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ORIGINAL PAPER

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Removal of trivalent chromium from tannery waste waters using bone charcoal

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Abstract The ability of bone charcoal to remove Cr(III) from aqueous solutions by adsorption has been investigated. The adsorbent used was first characterised and then the adsorption was studied as a function of time and amount of charcoal. Tests were carried out with synthetic solutions whose Cr concentrations (500 mg L^{-1}) were similar to those found in some effluents of Moroccan tannery industries. Cr removal efficiencies higher than 90% were obtained at pH 3.5 using 3 g of bone charcoal and a stirring time of about 30 min. Results of Cr removal by all sieved fractions of bone charcoal had shown the same interesting capabilities for Cr(III) retention. The cross interference with other elements was also investigated. Pretreatment of bone charcoal by nitric acid led to an increase in its specific surface area but induced a drastic reduction in its Cr elimination abilities. Adsorption tests were also carried out using calcinated bone charcoal. The results obtained showed a similar percentage of Cr retention to those found with untreated bone charcoal. On the other hand, a double treatment of bone charcoal with HCl and NaOH provided an enhancement of Cr(III) retention. The role played by the mineral fraction of the solid phase of bone was thus evidenced.

Keywords Tannery wastewaters · Chromium · Bone charcoal · Chemical treatment · Thermal treatment

Introduction

Cr is present in aqueous solutions mainly in two oxidation states, Cr(III) and Cr(VI), and due to the difference in toxicities of hexavalent and trivalent chromium, many attempts have been made to discriminate between the two species [1, 2, 3, 4, 5].

Depending on its oxidation state, Cr can be either toxic or beneficial [6, 7, 8]. Water soluble Cr(VI), is extremely irritating and toxic to human body tissue owing to its oxidising potential and easy permeation of biological membranes [2].

Cr in its trivalent form is an essential trace element for plants and animals; it is involved in glucose metabolism and nucleic acid synthesis [9]. However, Cr (III) has also been shown to be a potential hazard, especially in the aquatic environment. Mammalian in vitro tests have shown that trivalent chromium is a potential toxin, because it is a competitive inhibitor of many cellular processes [10].

The main sources of Cr pollution are mining, leather tanning, the cement industry, use in dyes, electroplating, production of steel, photographic material and corrosive paints [11]. The principal techniques for recovering or removing Cr from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents; such as activated carbon [11, 12, 13], *Pinus sylvestris* bark [14], fly ash and wollastonite [15], sphagnum moss peat [16] and bone charcoal [17], ion exchange [18, 19] and membrane technologies [20, 21]. Most of these methods suffer from some drawback such as high capital and operational costs. Therefore, there is a need for the development of low cost, easily available materials, which can adsorb Cr economically.

The main objective of this study was to evaluate the possibility of using bone charcoal as sorbent for the elimination of Cr(III) from polluted waters. Bone charcoal, commercially available in Morocco, is a product obtained

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from the calcination of bovine bones at high temperatures in the absence of air. In a previous work [17], we have shown that bone charcoal was an appropriate adsorbent for hexavalent chromium and that the process was dependent on pH, contact time and mass of bone charcoal.

First, a characterisation of bone charcoal by scanning electron microscopy, energy dispersive X-ray spectrometry (EDX) analysis and measurement of its specific area was done. Then, the parameters involved in the elimination of Cr(III) from aqueous solutions were determined. The influence of the most common ions present in tannery effluents on the Cr(III) removal was additionally investigated. Pre-treatments of bone charcoal by nitric acid and by HCl-NaOH were made in order to improve its sorption capacity towards Cr(III). Calcinated bone charcoal was also used as adsorbent in order to try to understand the mechanism of Cr elimination from aqueous solutions.

Materials and methods

Apparatus. The surface morphology and the qualitative composition of bone charcoal were determined using a JOEL 6400 scanning electron microscope equipped with a PGT EDX Analyser. Its specific surface area was determined by a Micromeritics 2100 E2 apparatus. All atomic absorption measurements were made using a Varian Spectr AA-10 flame atomic absorption spectrophotometer equipped with a Cr hollow cathode lamp.

