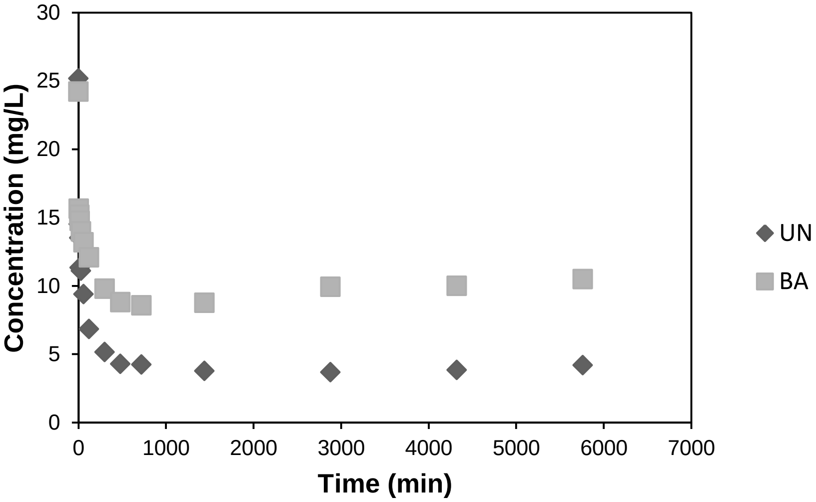

Fig. 9. Chromium concentration in solution as a function of time. Initial Cr(VI) concentration: 25 mg/L. Initial pH : 2.0 (BA) or 3.0 (UN).

Chromium sorption isotherms when using UN and BA are presented in Fig. 10. The experimental data were fitted to the Langmuir model (Equation 1) and its linearized form (Equation 2). The Langmuir parameters were calculated and are plotted together with the experimental data in Fig. 10. The $q_{\max}$, b, and the regression coefficient parameters are presented in Table 3.

$$q = (qmax \times b \times Ceq) \div (1 + b \times Ceq) \qquad (2)$$

$$1 \div q = 1 \div qmax + 1 \div (Ceq \times qmax \times b) \qquad (3)$$

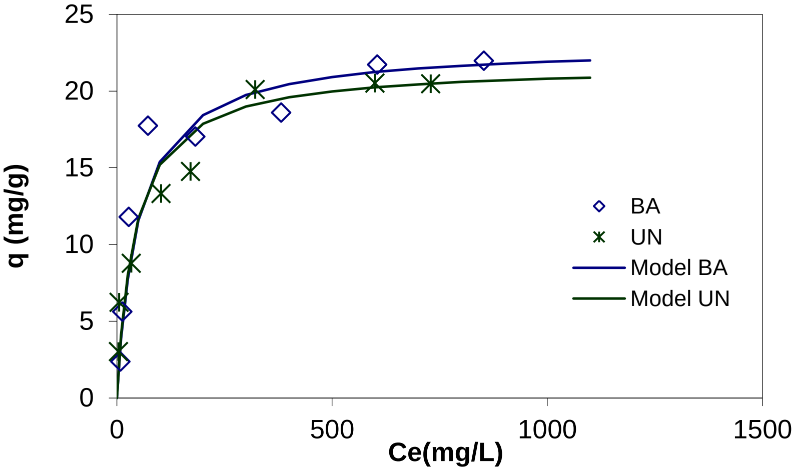

Fig. 10. Fitting of the Langmuir isotherm equation (lines) to the data gathered from the experiments (symbols). Initial pH: 2.0 (BA) or 3.0 (UN)

As can be observed, the experimental isotherm data fitted well with the Langmuir model, and the calculated maximum uptakes (q_{max}) were found to be 22.98 mg/g in BA and 21.69 mg/g in UN. Therefore, no significant differences were found in maximum sorption capacity between the two sorbents. The maximum uptake (q_{max}) values of both granules UN and BA were higher than that of untreated *Q. suber* cork (17.0 mg/g, Fiol *et al.* 2003) and comparable with other lignocellulosic materials like coconut shell (18.69) and saw dust (20.70) (Singha *et al.* 2011). The *b* values indicating the affinity of sorbents toward the metal were similar, although slightly lower in BA (0.023 and 0.020, respectively), *i.e.* having higher affinity.

