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Removal of Cr(VI) from water by cork waste

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Abstract The biosorption by cork powder is considered as *a promising* method for heavy metal removal from industrial waste waters such as chromium tanning factories. The aim of this study is to evaluate the efficiency extent of this method using cork powder as a biosorbent for Cr(VI). The Fourier Transform Infrared spectroscopy (FTIR) analysis permits to distinguish the type of functional groups likely to participate in metal binding. A linear form of BET isotherms for all the three used temperatures (i.e., 25, 35 and 45 °C) and a pseudo-second-order equation of adsorption kinetics are obtained. Other experimental results highlight the meaningful influence of parameters such as contact time, pH, concentration of Cr(VI) and the adsorbent particle size on Cr(VI) adsorption. 97% of Cr(VI) has been removed under definite conditions particularly a particle size of diameter $d < 0.08$ mm and pH of 2–3 values.

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1. Introduction

Cr(VI) compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection and chemical manufacturing, but, because of its hazardous properties by many exposure routes, it must be removed from water and wastewater. Several remediation methods have been used such as ion exchange (Dinesh et al., 2006), reverse osmosis, ultrafiltration, flotation and electrocoagulation. But most of these methods are expensive and ineffective at low Cr(VI) concentrations. Adsorption has evolved as the front line of defence for chromium removal. Selective adsorption by biological materials, mineral oxides, activated carbons or polymer resins has generated increasing excitement (Dinesh et al., 2006; Bailey et al., 1998).

Most cork companies consider cork powder as a waste product and use it only as an energy source because of its low economic value and high burning capacity. However, as biosorption has gained importance, the good performance and low cost of cork as a complexing material have become attractive.

For instance, adsorptive removal of heavy metals in wastewater is usually achieved using activated carbon, activated alumina or polymer resins, which are expensive materials. Thus a need exists for low cost, effective and regenerable adsorbent materials for this application. The fatty acid content of cork makes it a promising biosorbent for heavy metals such as Cu(II), Zn(II), Ni(II) and Cr(VI) (Silva et al., 2005).

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2. Materials and methods

Cork powder was obtained as a waste product from insulation panels of "EPE/Jijel Liège Etanchéité/SPA" factory at jijel (Algeria). The cork powder was washed and dried at 110 °C for two hours, then sieved to obtain different particle sizes.

The BET surface area of various particle sizes of cork (Cork 1 0.16–2 mm, Cork 2 0.08–0.16 mm and Cork 3 < 0.08 mm) was measured from the N_2 adsorption at 77 K with an Asorptiometer type ASAP 2010 B. Prior to these measurements, the samples were dried in an oven at 140 °C overnight and then quickly introduced into a testing tube. This later was heated to 200 °C and depressurised for 4 h.

The Infrared spectra of the adsorbent sample were measured as potassium bromide pellets using a Perkin Elmer model spectrum one FTIR Spectrometer.

Batch mode adsorption studies were carried out using a thermostated mechanical shaker (Hidolph RZR 2020) containing one litre of different Cr(VI) concentration solutions including one gram of different particle sizes of cork powder. The solutions were adjusted at different pH values and agitated at 250 rpm. Liquid and adsorbent were separated by filtration. The Cr(VI) concentration remaining in the supernatant was measured using a spectrophotometer (1601 Shimadzu) through the development of a purple-violet colour with 1,5-diphénylcarbazide in acidic solution at a wavelength of 540 nm.

Cr(VI) synthetic solutions were prepared by dissolving $K_2Cr_2O_7$ in distilled water.

Batch experiments were carried out in a glass beaker by adding 1 g of cork powder to 1 L of Cr(VI) synthetic solution at 5 mgL^{-1}. The pH and temperature were fixed at respectively 5.86 and 25 ± 1 °C. The contact time of the agitated mixtures varies from 1 min to 4 h. The adsorbent and adsorbate were separated by filtration before measuring the remaining Cr(VI) concentration.

The effect of particle size on the adsorption was investigated by using three domains of diameters (*d*): 0.16 < d < 0.2; 0.1 < d < 0.16; 0. and d < 0.08 mm at a temperature of 25 ± 1 °C and a Cr(VI) concentration of 0.5 mg L^{-1}.

The contact time was fixed at 3 h for all experiments.