Reagents. Bone charcoal with an average particle diameter between 0.05 mm and 0.8 mm was used as adsorbent. All the chemicals used were of analytical grade. A stock Cr(III) solution (500 mg L^{-1}) was prepared with distilled water using chromium alum [$CrK(SO_4)_2,12H_2O$]. The cross interference was studied using the following compounds: NaCl, NH_4Cl and Na_2SO_4, which were dissolved in the Cr solution at the required concentrations.

General procedure. Tests were carried out by mixing a given amount of bone charcoal with a fixed volume of a Cr(III) solution of known initial concentration. The samples were carefully stirred over a fixed time period, then filtered and the remaining Cr(III) determined in the solution by atomic absorption spectrophotometry.

Results and discussion

Adsorbent and its characterisation

Bone charcoal is a product obtained from the calcination of bovine bones at high temperatures in the absence of air. Scanning electron micrographs of this adsorbent are shown in Fig. 1.

It can be seen that the surface of bone charcoal is rough, with randomly dispersed micrometer-scale cavities. These cavities could potentially improve the adsorption of subsequent elements present in aqueous solutions.

The EDX analysis of bone charcoal gave the spectrum shown in Fig. 2. It indicated that bone charcoal contained phosphorus, carbon, oxygen, calcium, magnesium and sodium. Phosphorus, oxygen and carbon were the dominant constituents. The surface area of bone charcoal was determined by the BET method and it was evaluated to be 83 m^2/g.

