Chemical Engineering Journal 148 (2009) 473–479

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The effect of pH on the biosorption of Cr (III) and Cr (VI) with olive stone

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ARTICLE INFO

Article history:
Received 18 December 2007
Received in revised form 9 September 2008
Accepted 20 September 2008

Keywords:
Biosorption
Heavy metals
Chromium
Olive stone
Agricultural waste

ABSTRACT

In this work, the biosorption of trivalent and hexavalent chromium has been studied using olive stone, a low-cost natural sorbent, analysing the pH effect in the biosorption process. Removal of Cr (III) and Cr (VI) with olive stone is very sensitive to solution pH. The percentage of Cr (III) removed reaches a maximum at range pH between 4 and 6, reaching values close to 90%. However, at pH 3 the retention of Cr (III) is less than 50%. The percentage of Cr (VI) removed is higher than 80% when the pH is equal or lower than 2, whereas as the pH increases this percentage drops to values than 15%. Also, the results obtained for the final concentration of total Cr, Cr (VI) and Cr (III) indicate that a combined effect of biosorption and reduction is involved in the Cr (VI) removal specially when the pH value is lower than 3.

1. Introduction

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several ecosystems with the accumulation of many pollutants, especially heavy metals. Chromium is a highly toxic metal, considered as a priority pollutant because of its mutagenic and carcinogenic properties. The industrial use has increased, because of the extensive use of chromium in electroplating, tanning, metal finishing, textile industries, etc. Among its several oxidation states, trivalent and hexavalent species of chromium are mainly found in these industrial effluents [1,2].

The conventional physical–chemical methods for removal of heavy metals from effluents include precipitation, ion exchange, reverse osmosis, oxidation, which are, in some cases, highly expensive and ineffective at lower concentrations of metal ions [3,4]. The use of biological systems for the heavy metal elimination from diluted solutions has the potential to obtain better results and at low cost. Also, searching for a low-cost and easily available adsorbent has led to the investigation of materials from agricultural and biological origin, along with industrial by-products, as solid sorbents, which included apple residues [5], olive pomace [6,7], rice milling by-products [8], *Pinus sylvestris* sawdust [9], beer yeast [10] and olive stone [11].

Research into finding new uses for olive products, particularly by-products of olive oil production, is of great relevance not only to the economy, but also to the environment, in the towns where olives are grown. Olive stone results from olive oil and table olive production, and can be used as mainly a renewable energy source. The new designs of biomass boiler system facilitate the use of olive stone as fuel for the generation of heat and electricity [12,13].

In this work, olive stone has been used as trivalent and hexavalent chromium sorbent from aqueous solutions. The influence of solution pH has been analysed, which is one of the most important parameters for the elimination of metals present in aqueous media through biosorption. According to numerous authors, the pH variation can affect the characteristics and availability of the metal ions in solution, as well as modify the chemical state of the functional groups responsible for the biosorption [14,15]; also, the majority of research carried out on heavy metal biosorption indicates that the pH influence is due to the fact that H^+ ions are strong competitors of the corresponding ions of the sorbent [7,16–18].

2. Materials and methods

2.1. Biosorbent

In all the experiments, olive stones from the extraction plant for orujo oil “Cooperativa Nuestra Señora del Castillo” located in Vilches (Jaén), Spain, were used.

The olive stone was obtained through a separation process of the orujo by an industrial machine with a production capacity of 1500 kg/h and fitted to a 4-mm diameter using a sieve separator, which is the standard size used in this industrial process. The

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doi:10.1016/j.cej.2008.09.026

Table 1
Chemical characteristics of the olive stone.

Water, %	5.43
Fatty compounds, %	Negligible
Elemental analysis, %	
C	52.34
H	7.11
N	0.03
S	<0.1
O	40.47

original olive stone, with sizes ranging from 4 to 8 mm, was then ground in a hammer micromill and were sorted according to size with a high-vibration screen. For all experiments, the size selected was <1.0 mm.

The data of the chemical characteristics (elemental analysis and water and fat contents) of the olive stone are given in Table 1. The stone obtained contain between 5 and 10% humidity and amount negligible of fatty compounds. On the other hand, acid–base properties of olive stone were characterised by a mechanistic model denoting that this biosorbent is characterised by a main kind of active site (carboxylic groups) [19].

2.2. Solutions preparation

Cr (III) solutions and Cr (VI) solutions were prepared by dissolving chromium nitrate ($Cr(NO_3)_3$) and potassium dichromate ($K_2Cr_7O_2$) in distilled water, respectively. The pH of the solutions was adjusted with 0.1N solutions of sodium hydroxide and hydrochloric acid. All chemicals used in this work were of analytical grade (supplied by Merck).