The effect of pH on the Cr(VI) removal was investigated by testing five values of pH: 1–5 with 1 pH unit step at a temperature of 25 ± 1 °C and for 3 Cr(VI) concentrations: 0.5, 5 and 10 mg L^{-1}. The contact time was fixed at 3 h for all experiments.

Experiments were conducted by varying the initial Cr(VI) concentration in the range of 0.5–500 mg L^{-1} and agitating 1 L of the solution containing 1 g of cork powder during 3 h at different temperatures (i.e., 25, 35 and 45 °C). The system pH was adjusted between 2.5 and 3.

3. Results and discussion

3.1. Cork powder characterisation

3.1.1. BET surface area measurements

The BET surface area measurements (Table 1) show that, even if the diameters are very weak, we can see that the lower the cork particle size the higher the total contact surface area. The surface areas are considerably lower than those for the activated carbon presented in the literature. It can be attributed to that the

Table 1 Cork powder BET surface area vs. cork diameter.

Cork particle size	BET surface area (m^2 g)	Vm (cm^3 g) STP
Cork 1 (0.16–2 mm)	2.1095	0.484597
Cork 2 (0.08–0.16 mm)	2.8545	0.655722
Cork 4 (< 0.08 mm)	3.0245	0.694786

cork has probably a surface with macropores (diameters higher than 50 nm, according to IUPAC) (Domingues et al., 2005).

3.1.2. FTIR spectra

The FTIR spectra of the cork waste are shown in Fig. 1. The figure shows clearly that the spectra displays a number of absorption peaks, indicating the complex nature of the cork waste of Quercus Suber L. The bands at 3432 cm^{-1} representing bonded –OH groups. The bands observed at about 2922–2851 cm^{-1} could be assigned to the C–H stretch. The peaks around 1735 and 1631 cm^{-1} correspond to the C=O stretching. The C–O band absorption peak is observed to shift to 1036.02 cm^{-1}. Thus it seems that this type of functional group is likely to participate in metal binding. Among these absorption peaks particularly the bonded –OH groups, C=O stretching and carboxyl groups were especially involved in chromium biosorption (Malkoc et al., 2006).

3.2. Equilibrium time

At the fixed pH value of 5.86, the remaining Cr(VI) concentration decreased with the increase of the contact time until becoming constant after 3 h of contact with the solution. This highlights the reaching of an equilibrium at which the Cr(VI) concentration remains constant, in the solution, indicating a state of "cork saturation" with respect to Cr(VI), under the experimental conditions of the test (1 L of solution 5 mg L^{-1} Cr(VI), 1 g of cork), as shown in Fig. 2.

3.2.1. Adsorption kinetics

Kinetics of heavy metals adsorption was modelled by the first order Lagergren Eq. (1) (Kurniawan et al., 2006; Fontecha-Camara et al., 2008; Aroua et al., 2008; Khambhaty et al., 2009; Verma et al., 2006; Namasivayam and Sureshkumar, 2008; Khezami and Capart, 2005; Ho and Mackay,1998; Psavera et al., 2005; Makoc & Nuhoglu, 2007; Ünlü and Ersoz, 2006), the pseudo-second-order Eq. (2) (Namasivayam and Kadirvelu, 1999; Fontecha-Camara et al., 2008; Aroua et al., 2008; Khambhaty et al., 2009; Verma et al., 2006 and Namasivayam and Sureshkumar, 2008; Khezami and Capart, 2005; Ho and Mackay, 1998; Psareva et al., 2005; Malkoc and Nuhoglu, 2007; Ünlü and Ersoz, 2006).

$$\log(q_e - q_t/q_t) = \log q_e - k_1 t/2.303 \qquad (1)$$

$$t/q_t = 1/kq_e^2 + t/q_e \qquad (2)$$

where:

k_1 is the Lagergren rate constant of adsorption (min^{-1});