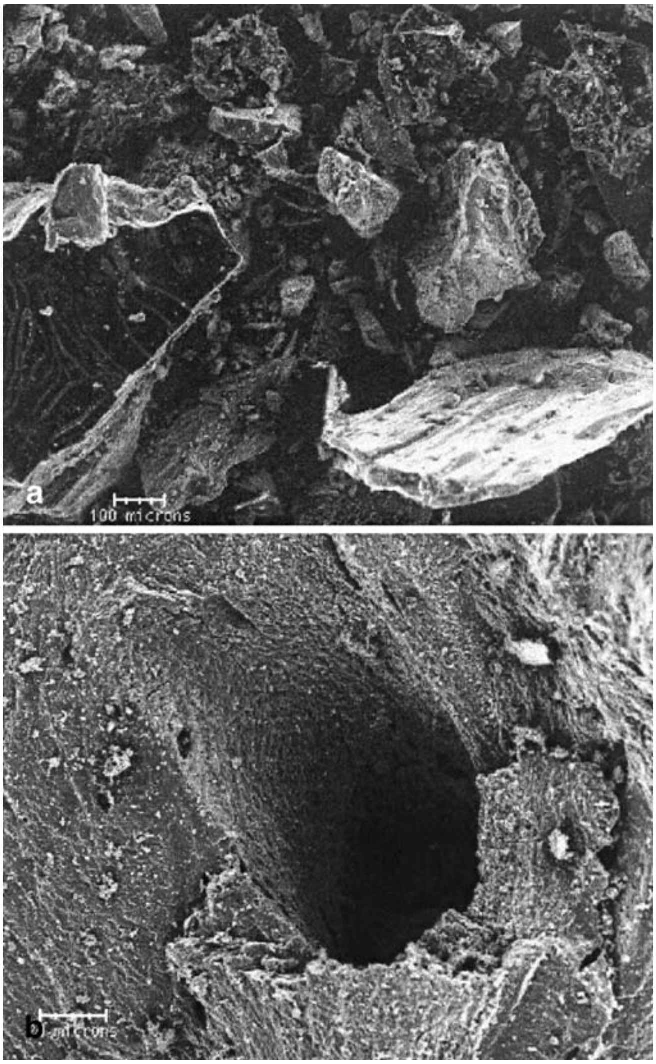


Fig. 1 Scanning electron micrograph images of bone charcoal

Effect of time contact

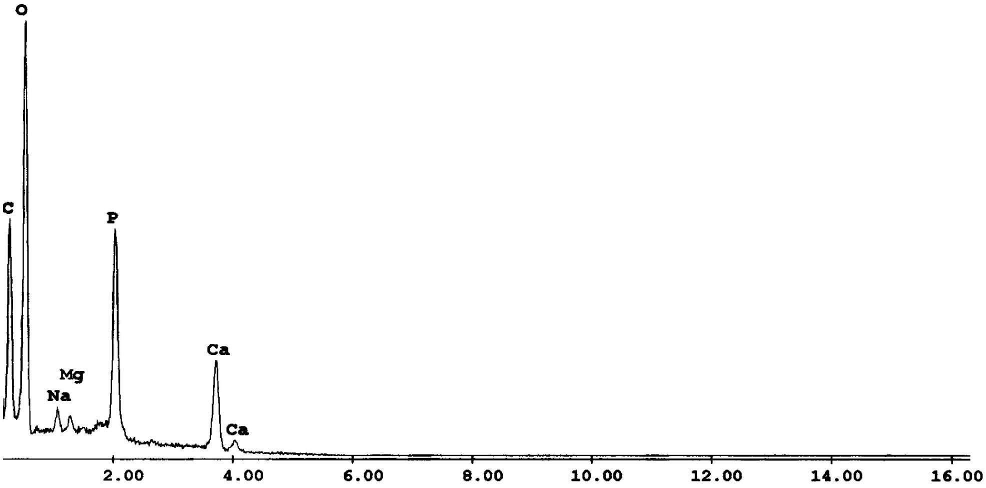
The adsorption time was varied from 10 to 40 min. Cr(III) was adsorbed on bone charcoal immediately and an increase in the adsorption time had no further influence on the adsorption. Figure 3 shows that the Cr(III) removal reached a constant level after 20 min.

It can be concluded that the treatment of 50 ml of 500 mg L^{-1} Cr(III) with 3 g bone charcoal at pH 3.5 can achieve the quantitative removal of Cr(III) within 30 min stirring.

The final pH values, obtained when studying the influence of the contact time, as well as the corresponding final values for blank tests are presented in Table 1.

The pH increase observed with the blank solution may be explained by the release of unremoved NH_3, which proceeds from the bone charcoal preparation process. It can be attributed, as well, to the presence of a CaO minoritary phase, which can appear clearly in calcinated bone charcoal and induce, in this case, a pH increase a little more significant than with bone charcoal.

Fig. 2 Energy dispersive X-ray spectrometry (EDX) analysis spectrum of bone charcoal



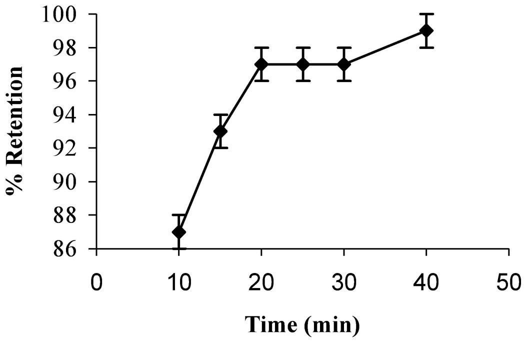


Fig. 3 Effect of stirring time on the Cr(III) retention by bone charcoal. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) were treated at pH 3.5 with 3 g of bone charcoal during different times of magnetic stirring

Table 1 Influence of contact time on final pH. The blank solution pH was adjusted by HNO_3 acid

$[Cr^{3+}]$ mg L^{-1}	Contact time min						
	0	10	15	20	25	30	40
0	3.5	9.41	9.57	9.63	9.66	9.69	9.72
500	3.5	6.1	6.14	6.26	6.20	6.42	6.55