2.3. Biosorption experiments

The experiments were performed by mixing 0.7 g of olive stone with a particle size <1.0 mm in 50 mL of the synthetic chromium ion solutions with a predetermined concentration of metal ion. These solutions were taken and placed in a 100-mL jacketed reactor that is connected to a thermostat-controlled bath. pH of the solution was adjusted at pH range studied and temperature set at 25 °C. The suspension was agitated with a shaker at a constant speed of 700 rpm for a contact time of 120 or 300 min that was confirmed to be more than adequate time for establishing sorption equilibrium at 25 °C for the biosorption of Cr (III) and Cr (VI), respectively [20].

Once the given operation time had elapsed, the liquid phase was removed from the reactor and centrifuged for 10 min and the liquid equilibrium concentration was analysed.

2.3.1. Biosorption of single Cr (III) and Cr (VI)

Experiments were carried out to verify the effect of pH in the biosorption of Cr (III) and Cr (VI) by olive stone, using a initial concentration of 10 mg/L and varying the pH from 3 to 11 according to previous studies [18].

Contact times of 120 and 300 min were chosen for Cr (III) and Cr (VI), respectively (previous studies have shown that Cr (VI) biosorption is produced slower than Cr (III) biosorption).

Atomic absorption spectrophotometry (PerkinElmer model 3100 fitted with a hollow cathode lamp and air-acetylene flame) was used to determine the Cr (III) concentration present in the solution for biosorption of single Cr (III).

For biosorption of single Cr (VI), the final total chromium (Cr (VI) + Cr (III)) concentration present in the solution was determined by atomic absorption spectrophotometry, and the final Cr (VI) concentration was determined by UV spectrophotometry (Thermo model Genesys 6 at a wavelength of 540 nm) using the 1.5-diphenyl carbazide method [21], obtaining, therefore, the final concentration of Cr (III) by difference.

On the other hand, to analyse the pH effect in the chromium solutions, some experiments were initially carried out without the biosorbent.

2.3.2. Biosorption of Cr (III)/Cr (VI) mixtures

Experiments were carried out using three mixtures Cr (III)/Cr (VI): 5/15, 10/10 and 15/5 mg/L, and varying the pH from 1 to 4. The rest of the parameters were adjusted in accordance with the results obtained previously, an olive stone concentration of 14 g/L, a contact time of 120 min and a temperature of 25 °C.

2.4. Fourier transform infrared spectroscopy

The chemical characteristics of native, Cr (III) and Cr (VI) bound olive stone were analysed and interpreted by FTIR spectroscopy. Each 1 mg dried sample (24 h P_2O_5) was mixed with 200 mg of KBr (Spectranal) and pressed under vacuum. The tablet recovered with a clip was immediately analysed with a spectrophotometer in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1}.

For studying the FTIR spectra after the Cr (III) and Cr (VI) biosorption, an initial chromium concentration of 10 mg/L, a biosorbent concentration of 14 g/L and the pH values 4 and 2 for Cr (III) and Cr (VI), respectively, were chosen.

3. Results and discussion

3.1. Biosorption of Cr (III)

Fig. 1a shows the final concentrations of Cr (III) obtained in a pH range of 3–11 for the experiments carried out in absence of the biosorbent. The final concentration present in the solution decreases as the pH increases until it reaches a minimum of pH 7, increasing again as the pH continues to rise. This indicates that the chromium precipitates in the form of $Cr(OH)_3$ at near-neutral pH values.

In this sense, it is well known that Cr^{3+} in water can undergo hydrolysis and/or complexation reactions whose extension mainly depends on the total Cr (III) concentration, the pH and the type of anions present in the solution. The simple Cr^{3+} hydrolysis can be shown as follows:

$$Cr^{3+} + H_2O \Leftrightarrow Cr(OH)^{2+} + H^+ \quad (1)$$

This reaction generates $Cr(OH)^{2+}$ and protons which contribute to the increase of the acidity of Cr (III) solutions. If Cr^{3+} is retained by the biomass, the reaction moves to the left, consuming protons and, therefore, increasing the pH of the media; however, if the biosorbent retains $Cr(OH)^{2+}$, the reaction moves to the right, releasing protons, which increases the acidity of the media. In the same way, the pH of the solution can also be modified due to the release or retention of protons on the part of the biosorbent.

On the other hand, it is important to know about the species that will be predominant in the solution as a function of the pH. Fig. 1b shows the speciation diagram for Cr (III) at 25 °C and 10 mg/L ion content [22–24]. The species that appear in $Cr(NO_3)_3$ aqueous solutions are the following:

- At pH values lower than 3 the predominant species is Cr^{3+}.
- At pH close to 4 approximately the same proportion of Cr^{3+} and $Cr(OH)^{2+}$ exists.
- At pH values close to neutrality, the chromium is mainly found precipitated as $Cr(OH)_3$.
- At a basic pH the predominant species is $Cr(OH)_4{}^-$.