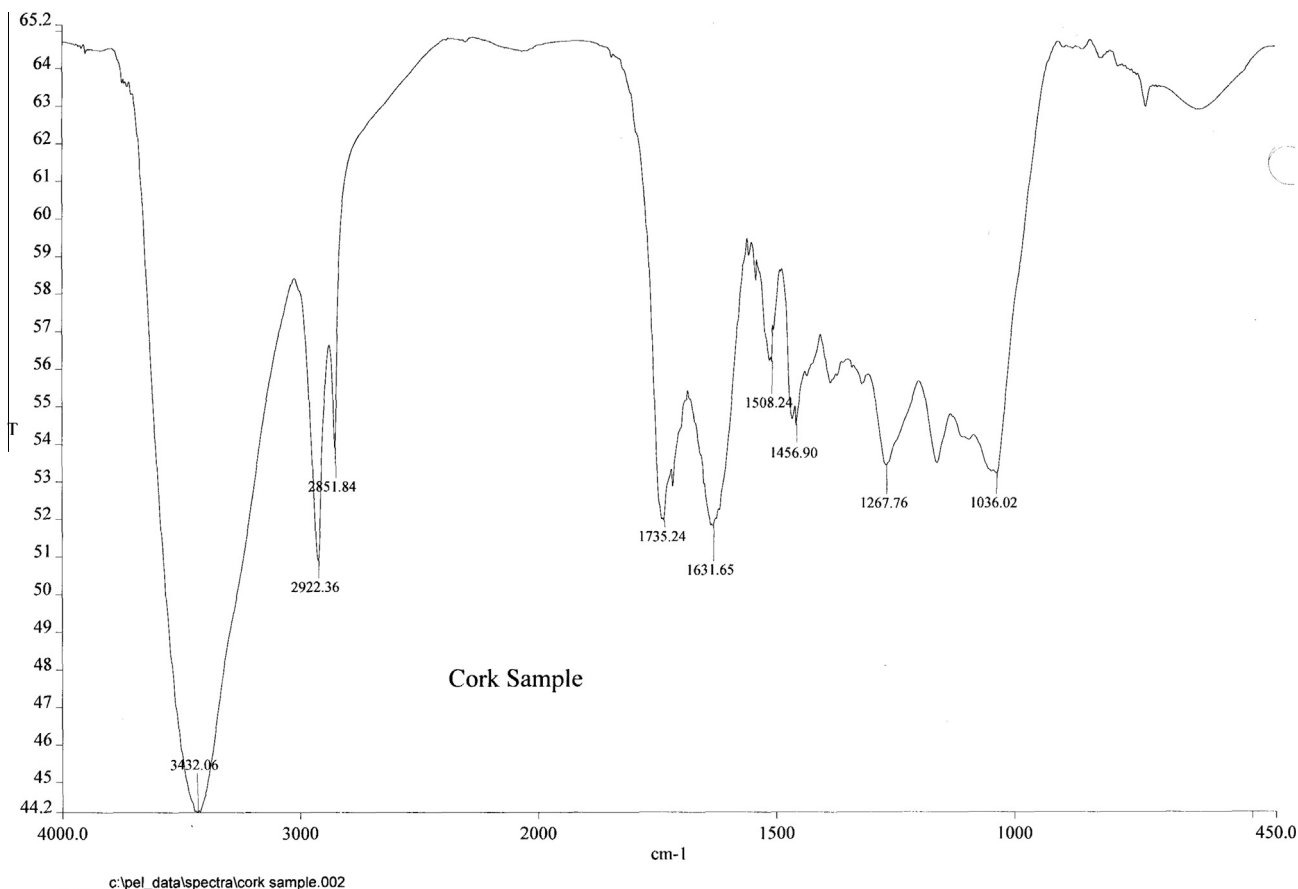k the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1});
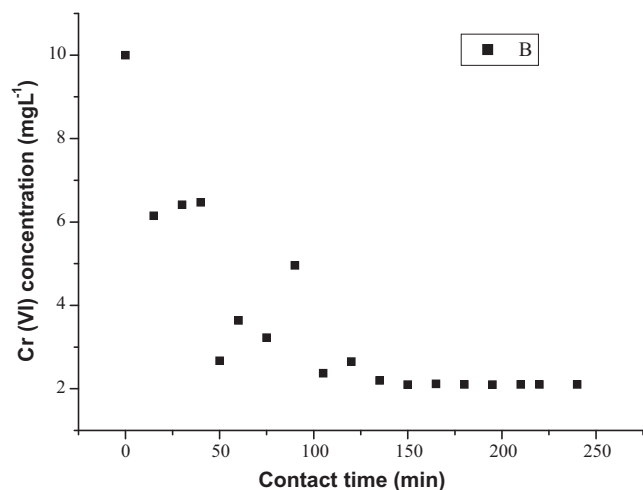
Figure 1 FTIR of cork powder.