Table 3. Langmuir Parameters for Cr(VI) Uptake

Sorbents	Calculated Langmuir Values		
	q_{max} (mg/g)	*b* (L/mg)	R^2
UN	21.69	0.023	0.9940
BA	22.98	0.020	0.9938

CONCLUSIONS

Removal of aqueous chromium(VI) by *Quercus cerris* and *Quercus suber* cork samples were performed. The following conclusions arise from this work:

1. Among the granules tested, untreated *Q. cerris* (UN) cork granules were the most efficient, followed by 200°C treated *Q. cerris* and black agglomerate *Q. suber* (BA) granules in the removal of Cr(VI) ions from aqueous solutions. Sorption was strongly dependent on initial pH of solution.
2. The experimental data were well fitted to the Langmuir model, and a similar maximum uptake was found (21.69 mg/g for UN and 22.98 mg/g for BA).
3. Heat treatment of *Q. cerris* cork at temperatures higher than 200°C resulted in a decrease of the total amount of chromium removed and Cr(VI) reduced.
4. FTIR spectra indicate that lignin plays a significant role in sorption of Cr(VI) onto both BA and UN. Suberin and polysaccharides also contribute to metal binding onto UN.
5. SEM–EDX analysis showed that chromium was homogeneously distributed on the cork granules surface.

These findings will be used in further works to optimize the experimental sorption conditions in continuous processes, since the results obtained in this study underline that the studied corks can be an alternative to more costly materials for the treatment of liquid wastes containing metals.

ACKNOWLEDGMENTS

This research was funded by the Spanish Ministerio de Ciencia e Innovación as part of the project CTM 2010-15185 and by the Strategic Project PEst-OE/AGR/UI0239/2011 by the Portuguese Fundação para a Ciência e Tecnologia (FCT).

REFERENCES CITED

Albadarin, A. B., Al-Muhtaseb, A. H., Walker, G. M., Allen, S. J., and Ahmad, M. N. M. (2011). "Retention of toxic chromium from aqueous phase by H_3PO_4-activated lignin: Effect of salts and desorption studies," *Desalination* 274, 64-73.

Chubar, N., Carvalho, J. R., and Correia, M. J. N. (2004a). "Cork biomass as biosorbent for Cu(II), Zn(II) and Ni(II),"*Colloid Surface A* 230, 57-65.

Chubar, N., Carvalho, J. R., and Correia, M. J. N. (2004b). "Heavy metals biosorption on cork biomass: Effect of pre-treatment,"*Colloid Surface A.* 238, 51-58.

Clesceri, S. L., Greenberg, A. E., and Eaton, A. D., (eds.). (1998). *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington DC, 65-67.

Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch J., and Serarols, J. (2003). "Biosorption of Cr(VI) using low cost sorbents,"*Environ Chem Lett.* 1, 135-139.

Fiol, N., Escudero, C., and Villaescusa, I. (2008). "Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark," *Bioresource Technol*. 99(11), 5030-5036.

Fiol, N., and Villaescusa, I. (2009). "Determination of sorbent point zero charge: Usefulness in sorption studies," *Environ. Chem. Lett*. 7, 79-84.

Hossain, M. A., Kumita, M., and Mori, S. (2010). "SEM Characterization of the mass transfer of Cr(VI) during the adsorption on used black tea leaves," *Afr. J. Pure Appl. Chem.* 4(7), 135-141.

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources.* 6(2), 2161-2287.

Jauberty, L., Gloaguen, V., Astier, C., Krausz, P., Delpech, V., Berland, A., Granger, V., Niort, I., Royer, A., and Decossas, J. L. (2011). "Bark, a suitable biosorbent for the removal of uranium from wastewater – From laboratory to industry," *Radioprotection* 46(4), 443-456

Kehinde, O. O., Oluwatoyin, T. A., and Aderonke, O. O. (2009). "Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr(VI) and Ni(II) from aqueous solution," *Afr. J. of Environ. Sci. Technol*. 3(11), 360-369.