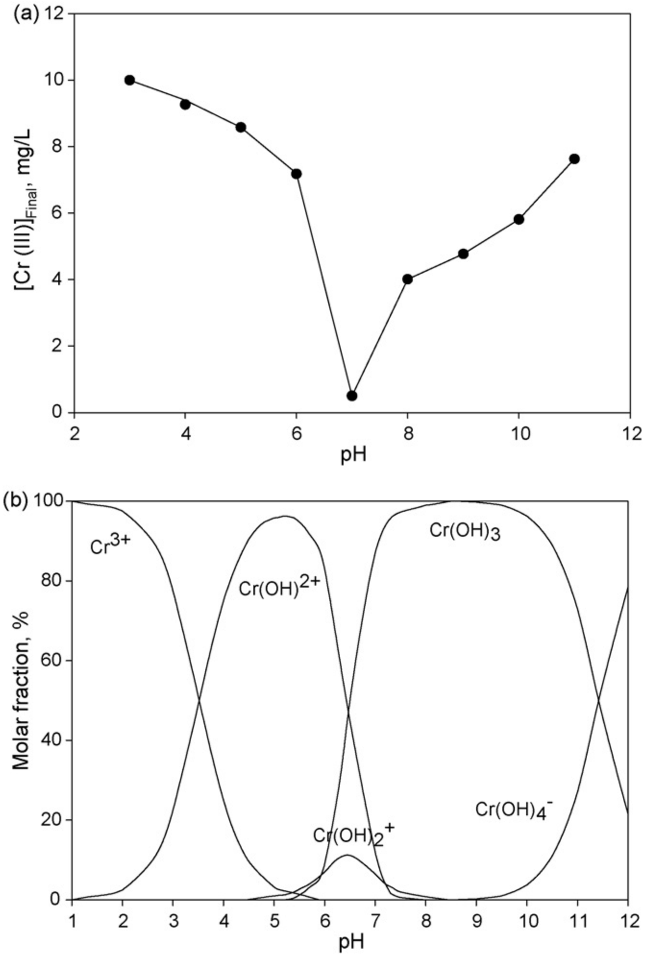

Fig. 1. (a) Final concentration of Cr (III) obtained in a pH range of 3–11 for the experiments carried out in absence of the biosorbent. (b) Speciation diagram for Cr (III) at 25 °C and 10 mg/L ion content.

Fig. 2 shows the effect of pH in the biosorption of Cr (III) by olive stone. The percentage of removed chromium reaches a maximum at a pH value of between 4 and 6, reaching values close to 90%. However, at pH 3 the percentage of removed chromium is less than 50%. These results may indicate that the retention of chromium ions by the olive stone is mainly due to the ionic attraction between metal ions and the biosorbent functional groups, mainly carboxylic groups. In this sense, some authors [7,22,25–29] indicate that at low pH values, H^+ ions and metal ions compete against each other, while at high pH values the retention can decrease due to the competition between the formation of the hydrated types of the metal and active biosorbent sites, the modification of the superficial charge of the solid and/or the corresponding salt precipitation.

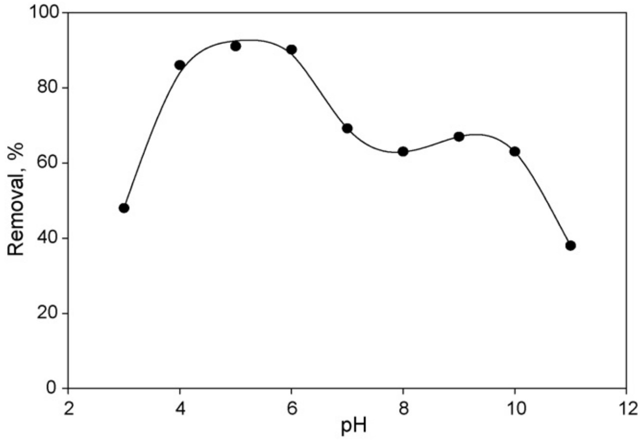

Fig. 2. Percentage of Cr (III) removed versus solution pH.

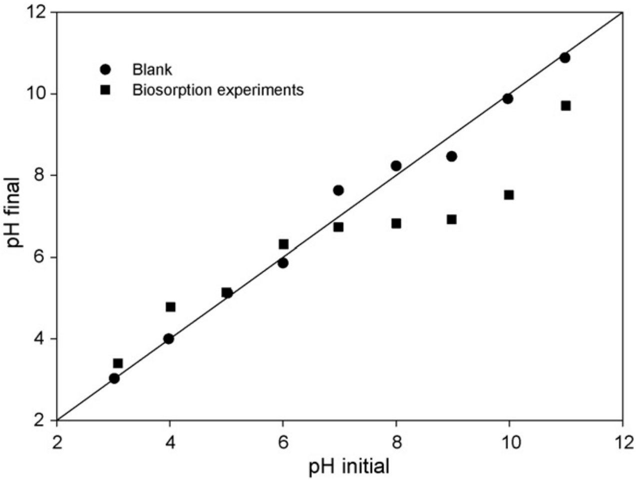

Fig. 3. pH variation in the blank experiments (without olive stone) and during the biosorption process of Cr (III).

