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Abstract: Exhausted ground coffee waste has been investigated as metal biosorbent for Cr(VI) from aqueous solution. Maximum metal sorption was found to occur at initial pH 3.0. Kinetic studies revealed that the initial uptake was quite rapid; nevertheless, it took five days to reach equilibrium. The value of the Langmuir maximum uptake was found to be 10.2 mg Cr(VI)/g waste. The sorbent is able to reduce hexavalent chromium to its trivalent form. A solution of 1 M NaOH was the most effective desorption agent and after 24 hours contact 42% of total chromium was desorbed in both hexavalent and trivalent oxidation states.

Keywords: Metal removal, chromium, low cost sorbent, sorption

INTRODUCTION

Hexavalent chromium is present in the effluents as a result of the electroplating, leather tanning mining, dyeing, fertilizer, and photography industries activities and its removal is of particular concern because of its great toxicity that causes severe environmental and public health problems. One of the classical techniques to remove Cr(VI) ions from effluents is precipitation of the previously reduced hexavalent chromium to its trivalent form followed by ion exchange or adsorption removal. These techniques, apart from being economically expensive,

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have disadvantages like incomplete metal removal, high reagent, and energy requirements and generation of toxic sludge or other waste products that require treatment or disposal. Therefore, efficient and environmentally friendly methods are thus needed to be developed to remove heavy metal from water streams. Biosorption of metallic elements, is a good alternative technique because it utilizes as sorbents inactive/dead biological materials which are generally available at low cost, are non hazardous, and abound in nature (1).

The re-use of waste materials that arise through various industrial processes for additional purposes, rather than simple disposal or combustion, makes both environmental and commercial sense. The food industry produces big amounts of wastes which are disposed or combusted.

During the last years, Cr(VI) removal using different sorbents based on food industry wastes i.e. wheat bran (2) coirpith and rice husk (3), pomace (4), or tea waste (5), has been investigated.

Exhausted ground coffee waste is available in big quantities from the manufacture of soluble instant coffee and at present this waste is mainly used in composting. This waste is a tannin-containing material with polyhydroxy polyphenol functional groups that are potentially good metal binding groups (6). However, studies on metal removal by using exhausted coffee residues are scarce. Among these studies, Cr(VI), Cd(II), and Al(III) sorption by Turkish coffee and exhausted coffee has been investigated by Orhan and Buyukgungor (7) and Utomo and Hunter (8) studied Cu(II), Zn (II), Cd(II), and Pb(II) sorption onto used exhausted coffee grounds. Results obtained in those studies, indicate that coffee waste offers considerable promise as low cost sorbent for waste water treatment. The aim of this work is to evaluate the usefulness of exhausted coffee waste generated in a soluble coffee production industry as sorbent material for the removal of hexavalent chromium from aqueous solution.

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EXPERIMENTAL

Materials and Reagents

Exhausted ground coffee wastes were supplied by an industry of soluble coffee production from Girona, Spain. The wastes were dried in an oven at 105°C until constant weight. Once dried, they were sieved for a particle size of 0.75–1.5 mm. Cr(VI) solutions were prepared by dissolving appropriate amounts of $K_2Cr_2O_7$ in distilled water. NaOH and HCl solutions were used for pH adjustment and desorption experiments. All reagents were analytical grade and were purchased from Panreac (Barcelona, Spain).

Chromium standard solutions of 1000 mg/L also purchased from Panreac were used for Flame Atomic Absorption Spectroscopy (FAAS) calibration.

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Characterization of Exhausted Ground Coffee Wastes

Porosimetric Analysis

A mercury porosimeter Pascal 240 from Thermo Electron Corporation was used to determine the total specific surface area (7.5 m^2/g), the average pore radius (20.67 micron), total porosity (69.75%), bulk density (0.426 g/cm^3) and apparent density (1.41 g/cm^3) of the exhausted ground coffee waste.

Elemental Analysis

Elemental analysis of exhausted ground coffee waste performed with an elemental analyzer (EA1110 CE Instruments) showed the material composition: 57.50% C, 7.39% H, 2.06% N, and $<0.3\%$ S.