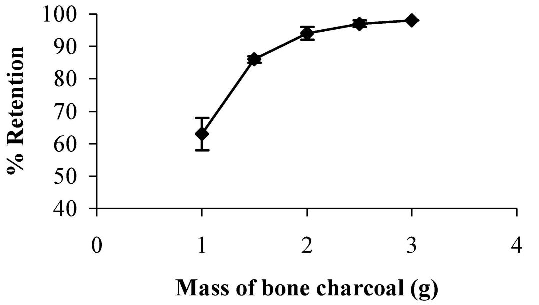


Fig. 4 Effect of bone charcoal mass on the Cr(III) retention. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) were treated at pH 3.5 for 30 min at different levels of adsorbent

Effect of the bone charcoal mass

The effect of the mass of bone charcoal on the retention of Cr(III) was studied using 50 ml of 500 mg L^{-1} Cr(III) solutions at pH 3.5 treated with bone charcoal masses from 1 to 3 g for 30 min. Figure 4 shows the effect of the bone charcoal amount on the Cr(III) retention. The quantity of adsorbed Cr from aqueous solution initially increased with the amount of bone charcoal and the quantitative

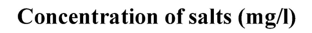
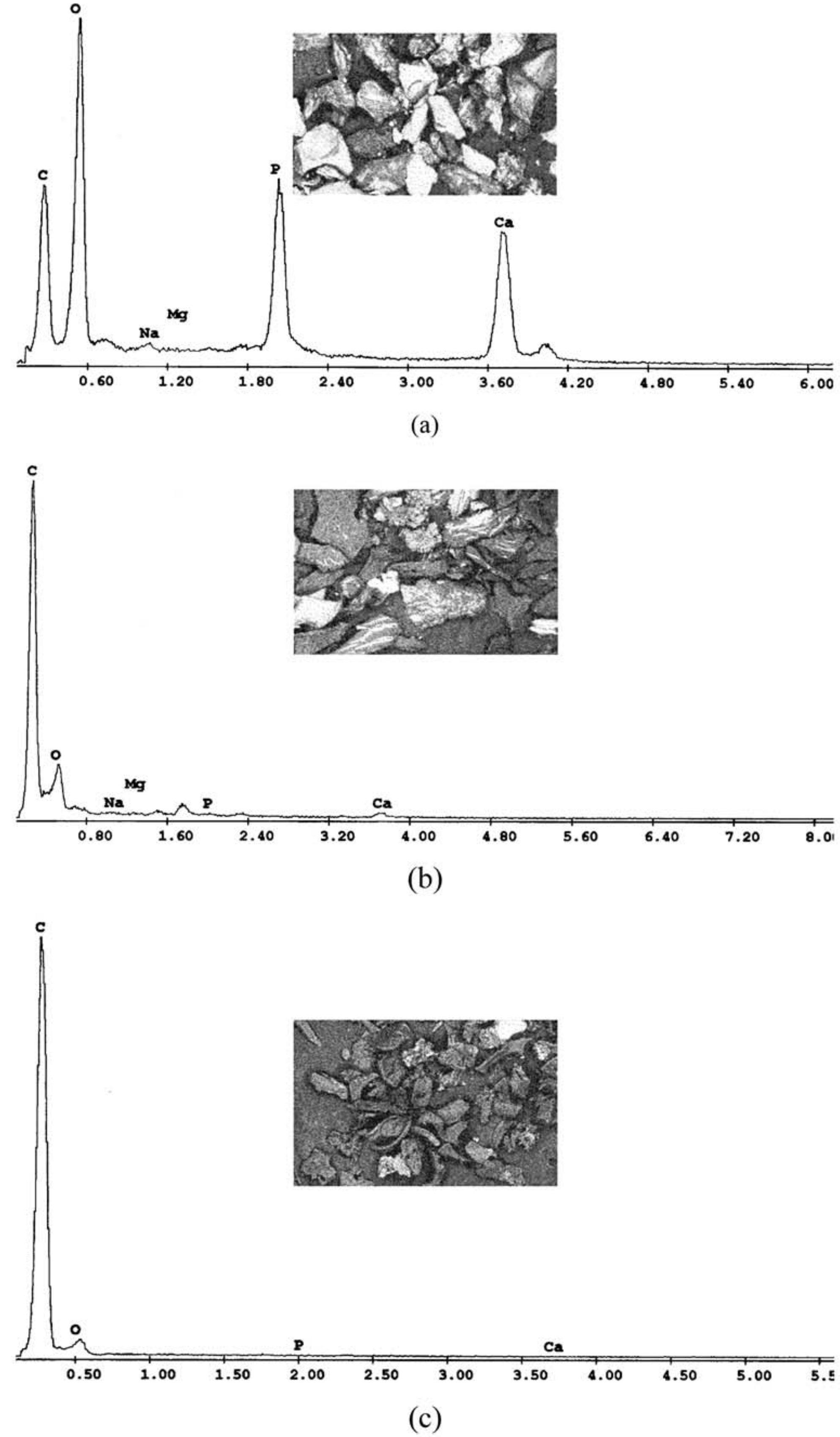