On the other hand, the pH value also affects the ionic state of the functional groups presented in the biosorbent and involved in the metal binding. So, the effect of pH also can be explained in terms of pH of the point of zero charge, pH_{pzc}. Previous pH drift tests indicated that the zero point of charge of the olive stone was at pH 4.38 [30]. From an electrostatic interaction point of view, the biosorption of the Cr (III) species on the olive stone at pH below 4.38 would be electrically unfavourable or repulsive because, at these pH values, the surface charge of olive stone is positive. However, when the pH values increase and pH is higher than pH_{pzc}, the surface charge of the sorbent is negative and to bind Cr (III) cation is favoured. This explains the observed increase of biosorption of the Cr (III) on the olive stone for pH increase from 3 to 6 (see Fig. 2).

Finally, during the 120-min duration of the experiment, the pH was also observed in both blank (without olive stone) and biosorption experiments. The results are shown in Fig. 3.

In the experiments without the olive stone the pH is practically constant, with a small fluctuation of pH values between 6 and 8, where, as illustrated in Fig. 1, the highest chromium hydroxide precipitation occurs. Nevertheless, in the biosorption experiments, at pH values of between 3 and 6, the final pH is slightly higher than the initial one, which may be justified by the retention of H^+ ions by the biosorbent. Starting from pH 6, a decrease in pH is clearly observed as a function of contact time which, as previously mentioned, could be related to the formation of hydrated types and their retention by the olive stone with the consequent release of H^+ ions.

Therefore, for the study of the biosorption process it is necessary to work with pH values lower than 5, because to work at higher pH values produces a combined biosorption–micro-precipitation process with predominance of the latter, in some cases.

3.2. Biosorption of Cr (VI)

The oxidation state of chromium and the pH are two of the factors, which most affect the biosorption process. It has been verified that Cr (VI) can be easily reduced to Cr (III) in the presence of particular solid sorbents and in acid media. Although the studies carried out on chromium elimination by biosorption are numerous, few of them have analysed the combined effect of the retention of Cr (VI) by the solid sorbent and its reduction to Cr (III). Therefore, it can be stated that the mechanism for chromium retention would really imply two simultaneous processes [31–33]:

- The reduction of Cr (VI) to Cr (III) in presence of the biosorbent and in acid media.
- The retention of the initially present Cr (VI) by the biosorbent, as well as of the Cr (III) formed during the reduction process.

To analyse the pH effect in Cr (VI) biosorption by olive stone, experiments were first carried out in absence of the biosorbent. The results show that the total Cr and Cr (VI) practically coincide in all the pH range, with only the normal differences between them resulting from the use of two different analytical techniques for their determination, which indicates that, in absence of the olive stone, a reduction of Cr (VI) to Cr (III) does not occur. In the same way, the final chromium concentration in the solution is practically equal to the initial one (10 mg/L), therefore, a precipitation does not occur as in the case of Cr (III).

On the other hand, Cr (VI) is easily hydrolysed in water. The predominant Cr (VI) species for concentrations less than 500 mg/L are the $HCrO_4^-$ and CrO_4^{2-} anions. The equilibrium reaction between the two species is greatly dependent on the pH.

$$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-} \tag{2}$$

At low pH values, $HCrO_4^-$ is the predominant species, whereas CrO_4^{2-} is mainly present at higher pH values. On the other hand, other species of chromium coexist in the acid media ($Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$), so that a decrease in pH would lead to the formation of different oxidised chromium species [23,31,34,35].

Therefore, as all Cr (VI) species are negatively charged, a decrease in pH causes the sorbent surface to charge positively due to the protonation of the active groups, creating a strong attraction for the negatively charged Cr (VI) ions. However, as the pH increases, the H^+ concentration decreases and the surface charge of the sorbent becomes negative, which would prevent the retention of the chromium species. This would justify a decrease in Cr (VI) biosorption as the pH increases in the media [35,36].

Experiments were carried out to verify the effect of pH in Cr (VI) biosorption by olive stone. Fig. 4a shows the final concentration of the total Cr, Cr (VI) and Cr (III) in a pH range of 1–4, and Fig. 4b shows the percentage of removed total Cr and Cr (VI) as a function of pH to illustrate more clearly the results obtained.

The percentage of removed Cr (VI) is higher than 80% when the pH is equal or lower than 2, whereas when the pH increases this percentage drops to values less than 15%. Similarly, the percentage of removed total Cr is close to 50% at a pH of 1, 1.5 and 2, decreasing notably when the pH increases.