Point of Zero Charge Determination

Potentiometric mass titrations (PMT) were performed to determine the pH of point of zero charge of coffee waste. Potentiometric titrations using an automatic titrator (Orion 960) were performed for a blank solution and suspensions of three different masses of coffee waste at constant ionic strength following the methodology proposed by Bourikas et al. (9). Point of zero charge of coffee waste was found to be at pH 3.9.

Analysis of Chromium

The total concentration of chromium, i.e., Cr(VI) + Cr(III) was determined by flame atomic absorption spectroscopy (FAAS) (Varian SpectrAA 220FS). Hexavalent chromium was analyzed by the standard colorimetric 1,5 diphenylcarbazide method (10) in a spectrophotometer (Cecil, CE2021). The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentrations, respectively. For comparison sake, the Cr(VI) standard used in diphenylcarbazide method was analysed by FAAS. Analytical measurements made by the two techniques were comparable within 5%.

General Metal Uptake Procedure

Batch experiments were carried out at 20 ± 2°C in stoppered glass tubes. The experiments consisted on shaking a fixed mass of 0.1 g of dry exhausted coffee (EC) with 15 mL of Cr(VI) solution at 30 rpm in a rotary mixer (Rotator STR4, Stuart Scientific) until equilibrium was reached.

After agitation the solid was removed by filtration through a 0.45 μm cellulose filter paper (Millipore Corporation). The final metal concentration in the filtrates as well as in the initial solution was determined by either FAAS or DPC colorimetric method. The sorbed metal concentration was obtained from the difference between initial and final metal concentrations in solution.

When the initial pH of metal solutions was adjusted to the desired value no efforts were made to maintain the solution pH while metal ions were being sorbed. Measurement of pH (Crison Model Digilab 517 pH meter) at the beginning and at the end of the experiments was performed.

Each experiment was carried out in duplicate and the average results are presented in this study.

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Sorption Kinetics

Previous experiments were carried out to determine the contact time needed by the coffee waste-metal system to achieve equilibrium. The experiments were carried out at two different initial pHs 2.8 and 5.0. Metal initial concentration was around 50 mg/L. Samples were drawn at predetermined intervals of time for metal concentration analysis. The amount of metal sorbed by weight of dry wastes was calculated as $q_t = (C_i - C_t)V/w$, where V(L) is the solution volume, C_i and C_t (mol/L) are the initial and at time t metal solution concentration, respectively and w (g) is the dry weight of the sorbent.

Effect of pH

The pH of metal solutions has been identified as the most important variable governing biosorption (1). This is partly due to the fact that the distribution of metal chemical species in solution varies with the pH and partly that this parameter influences on the net charge of the sorbent.

The effect of pH on the sorption was studied by adjusting the initial solution pH within the range 1.0–9.0. In these experiments, metal initial concentration was around 50 mg/L.

In order to know the chemical species in solution in the experimental conditions used in this work, chromium species distribution diagrams at a fixed metal concentration (around 50 mg/L) as a function of different pH values, were performed using equilibrium constants in aqueous solutions given in the literature (11) and a specially made computer program (12).

Sorption Isotherm

For the adsorption isotherm experiments, the initial metal concentration was varied within the range 3.65–239 mg/L, temperature was 20 ± 2°C and initial pH 3.0. This pH was selected based on batch tests conducted to determine the effect of pH on sorbent capacities. The classical model of Langmuir was used to model sorption equilibrium data.

Desorption Experiments

The elution of metallic elements from the sorbent allows both recovery of metal ions and recycling of the sorbent for subsequent uses. For all desorption experiments, coffee waste was pre-loaded by contacting the sorbent with a 500 mg/L Cr(VI) solution at pH 3.0 and following the above-mentioned general metal uptake procedure. The amount of metal loaded on exhausted coffee waste was around 10 mg Cr/g dry sorbent. Aliquots of metal-loaded exhausted coffee (0.1 g), after gently washing with distilled water, were contacted for 24 hours with 15 mL of either HCl and NaOH solutions of different concentration within the range (1.0×10^{-2}–1.0 mol/L).

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SEM-EDX Analysis

The surface structure and local elemental composition of the exhausted ground coffee before and after chromium sorption was analyzed by Scanning Electron Microscopy (Zeiss DSM 960 A) and Energy Dispersive X-ray Analysis (Oxford Link Isis Pentafet) respectively. Digital images were processed by using Quartz PCI program.