Figure 2 Equilibrium time of Cr(VI) concentration vs. contact time.

q_e and q_t are the amounts of metal ion adsorbed on the sorbent (mg g^{-1}) at equilibrium and at time t, respectively.

Linear plots of t/q_t vs. time are shown in Fig. 3. It was evident from this figure that the Cr(VI) adsorption by cork followed pseudo-second-order kinetics. From this curve we can determine the slope $1/q_e$ then q_e and the intercept $(1/k \ q_e^2)$ which gives k, the pseudo second order rate constant.
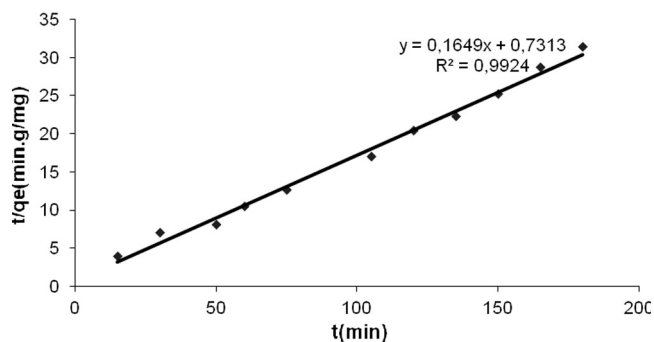

Figure 3 Pseudo-second-order adsorption kinetics.

Calculations give the following results: $q_e = 6.064$ mg g^{-1} and $k = 0.037$ g mg^{-1} min^{-1} (Gupta et al., 2001, Khezami and. Capart 2005, Ho and Mackay, 1998; Psareva et al., 2005; Malkoc and Nuhoglu, 2007 and Ünlü and Ersoz, 2006).

3.3. Particle size effect

The effect of varying particle size on the Cr(VI) adsorption is shown in Fig. 4. We can notice that particle size plays a very important role on the Cr(VI) adsorption. The adsorption percentage increased as the particle size is lowered. Indeed, the best rate is 77% for the particle size $d < 0.08$ mm.
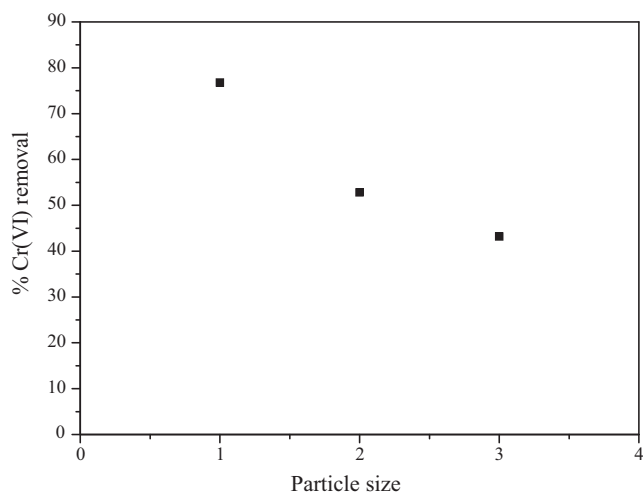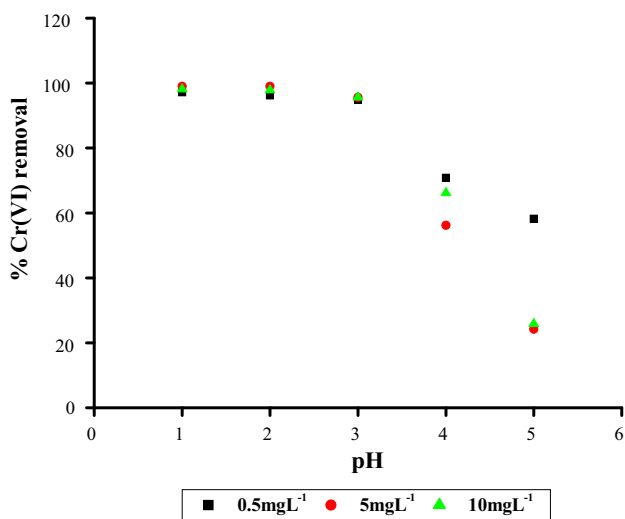
Figure 4   Cork particle size effect on Cr(VI) adsorption.