These results indicate that the biosorption process of Cr (VI) by olive stone is greatly dependent of the solution pH, since it varies from being almost totally removed to practically nothing being removed in a very narrow pH range. These results agree with those obtained by numerous authors using other solid sorbent, which justify that the Cr (VI) biosorption is only produced in very acid media (pH < 2), because the active groups of the biosorbent are protonated, acquiring a positive charge, and therefore, are able to attract Cr (VI) species which are negatively charged [36–39].

On the other hand, the results obtained for the final concentration of total Cr, Cr (VI) and Cr (III), indicate that, at pH values lower than 3, a combined effect of the Cr (VI) biosorption by the olive stone and its reduction to Cr (III) is produced. At pH values lower than 2, approximately 50% of Cr (VI) is removed and the other 50% is reduced, being both processes of equal importance. The chromium reduction can take place through various reactions, mainly the following:

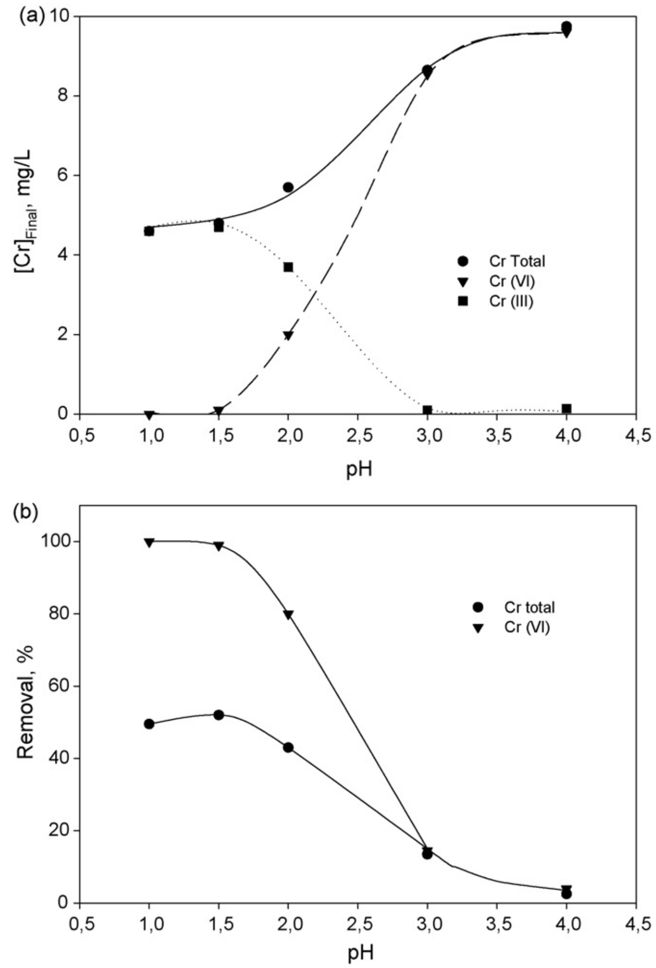

Fig. 4. (a) Final concentration of total Cr, Cr (VI) and Cr (III) in a pH range of 1–4. (b) Percentage of total Cr and Cr (VI) removed versus solution pH.

$$HCrO_4^- + 7H^+ + 3e^- \Leftrightarrow Cr^{3+} + 4H_2O \tag{3}$$

$$CrO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Cr^{3+} + 4H_2O \tag{4}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \Leftrightarrow 2Cr^{3+} + 7H_2O \tag{5}$$

All these reactions are influenced by the structure of the reagent, the nature of the media where the reaction takes place and its pH. Proton consumption is produced in all of them; thus, the reduction of Cr (VI) to Cr (III) is produced in strongly acidic media [40].

To verify the pH variation during the biosorption process, the initial pH against the final pH (corresponding to the experiments shown in Fig. 4) has been represented in Fig. 5.

pH remains almost constant when the media is strongly acidic (pH < 2) although there is a slight tendency to increase at pH 1. In very acidic media a removal of protons occurs due to the presence of functional groups with acid–basic properties in the olive stone and the reduction from hexavalent to trivalent chromium that also consumes protons. However, an increase of pH is not appreciated, probably because in a strongly acidic solution, the proton concentration is very high and this effect is not significant.

However, at pH values of 3 and 4 an increase in pH during the experiment is clearly observed, which could be justified by the removal of protons of the media by the biosorbent, since at these pH values the reduction of chromium is practically insignificant.