SEM-EDX analysis of the surface of the sorbent was carried out after sorbent treatment with a 500 mg/L Cr(VI) solution at initial pH 3.0. In order to compare, a blank was carried out by contacting the sorbent with aqueous solution at pH 3.0. Before analysis, blank and chromium-laden exhausted coffee were washed with deionized water and dried in an oven at 75°C until constant weight. For these analyses, samples were mounted on a stainless stub using a double-stick tape coated with a thin layer of carbon.

FTIR-ATR Analysis

Exhausted ground coffee is a complex material whose major constituents are lignin and cellulose. The sorption of metals by this kind of materials is supposed to occur by the polar functional groups of lignin (alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers) and others acting as chemical bonding agents (13–15). To give a qualitative and preliminary analysis of the main functional groups that might be involved in Cr(VI) uptake, a Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis in solid phase was performed using a Fourier Transform Infrared Spectrometer (Mattson Satellite with MKII Golden Gate Reflection,

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ATR System). Same samples used for SEM analysis were used for FTIR-ATR analysis.

RESULTS AND DISCUSSION

Sorption Kinetics

The amount of Cr(VI) sorbed onto the coffee ground waste as a function of contact time is plotted in Fig. 1. As can be seen, for the two initial pH studied, there is a visible increase of the amount of chromium sorbed during the first 30 hours; however, after this time, metal uptake slowly increases until the sorption process is completed (around 120 minutes) and the curve becomes flattened. Taking into account these results, a shaking time of 5 days was used in all further sorption experiments to ensure equilibrium. In the same figure, it can also be observed that metal removal is higher at pH 2.8 suggesting that acidic media might favor metal removal.

In order to investigate the sorption rate law of metal sorption, the kinetic data obtained from batch experiments, have been analyzed using the pseudo-second order equation proposed by Ho et al. (16). The differential equation that describes the pseudo-second order is the following:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

where q_e is the amount of metal sorbed at equilibrium (mg/g), k is the rate constant of sorption (g/mg h) and q_t is the amount of metal sorbed on the surface of the sorbent at any time, t, (mg/g).

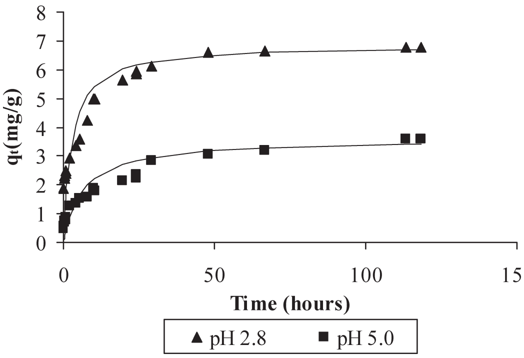

Figure 1. Chromium sorbed onto exhausted coffee waste as a function of contact time. Predicted data by pseudo-second-order kinetic model (lines) and experimental data (symbols). Initial pH 2.83 and 5.02. Cr(VI) initial concentration: 50 mg/L.

Separating the variables and integrating for the initial conditions $t = 0$, $q_e = 0$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{2}$$

which is the integrated rate law for a pseudo-second order reaction. Equation (2) can be rearranged to obtain the linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{3}$$

When the experimental data were introduced into the Equation (3), straight lines were obtained by plotting t/q_t against t, indicating that the process follows the pseudo-second order rate equation. From the equations of the different obtained linear plots, the equilibrium metal sorption, q_e, the values of the rate constant, k, and the coefficients, R^2, were calculated and are presented in Table 1.

As seen in Table 1, the best fit to the pseudo-second order kinetic model for Cr(VI) sorption onto the coffee waste was obtained for sorption data at pH 2.8. Nevertheless, R^2 in both cases is greater than 0.97. Furthermore, the calculated q_e showed in Table 1 are in good agreement with the observed experimental ones. The lower q_e and K values in the case of pH 5.0 confirms the dependence of Cr(VI) sorption on pH.

The well-suitability of pseudo-second order to model sorption of Cr(VI) can be observed in Fig. 1, where the calculated pseudo-second order curves are superimposed to the experimental data. The good compliance between experimental and calculated values suggests that chemisorption may be the rate-limiting step involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate (17, 18).