Even if the specific surface areas are very low, the considerable increase in the adsorption efficiency can be attributed to the active sites for adsorption density at the surface of cork powder which will increase even with a slight increase of particle surface area.
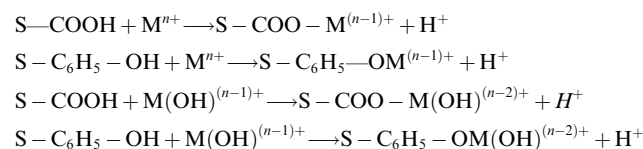
3.4. pH effect

The effect of solution pH on the adsorption of Cr(VI) on cork is shown in Fig. 5, where we can note that, for the three initial Cr(VI) concentrations used, the pH plays a very important role. Each point of the curve is obtained when the adsorption had reached the equilibrium state, that is to say when the Cr(VI) concentration becomes constant in the solution. We can observe that the Cr(VI) removal ratio is found between pH values of 1 and 3 for the three tests series. This ratio decreases rapidly to 60% when pH increases towards 4, then until 30% when the pH value reaches 5. The high adsorption capacity of Cr(VI) in lower pH ranges has been reported by many authors. However if pH decreases under 2.5, Cr(VI) removal becomes inefficient.
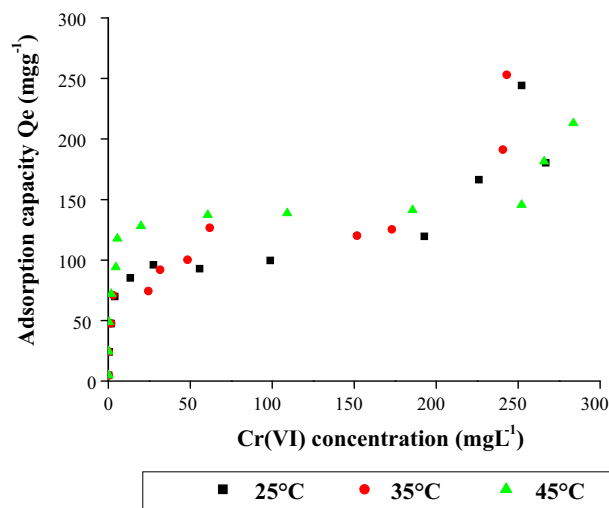
This can be attributed to the reduction of Cr(VI) to Cr(III) at low pH values on the surface of cork, encouraging the adsorption phenomena on one hand, and electrostatic attraction of the highly protonated cork surface to the major chromium species ($HCrO_4^-$) encouraging the complexation phenomena, on the other hand. Under this pH, according to (Ranganathan, 2000), the chromium ions are in solution.

Uptake of hexavalent chromium at pH between 2.0 and 6.0 is a H^+–M^{n+} exchange process. The possible sites on the adsorbent include groups which are the source of H^+ ions ($-C_6H_5-OH$ and $-COOH$ functional groups) where protons can be exchanged for cations:

$$S-COOH + M^{n+} \longrightarrow S-COO-M^{(n-1)+} + H^+$$

$$S-C_6H_5-OH + M^{n+} \longrightarrow S-C_6H_5-OM^{(n-1)+} + H^+$$

$$S-COOH + M(OH)^{(n-1)+} \longrightarrow S-COO-M(OH)^{(n-2)+} + H^+$$

$$S-C_6H_5-OH + M(OH)^{(n-1)+} \longrightarrow S-C_6H_5-OM(OH)^{(n-2)+} + H^+$$

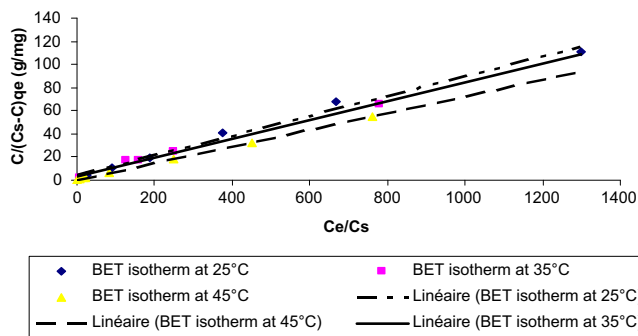S denotes the surface.