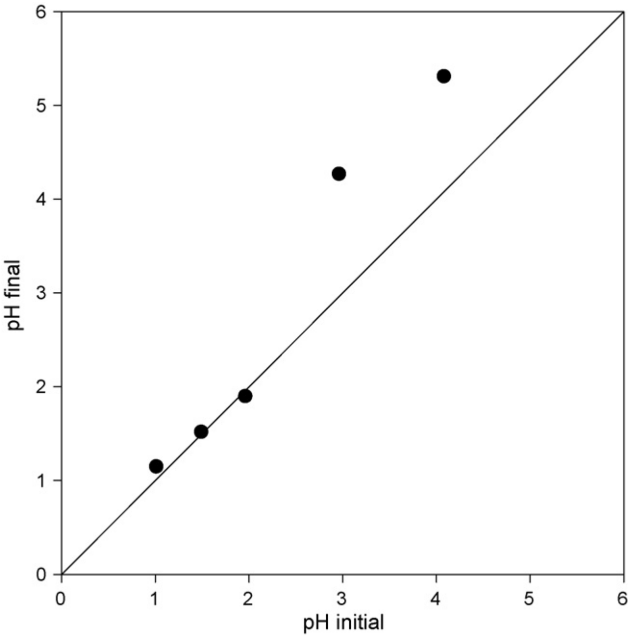

Fig. 5. pH variation during the biosorption process of Cr (VI).

These results agree with those obtained by numerous researchers, indicating that, although the protonation of the sorbent and the reduction of chromium are the main causes for the pH alteration in the media, the various pH-dependent equilibria that chromium may present when found in aqueous solutions and the interactions with solid sorbent active groups should also be considered [31,40–43].

3.3. *Biosorption of Cr (III)/Cr (VI) mixtures*

Once Cr (III) and Cr (VI) biosorption have been studied separately, the effect of pH in different Cr (III)/Cr (VI) mixtures was analysed. Fig. 6 shows the final chromium concentration as a function of pH for three mixtures Cr (III)/Cr (VI): 5/15, 10/10 and 15/5 mg/L.

For mixture 1 (5 mg/L Cr (III)/15 mg/L Cr (VI)), as the pH increases, Cr (VI) remained in the solution increases significantly, while Cr (III) decreases. If the extreme values are compared, 3.4 mg/L of Cr (VI) remained in solution at pH 1, which results in a 77.3% of Cr (VI) removed and there are 8.7 mg/L of Cr (III) in the solution, which indicates that not only any Cr (III) has been removed but also there is a greater Cr (III) concentration as a result of the Cr (VI) reduction. At pH 4, the effect is opposite, since 14.3 mg/L of Cr (VI) remain in the solution, which implies that nothing has been removed and there are 1.1 mg/L of Cr (III) (78% removal), considering that at this pH value, a Cr (VI) to Cr (III) reduction does not take place. In the other two chosen mixtures, the behaviour is similar, though proportional to the initial Cr (III) and Cr (VI) quantities in the media.

If the results obtained for the total Cr are compared, it can be observed that as the proportion of Cr (III) in the mixture increases and the pH in the media increases, the total Cr in the solution notably decreases, thus, the total removed percentage increases, which means that the olive stone has a greater Cr (III) retention capacity than that of Cr (VI), as it has been illustrated through their separate studies.

A continuous study of the pH was also carried out during the operational time with the objective to see possible changes that occur in the pH and compare them to what has been obtained through the experiments carried out separately. The results are illustrated in Table 2.