Effect of pH

Results of Cr(VI) sorption as a function of initial pH are presented in Fig. 2. The percentage of Cr(VI) species present in solution is superimposed on the same figure. As can be seen, when the pH of the solution increases from 1.0 to 3.0, the adsorption of Cr(VI) increases and maximum sorption is found at pH 3.0. From this pH to pH 6.0, the amount of Cr(VI) sorbed is similar,

Table 1. Kinetic parameters of pseudo-second order kinetic model for Cr(VI) sorption onto exhausted coffee waste at 20 ± 2ºC. Cr(VI) initial concentration: 50 mg/L

pH	R^2	q_e (mg/g)	K (g/mg h)
5.0	0.972	3,59	0,043
2.8	0.997	6,86	0,053

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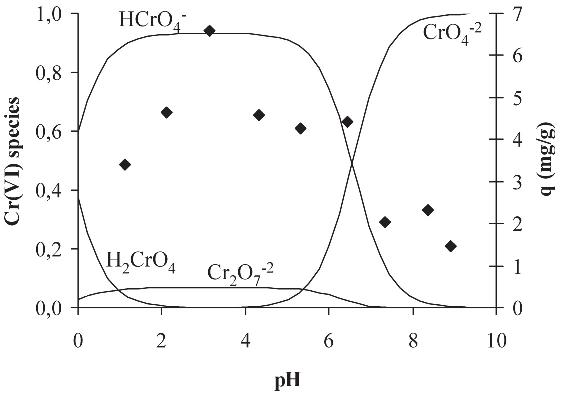

Figure 2. Chromium uptake by exhausted coffee waste as a function of initial H (symbols). Initial metal concentration was 50 mg/L. The species distribution diagram of Cr(VI) (50 mg/L) is superimposed (lines).

whereas as the pH increases from 6.0 to 9.0, Cr(VI) sorption decreases significantly.

One of the common proposed mechanism for Cr(VI) sorption by biosorbents is electrostatic attraction between sorbent and sorbate (19, 20). As seen in Fig. 2, only the negative Cr(VI) charged species ($HCrO_4^-$ and $Cr_2O_7^{2-}$ and CrO_4^{2-}) are present in solution at the studied pH range (1.0–9.0). Therefore, the adsorption observed at pH lower than pH_{pzc} (3.9) when the sorbent surface is charged positively may be explained by the electrostatic attraction between sorbent and negatively charged species ($HCrO_4^-$ and $Cr_2O_7^{2-}$). Nevertheless, electrostatic attractions cannot explain neither the decrease of adsorption when decreasing pH from 3.0 to 1.0 nor the metal uptake at pH higher than pH_{pzc} as at these pH values the sorbent surface is charged negatively with the subsequent repulsion between negative charges. Thus, other mechanisms must be involved in metal uptake.

Several authors have reported that, at acidic pH, Cr(VI) can be reduced to Cr(III) after contact with lignocellulosic materials (2, 21). Reduction of Cr(VI) is a protons consuming reaction and is favored at low pH; thus, if exhausted ground coffee waste has the ability to reduce Cr(VI) to Cr(III), reduction would be more favored at pH 1.0 than a pH 3.0. Moreover, the reduced form of chromium (Cr(III)) could be released into the solution where it would be present as the species Cr^{3+} cation and $Cr(OH)^{2+}$ and these species would not be attracted by the positively charged surface of the sorbent. Taking into account these considerations, a highest reduction ratio at pH 1.0 would explain the lowest metal adsorption observed at this pH.

Reduction could also be responsible in part for the adsorption observed at pH higher than pH_{pzc}. Although the ratio of reduction at this pH range was

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lower than at the very high acidic pH, the Cr(III) formed species could be attracted electrostatically by the negatively charged sorbent surface. Nevertheless, reduction is not able to explain the obtained results at pH higher than pH_{pzc}. Therefore, other mechanisms than redox reaction and electrostatic attractions must be involved in metal uptake.

As seen in Fig. 2, initial pH 3.0 resulted to be the most favorable for Cr(VI) sorption onto the sorbent. At this pH, both postulated mechanisms, electrostatic attraction of the anionic Cr(VI) species, and the reduction of Cr(VI) to Cr(III) take place. When analyzing total chromium and Cr(VI) in the remaining solution after contact of 50 mg/L (pH 3.0) with exhausted ground coffee, 68.5% of total chromium was Cr(VI) and 31.5% was Cr(III). These results confirm the coexistence of chromium in both oxidation states.