Fig. 5 Effect of the presence of salts on Cr(III) retention by bone charcoal. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) in the presence of different concentration of interfering elements were treated at pH 3.5 with 3 g of bone charcoal for 30 min

Table 2 Effect of bone charcoal granulometry on Cr(III) retention. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) were treated at pH 3.5 with 3 g of bone charcoal for 30 min. Results reported are the average±the corresponding standard deviation of two independent assay solutions containing 25 mg Cr(III) treated at pH 3.5 with 3 g of bone charcoal under magnetic stirring for 30 min

Sieved fraction µm	Retention %	S^a
$\phi>630$	84	12
$315<\phi<630$	80	6
$100<\phi<315$	97	2
$40<\phi<100$	97	1
$\phi<40$	98	1

Fig. 6a–c Effect of the treatment of bone charcoal by nitric acid. **a** 1 M. **b** 2 M. **c** 5 M



retention was reached for an adsorbent mass at around 2 g.

Influence of other ions on the retention of Cr(III)

Since the purpose of this work was to investigate the application of bone charcoal in tannery waste waters treatment, tests were performed in order to investigate the influence of the presence of metal ions that are expected to appear in this kind of effluent. So, a study of the influence of NaCl, NH_4Cl and Na_2SO_4 on Cr(III) retention by bone charcoal was investigated. Solutions of 500 mg L^{-1} Cr(III) were treated with 3 g of bone charcoal for 30 min in presence of the above-mentioned compounds with concentrations in the range 200–2000 mg L^{-1} and the results obtained were evaluated in terms of Cr retention. From Fig. 5, it can be noted that no obvious influence on the sorption rate of Cr(III) was observed. The same behaviour was observed when synthetic solutions of hexavalent chromium were treated with bone charcoal in the presence of the same interfering compounds [17].

Effect of bone charcoal granular size

The effect of the specific surface areas of different sieved fractions was evaluated by adsorption tests carried out by putting 50 ml of 500 mg L^{-1} Cr(III) in contact with 3 g of each sieved fraction. Table 2 shows that all sieved fractions tested showed very interesting Cr(III) retention capabilities. Taking into account the precision of the measurement, the granular size of bone charcoal did not affect the retention rate of Cr(III) significantly.

Effect of bone charcoal treatment

Chemical treatment. Several tests were made in order to investigate the possibility of increasing the bone charcoal Cr removal capacity by means of prior activation treatment. Bone charcoal was treated with nitric acid at different concentrations (1 M, 2 M, and 5 M) for 2 h, washed with distilled water and dried at 80 °C for 1 h.

To understand the reaction between the adsorbent and nitric acid, treated bone charcoal was characterised by SEM on retro-diffused electrons and by EDX analysis. Figure 6 shows the results obtained. It can be seen that all the mineral components of bone charcoal are solubilised by nitric acid except the carbon. Nitric acid does not oxidise carbon under the above-cited conditions.