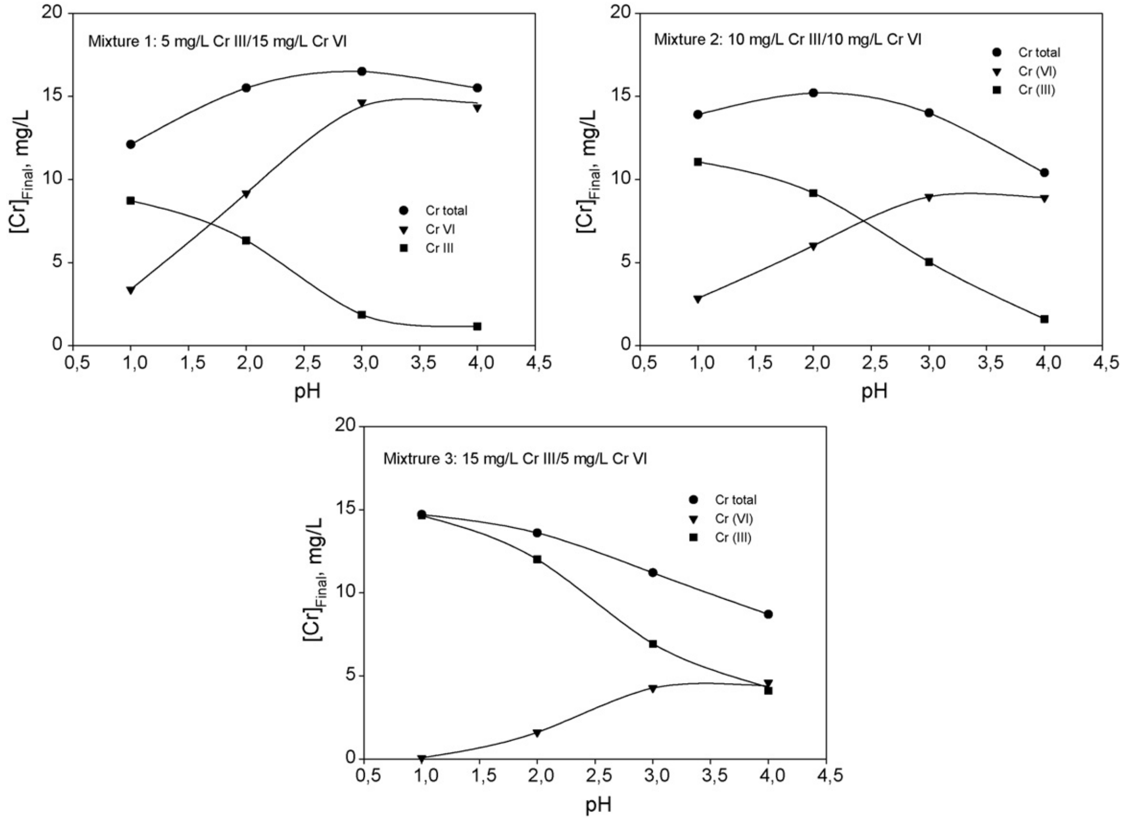

Fig. 6. Final concentration of total Cr, Cr (VI) and Cr (III) versus pH for Cr (III)/Cr (VI) mixtures.

Table 2
pH variation during the biosorption process of Cr (III)/Cr (VI) mixtures.

Mixture 1, 5 mg/L Cr (III)/15 mg/L Cr (VI)	Mixture 2, 10 mg/L Cr (III)/10 mg/L Cr (VI)	Mixture 3, 15 mg/L Cr (III)/5 mg/L Cr (VI)
pH initial/pH final		
1.03/1.02	0.99/0.92	1.04/1.06
2.04/2.24	2.08/2.21	2.01/2.16
3.01/4.42	3.03/3.89	3.05/4.08
4.07/5.09	3.95/5.03	3.96/4.90

The results are very similar to those obtained in the Cr (VI) biosorption experiments (Fig. 5), where, in all cases, a tendency for an increase in pH during the operational time exists, especially at pH 3 and 4, which is mainly justified by the removal of H^+ by the biosorbent in the media.

According to the results, the simultaneous presence of Cr (III) and Cr (VI) in the solution does not affect to the biosorption process. The results are similar to the obtained ones from the single-ion system, being the pH the main parameter of chromium removal by olive stone. Park et al. [43] reached to the same conclusion in their studies with *Ecklonia* biomass.

Subsequently, a series of experiments were performed with the objective to determine if a change in the pH during the process would allow the removal of a high quantity of chromium. Thus, it was carried out as follows: initially a mixture of Cr (III)/Cr (VI) is divided in the proportions previously considered with an initial pH equal to 1; an operational time of 120 min passes and subsequently the pH is increased to 4, continuing the experiment for another 120 min. Next, the total chromium and Cr (VI) are analysed, obtaining the results illustrated in Fig. 7, where an experiment in which the initial solution only contains Cr (VI) is included.

In the mixture where there is initially no Cr (III) (mixture 0), in the first 120 min (pH 1), Cr (VI) retention by olive stone and reduction to Cr (III) occur, since 6.71 mg/L of Cr (III) appear in the solution; during the next 120 min (pH 4), a slight decrease of both Cr (VI) and formed Cr (III) takes place, thus, at the end of the experiment 65% of Cr (VI) has been removed (including biosorption and reduction) and a 35.5% of the total Cr.

In mixtures 1, 2 and 3, a similar result is obtained during the first stage of the experiment (pH 1), since both biosorption and Cr (VI) reduction are observed, except in mixture 3 where the initial Cr (VI) concentration is very low (5 mg/L) and the reduction process is not significant. However, by increasing the pH to 4 (second phase of the experiment) a greater Cr (III) retention occurs, reaching to, in mixture 4, a 100% retention of Cr (VI) and a 45.5% retention of Cr (III) initially present in the solution.

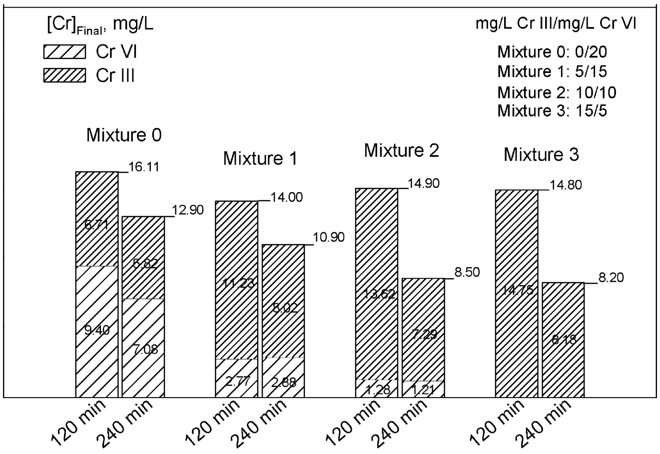

Fig. 7. Final concentration of Cr (VI) and Cr (III) for Cr (III)/Cr (VI) mixtures in the experiments carried out in two stages.