Sorption Isotherms

The sorption equilibrium data were fitted by the non-competitive Langmuir model:

$$q = \frac{q_{max} b\ C_e}{1 + b\ C_e} \tag{4}$$

where q, is the amount of metal sorbed per unit mass of sorbent, q_{max} is the maximum metal uptake per unit mass of sorbent (mg/g), C_e is the equilibrium concentration of sorbate in solution (mg/g), and b is the Langmuir constant related to energy of sorption (L/mg) which reflects quantitatively the affinity between the sorbent and the sorbate.

From the experimental equilibrium data, a non-linear fit was performed by means of the program MATLAB in order to obtain the Langmuir model parameters. This program minimizes the sum square of residuals (SSR):

$$SSR = \sum_{i=1}^{N} \left(q_i - \frac{q_{\max}\, b\, C_i}{1 + b\, C_i} \right)^2 \tag{5}$$

The obtained results for the Langmuir parameters were q_{max} 10.17 mg/g and b 0.125 L/mg (*SSR* 18.82). The experimental data of Cr(VI) sorption and the Langmuir curve calculated from the model parameters are plotted in Fig. 3. In this figure, it can be observed that experimental data points have a good compliance with the calculated Langmuir isotherm curve, this fact indicates monolayer coverage on the exhausted coffee surface by chromium.

The q_{max} (10.17 mg/g) obtained in this study for Cr(VI) sorption onto exhausted ground coffee was compared to the reported in the literature for some lignocellulosic sorbents. Similar results were found for sugar cane bagasse (13.4 mg/g), maize cob (13.8 mg/g) and sugar beet pulp

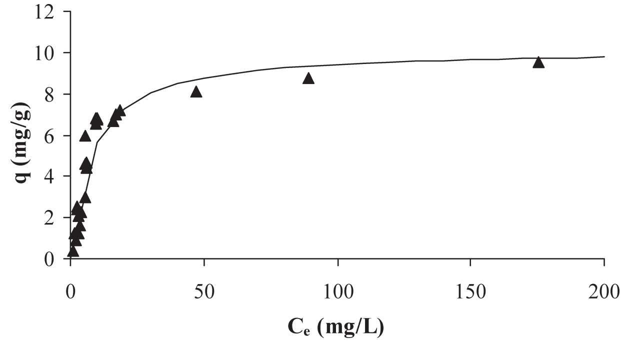

Figure 3. Fitting of the Langmuir isotherm equation to the data gathered from the equilibrium sorption experiments (symbols). Initial pH: 3.0, Temperature 20 ± 2 °C.

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(17.2 mg/g), (23), cork (17.0 mg/g) and olive stones (9.0 mg/g) (19). Nevertheless, notably higher capacity values of Cr(VI) adsorption were reported for black tea leaves (455 mg/g) (22), for sawdust (39.7 mg/g) (23), eucalyptus bark (45.0 mg/g) (24), yohimbe bark (42.5 mg/g), and grape stalks (59.8 mg/g) (19).

Desorption Experiments

Desorption experiments put into evidence that after 24 hours contact NaOH solutions were more efficient than HCl solutions to desorb chromium for the sorbent (Fig. 4). As seen, the highest chromium desorption percentage (47.0%) was obtained for the highest NaOH concentration (1.0 mol/L) used. It must be pointed out that when NaOH was used as desorbent agent,

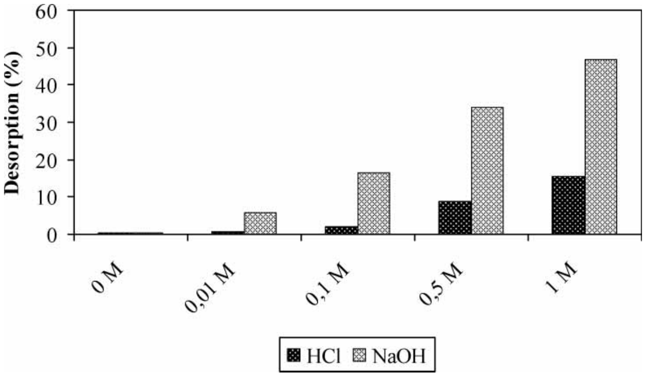

Figure 4. Desorption percentage of chromium from exhausted coffee using different HCl and NaCl concentrations as stripping solutions.