Adsorption tests were carried out with the activated bone charcoal. Table 3 shows the Cr(III) removal obtained and also the specific surface area of treated bone charcoal. The surface area of bone charcoal increased with the concentration of nitric acid, but its Cr retention capacity diminished drastically. This finding could suggest that retention of trivalent chromium onto bone charcoal is due to its reaction with phosphates or oxides rather than with carbon.

Table 3 Effect of bone charcoal treatments on Cr(III) retention. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) were treated at pH 3.5 with 3 g of adsorbent for 30 min

Concentration of nitric acid	Specific surface area m^2/g	Retention %	Weight loss %
1 M	190	93	30
2 M	326	74	64
5 M	630	13	84

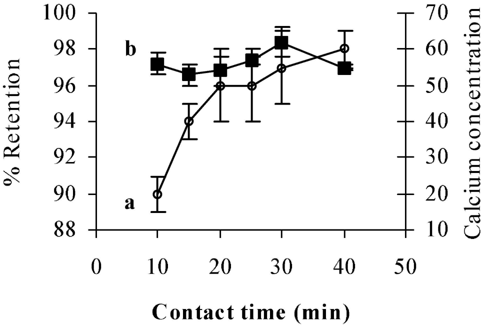


Fig. 7 **a** Adsorption tests of Cr(III) on calcinated bone charcoal. Experimental conditions: 50 ml of 500 mg L^{-1} Cr(III) were treated at pH 3.5 with 3 g of calcinated bone charcoal during different times of magnetic stirring. **b**. Evolution of calcium concentration during different contact time with calcinated bone charcoal

Thermal treatment. To confirm the last suggestion, adsorption tests were carried out using calcinated bone charcoal at a temperature of 950 °C, in the presence of air oxygen, in order to eliminate its carbon content. Results obtained are shown in Fig. 7.

Figure 7 shows that calcinated bone charcoal can achieve a quantitative Cr (III) removal within a little more than 20 min. The calcium content of the solution was also analysed with the aim of ascertaining whether elimination of Cr from aqueous solution is due to an ion exchange process.

From Fig. 7 it can also be noted that when contact time with calcinated bone charcoal increased, the calcium concentration remained at the same level while the Cr concentration decreased. This indicates that metal retention is due to interactions with mineral components of bone charcoal via a mechanism other than ion exchange.

On the other hand, to verify the aforementioned hypothesis, bone charcoal was treated with 1 M HCl and, after 1 h, with 1 M NaOH for an additional 1 h. The product obtained was cleaned with 2 L of pure water using a vacuum filtration system and then dried at 80 °C for 2 h. The retention percentage of a 500 mg L^{-1} Cr(III) solution treated with 1.5 g of bone charcoal in a total volume of 50 ml for 1 h was 99±1%. So, it can be concluded that Cr(III) is totally retained by the mineral components of bone charcoal, the benefits obtained by the successive treatments with HCl and NaOH coming from the fact that it provides a surface of the solid phase covered by mixed oxides, thus enhancing the adsorption-ion exchange processes. It should be noted that bone charcoal treated with