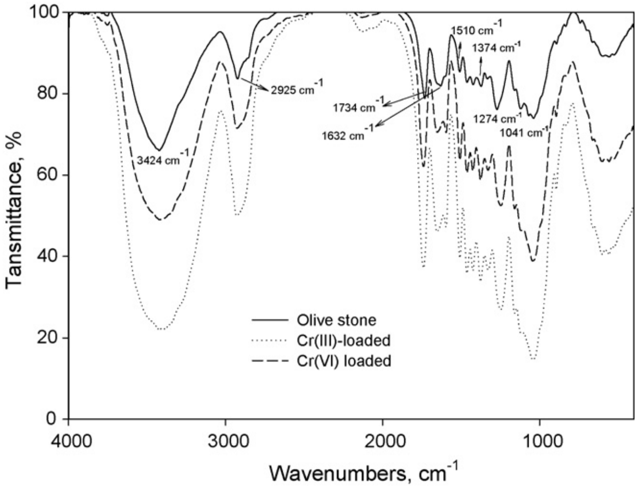

Fig. 8. FTIR spectra for native and chromium-loaded olive stone.

If these results are compared to those of Fig. 6 it can be deduced that, at pH 1, the behaviour is similar, whereas by increasing the pH to 4 a lower Cr (III) biosorption occurs during the two-stage experiments, which could be justified by the fact that, initially, by lowering the pH to 1, a protonation of the olive stone is produced, causing a change in the surface charge, which allows the retention of the Cr (VI) present to remain in an anionic form. However, by increasing the pH to 4 during the second phase of the experiment, a change in the surface properties of the sorbent is not obtained, thus, Cr (III) retention decreases.

3.4. FTIR spectra

The interactions of Cr (III) and Cr (VI) with the functional groups of olive stone were elucidated on the basis of the FTIR analyses, so FTIR spectra of chromium-loaded biomass were compared with that of the native biomass. As shown in Fig. 8, the FTIR spectrum of the native olive stone displays a number of absorption peaks, indicating the complex nature of this sorbent.

IR spectra of olive stone after the biosorption of Cr (III) and Cr (VI) denoted that main peaks observed for native olive stone are preserved; nevertheless some perturbations are induced. The transmittance decreases and some peaks change their wavenumbers. The peak around 1734 cm^{-1} (C=O stretching) shifted to higher frequencies (1741 cm^{-1}) in both cases (Cr (III) and Cr (VI)), also the peak around 1632 cm^{-1} (C=O chelate stretching) shifted to 1654 cm^{-1} [24]. The peak around 1274 cm^{-1} (C–O–C stretching) shifted to lower frequencies (1248 cm^{-1}) [44]. This result suggested that carboxyl groups could be the main groups involved in the binding of chromium during Cr (III) and Cr (VI) biosorption by olive stone.

However, significant peaks at 3424 cm^{-1} (O–H and N–H stretching), 2925 (–CH stretching), 1510 cm^{-1} (aromatic C, C=C ring stretching), 1374 cm^{-1} (COO, CH_3 stretching or OH stretching) and 1041 cm^{-1} (C–O stretching of alcoholic groups of polysaccharide) are preserved [45–47].

Finally, the pH_{pzc} value for olive stone reasonably agrees with the pK_a of carboxyl groups in biomolecules [30], which seem to be the main binding sites on the cell wall according to this characterisation of olive stone by infrared spectroscopy.

4. Conclusions

(1) The percentage of removed Cr (III) reaches a maximum at a pH of between 4 and 6, reaching values close to 90%; however, at pH 3 the percentage of removed Cr (III) is less than 50%. These results may indicate that the retention of chromium ions by the olive stone is mainly due to the ionic attraction between metal ions and the biosorbent functional groups, mainly carboxylic groups.

(2) The biosorption process of Cr (VI) by olive stone is greatly dependent of solution pH, since the percentage of removed Cr (VI) is higher than 80% when the pH is equal or lower than 2, whereas when the pH increases this percentage drops to values less than 15%.

(3) The results obtained for the final concentration of total Cr, Cr (VI) and Cr (III), indicate that, at pH values lower than 3, a combined effect of the Cr (VI) biosorption by the olive stone and its reduction to Cr (III), being both processes of equal importance in some cases.

(4) The results obtained for the biosorption of Cr (III)/Cr (VI) mixtures indicated that the optimum operational conditions should be chosen in each particular case depending on the initial concentration of both and taking into consideration the toxicity and the permitted disposal levels.

Acknowledgments

The authors are grateful to the Ministerio de Educación y Ciencia for financial support received (Project CTM2005-03957/TECNO) in the realization of this work.

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