Marques, A. V., Pereira, H., Meier, D., and Faix, O. (1994). "Quantative analysis of cork (*Quercus suber* L.) and milled cork lignin by FTIR spectroscopy, analytical pyrolysis and total hydrolysis," *Holzforschung* 48 (suppl.), 43-50.

Oh, M., and Tshabalala, M. A. (2007). "Pelletized ponderosa pine bark for adsorption of toxic heavy metals from water," *BioResources* 2(1), 66-81.

Olivella, M. À., Jové. P., Şen, A., Pereira, H., Villaescusa, I., and Fiol, N. (2011). "Sorption performance of *Quercus cerris* with polycyclic aromatic hydrocarbons and toxicity testing," *BioResources* 6(3), 3363-3375.

Park, D., Ahn, C. K., Kim, Y. M., Yun, Y. S., and Park, J. M. (2008). "Enhanced abiotic reduction of Cr(VI) in a soil slurry system by natural biomaterial addition," *J. Hazard. Mater*. 160, 422-427.
Pereira, H., and Ferreira, E. (1989). "Scanning electron microscopy observations in insulation cork agglomerates," *Mater. Sci. Eng*. A 111, 217-225.
Pereira, H. (1992). "The thermochemical degradation of cork," *Wood Sci. Techno*. 26, 259-269.
Pereira, H. (2007). *Cork: Biology, Production and Uses,* Elsevier Public., Amsterdam.
Sarin, V., and Pant, K. K. (2006). "Removal of chromium from industrial waste by using eucalyptus bark," *Bioresour. Technol*. 97, 15-20.
Şen, A., Miranda, I., and Pereira, H. (2012a). "Temperature-induced structural and chemical changes in cork from *Quercus cerris,*" *Ind. Crop. Prod*. 37, 508-513.
Şen, A.,Velez Marquez, A., Gominho, J., and Pereira, H. (2012b). "Study of thermochemical treatments 1 of cork in the 150-400ºC range using colour analysis and FTIR spectroscopy," *Ind. Crop. Prod.* 38, 132-138.
Seng, C. E., Lee, C. G., and Liew, K. Y. (2001). "Adsorption of chromium (VI) and nickel (II) ions on acid- and heat-activated deoiled spent bleaching clay," *J. Am. Oil Chem. Soc.* 78, 831-835.
Shen, Y. S., Wang, S. L., Huang, S. T., Tzou, Y. M., and Huang, J. H. (2010). "Biosorption of Cr(VI) by coconut coir: Spectroscopic investigation on the reaction mechanism of Cr(VI) with lignocellulosic material," *J. Hazard. Mater*. 179(1-3), 160-165.
Singha, B., Naiya, T. K., Bhattacharya, A. K., and Das, S. K. (2011). "Cr(VI) ions removal from aqueous solutions using natural adsorbents-FTIR studies" *JEP*. 2, 729-735.
Üstün, G. E. (2009). "Occurence and removal of metals in urban wastewater treatment plants," *J. Hazard. Mater*. 172(2-3), 833-838.
Villaescusa, I., Fiol, F., Cristiani, F., Floris, C., Lai, S., and Nurchi, V. M. (2002). "Copper(II) and nickel(II) uptake from aqueous solutions by cork wastes: A NMR and potentiometric study," *Polyhedron*. 21, 1363-1367.
Villaescusa, I., Fiol. N., Martínez, M., Miralles, N., Poch, J.,and Serarols, J. (2004). "Removal of copper an nickel ions from aqueous solutions by grape stalks wastes," *Water Res*. 38, 992-1002.
Vinodhini, V., and Das, N. (2009). "Mechanism of Cr(VI) biosorption by neem sawdust," *AEJSR*. 4(4), 324-329.
Yılmaz, S., Türe, M., Sadıkoğlu, M., and Duran, A. (2010). "Determination of total Cr in wastewaters of Cr electroplating factories in the I. organize industry region (Kayseri, Turkey) by ICP-AES," *Environ. Monit. Assess.* 167, 235-242.

Article submitted: February 20, 2012; Peer review completed: June 2, 2012; Revised version received: June 29, 2012; Second revision: July 5, 2012; Third revision received and accepted: August 10, 2012; Published: August 15, 2012.