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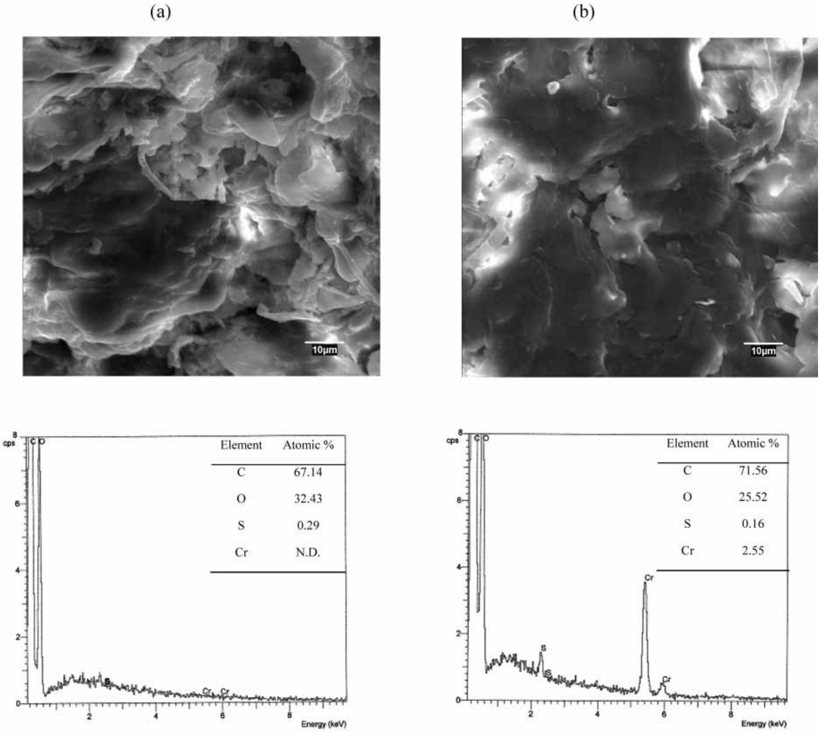
chromium was desorbed from the exhausted ground coffee in both chromium oxidation states, Cr(VI) and Cr(III). This fact evidences that chromium is bound in both forms, thus confirming that the sorbent is able to reduce hexavalent chromium to its trivalent form.

SEM-EDX Analysis

Electron micrographs and EDX spectra of exhausted ground coffee after contact with an aqueous solution at pH 3.0 and 500 mg/L of Cr(VI) solution are shown in Fig. 5 (a and b), respectively.

The micrographs put into evidence the heterogeneous morphology of the sorbent. EDX spectrum reveals that C and O constitute the two major elements of the lignocellulosic sample and, after treatment with Cr(VI) solution, Cr signal is clearly observed.



(a)

Element	Atomic %
C	67.14
O	32.43
S	0.29
Cr	N.D.

(b)

Element	Atomic %
C	71.56
O	25.52
S	0.16
Cr	2.55

Figure 5. Scanning electron micrograph and Energy dispersive X-Ray analysis of exhausted coffee waste (a) and Cr(VI)-laden exhausted coffee (b) Magnification: 1000 X.

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FTIR-ATR Analysis

Figure 6 shows the infrared spectra of the exhausted ground coffee and the material after being contacted for 24 hours with an initial metal concentration of 500 mg/L. The characteristic IR bands for lignocellulosic materials can be divided into four regions: the broad hydroxyl bands (3200–3600 cm^{-1}), the stretching bands of CH_2 and CH_3 (2800–3000 cm^{-1}), the stretching bands of carbonyl groups (1550–1750 cm^{-1}) and the fingerprint region (below 1550 cm^{-1}) in which the assignment of peaks is not clear because of the complex interactions of their vibration systems (25).