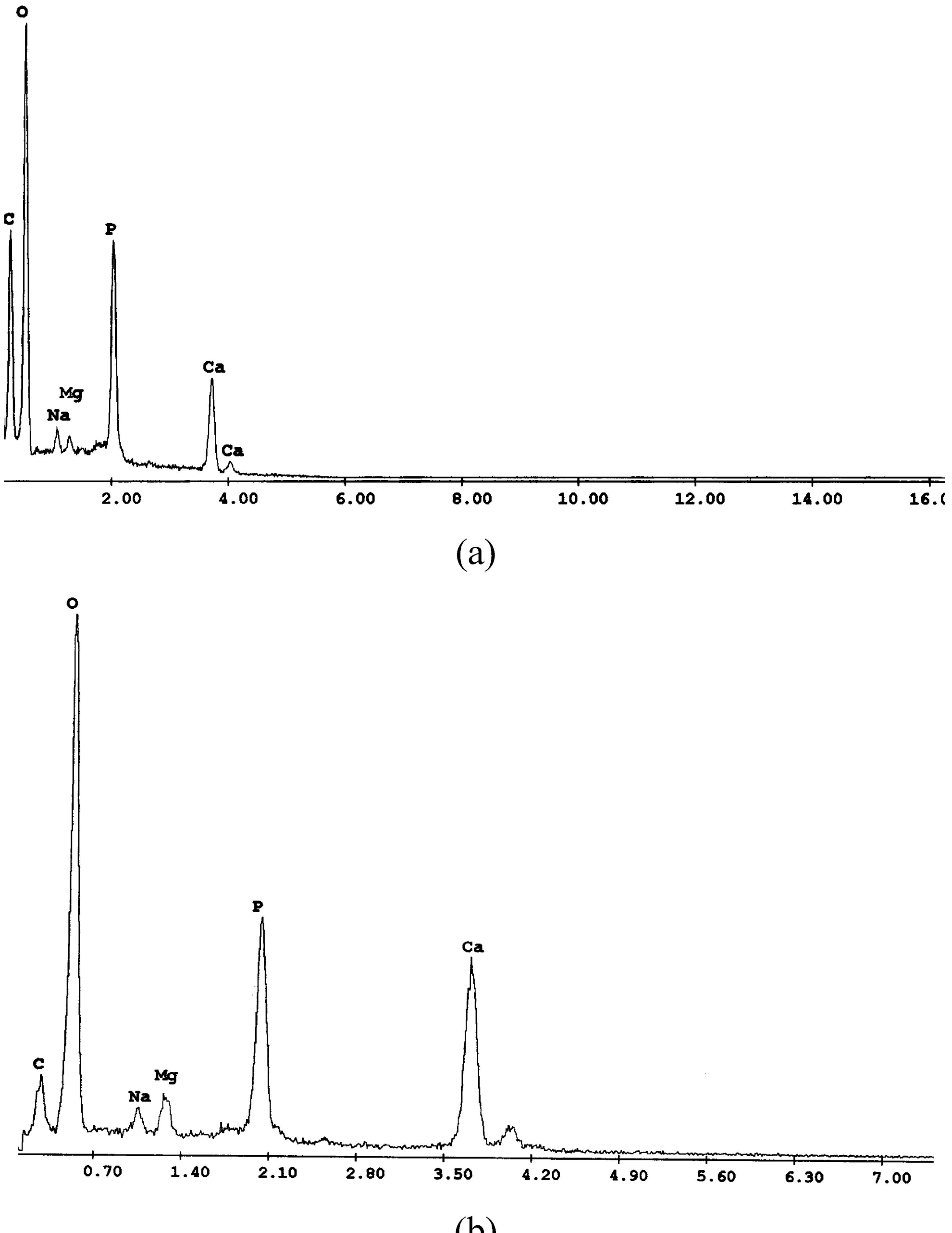


Fig. 8a, b EDX spectra of bone charcoal without (**a**) and with (**b**) HCl+NaOH treatment

HCl and NaOH only involves a 3% mass loss of the solid phase, thus improving the benefits of the treatment in order to obtain a good efficiency of control products for water decontamination.

Figure 8 shows the EDX spectra obtained for bone charcoal samples before and after HCl+NaOH treatment. These may indicate the increasing of the oxides proportion in the treated sample, which justifies the enhancement of bone charcoal capacity for Cr elimination from water solutions.

In conclusion, bone charcoal can be used successfully in the removal of trivalent chromium from tannery wastewaters. The amount of bone charcoal necessary to perform a Cr removal ≥90% is about 60 g L^{-1} for Cr concentrations of 500 mg L^{-1} at a pH of 3.5 for 30 min of stirring time. There were no marked differences between any of the bone charcoal sieved fractions for Cr retention. The presence of other elements had practically no influence on Cr elimination. Pre-treatment of bone charcoal by nitric acid led to an increase in its specific surface area, but decreased drastically its Cr retention capacity. Calcinated bone charcoal revealed a very interesting Cr removal capacity. According to the results obtained, the retention of Cr seems to be due to the mineral phase of bone rather than carbon.

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