In the solution, the reaction of metal ions with the biomass can be described by the following equilibrium:

$$H_nB/M^{n+} <=> MB/nH^+ \tag{3}$$

Figure 6   Adsorption isotherms at: D 25 °C, B 35 °C and C 45 °C.

Figure 5   Effect of pH on Cr(VI) adsorption on cork at different initial Cr(VI) concentrations.

Figure 7   BET isotherm sets: at 25 °C (set 1), 35 °C (set 2) and 45 °C (set 3).

Table 2 BET constants at different temperatures.

Temperature (°C)	$(B-1)/q_mB$	$1/q_mB \times 10^6$	R^2	B	q_m (mg/g)
25	0.0087	4	0.9869	2176	114.89
35	0.0079	3	0.9927	2634.42	126.53
45	0.0071	0.7	0.9984	10143.94	140.83

where M represents the metal, n its charge and B the biosorptive active centres.

Taking into account the reaction (3), the pH should influence the metal ion biosorption because of the competition between the metal and H^+ ions for the active biosorption sites. Furthermore, the pH dependency on the metal ion uptake by the biomass can also be justified by the association-dissociation of certain functional groups, such as carboxylic groups. In fact, it is known that at low pH, most of these groups cannot bind the metal ions in solution, although they may take part in complexation reactions (Chubar et al., 2004).

3.5. Adsorption isotherms

Increasing Cr(VI) concentration decreased the removal ratio at $2 <$ pH < 3 after four hours of experience, but the amount per gram of cork increased. In this case it is more interesting to plot adsorption isotherms in terms of the adsorption capacity q_e (ml of Cr(VI) per grams of cork) versus the Cr(VI) equilibrium concentration C_e (mg L^{-1}).

Fig. 6 presents these experimental adsorption isotherms at three temperatures (i.e. 25, 35 and 45 °C $\pm$ 1 °C) with an initial concentration of metal ions in solution varying from 0.5 to 500 mg L^{-1}.

All the adsorption isotherms are type IV, which can be explained by the fact that the adsorption occurs in multilayer form. The first zone describes the first lay adsorption which can be physically or chemically adsorbed with a strong adsorbate/adsorbent interaction and the second zone describes adsorption on the next lays physically adsorbed after the first lay saturation.

As seen in Fig. 6, we have a multilayered type adsorption, so the BET model is the most appropriate in this case. Fig. 7 shows the linear form of BET isotherms for all the three used temperatures.

The BET isotherm is based on the simplifying assumptions that each molecule, in the first adsorbed layer, serves as the site for the adsorption of a molecule into the second, and so on.

The resulting equation for the BET equilibrium isotherm for the adsorption from solution takes the form (Faust and Aly, 1987):

$$q = \frac{q_m B C_e}{(C_s - C_e)[1 + (B-1)\frac{C_e}{C_s}]} \quad (4)$$

Where: $q = x/m$: the amount of adsorbed solute x per unit weight adsorbent m; C_e: equilibrium concentration of the solute; q_m: amount of solute adsorbed per unit weight of adsorbent required for a monolayer capacity; C_s: concentration of the solute in water at a specified temperature; B: a constant. Transforming Eq. (4) to Eq. (5):

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_mB} + \frac{[(B-1)]}{q_mB}\frac{C_e}{C_s} \quad (5)$$

shows that a plot of the left side against C_e/C_s should give a straight line having slope $(B-1)/q_mB$ and intercept $1/q_mB$. Table 2 shows R^2, B and q_m for each work temperature (Chubar et al., 2004).

4. Conclusions

The results demonstrated that cork biomass, a waste material from cork board factories, is an efficient adsorbent for Cr(VI) from aqueous solutions. The removal percentage depended on contact time, particle size, temperature, initial Cr(VI) concentration and the pH of the system. Among all parameters of the survey, the pH is the most influential on Cr(VI) adsorption. The highest Cr(VI) adsorption was around 97% at system pH between 2.5 and 3. So we can say that this last parameter plays a very important role in the biosorption of Cr(VI) mechanism onto cork biomass. This biosorption is of type multilayered and the BET model is applicable.

The results obtained in this work indicate that cork wastes may be used as cheap natural sorbent for Cr(VI).

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