The peaks observed in the virgin and Cr(VI) treated material were attributed to lignin components: guaiacyl (1033, 1162, and 1236 cm^{-1}) and syringyl units (1317 cm^{-1}) and the bands at 1457 and 1521 cm^{-1} to methoxy deformation and to the vibration of the aromatic skeleton, respectively. (2) The bands located at 1725 and 1739 were attributed to the stretching vibration of C=O motion in carboxyl groups (26). Characteristic bands of cellulose units were found at 1058, corresponding to the skeletal vibration of C-O-C on pyranose, and 1376, attributed to O-H bending (27).

The modification of both cellulose and lignin characteristic bands indicates that both units are involved in Cr(VI) sorption. The general trend observed after Cr(VI) treatment in acidic conditions was a decrease of oxygenated functions bands intensity, except in the case of the band corresponding to a carboxylic function (1725 cm^{-1}), where an increase of the intensity was

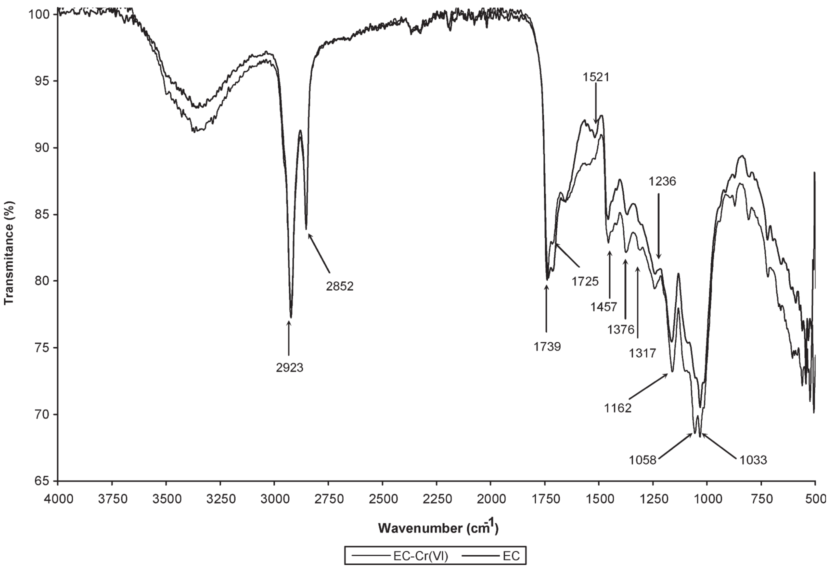

Figure 6 Infrared analysis of exhausted coffee waste (EC) and exhausted coffee contacted with acidic Cr(VI) solution (EC-Cr(VI).

observed. This fact could be explained by considering that the reduction of Cr(VI) to Cr(III) that takes place in acidic pHs, with subsequent oxidation of the solid surface of the sorbent, that would provoke the conversion of some of the alcoholic groups of the sorbent in carboxylic functions.

In a FTIR spectrum, fatty acids are characterized by two aliphatic vibrations at 2923 and 2852 cm.$^{-1}$ These two bands were not modified neither in intensity nor in position, indicating that these moieties are not involved in Cr(VI) sorption.

CONCLUSIONS

Exhausted ground coffee waste was investigated for the removal of hexavalent chromium from aqueous solution and the following conclusions can be drawn from the results of the present study:

- Kinetics of Cr(VI) sorption onto exhausted ground coffee waste follows pseudo-second order rate expression.
- Metal sorption is pH-dependent and maximum sorption was found to occur at initial pH 3.0. At this pH, electrostatic attraction of the anionic Cr(VI) species and reduction of Cr(VI) to Cr(III) take place.
- The sorption data were fitted by the Langmuir isotherm model. Calculated q_{max} was found to be 10.17 mg Cr/g exhausted ground coffee.
- SEM-EDX analysis confirms the presence of chromium on sorbent surface and FTIR analysis shows modification on cellulose and lignin characteristic bands indicating that both units are involved in Cr(VI) sorption.

In summary, exhausted coffee wastes a part from being a suitable low cost sorbent for chromium, has the advantage of converting Cr(VI) to the less toxic Cr(III), so, they can be used for the removal of chromium from wastewaters through a cost-effective and environmentally friendly process. Furthermore, the potential of using the studied wastes as cheap reducing agent for the reduction of Cr(VI) to Cr(III) deserves to be investigated.

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