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Removal of hexavalent chromium from wastewaters by bone charcoal

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Abstract The adsorption of hexavalent chromium onto bone charcoal was studied as a function of time, amount of charcoal, pH, concentration of chromium and sample volume. The cross interference with other elements was also investigated. Tests were carried out with solutions of chromium(VI) at concentrations between 5 and 25 mg · L⁻¹. Chromium removal efficiencies higher than 90% were achieved at pH = 1 using 2 g of bone charcoal and a stirring time in the order of 30 min. Acid and alkaline pretreatments of bone charcoal did not improve the sorption capacity of bone charcoal against Cr(VI). The presence of other ions had practically no influence on the chromium removal. The presence of a matrix of tannery effluents did not reduce the removal capacity of bone charcoal for Cr(VI), but it was confirmed that only 47% of Cr(III) can be removed using these conditions.

Introduction

Chromium is an essential nutrient for plant and animal metabolism. However, when accumulated at high levels, it can generate serious trouble and diseases [1].

Chromium is present in aqueous solutions mainly in two oxidation states, Cr(III) and Cr(VI), and because of the difference in toxicity of hexavalent and trivalent chromium, many attempts have been made to discriminate between the two species [2–4]. The maximum levels permitted in wastewater, 5 mg · L⁻¹ for Cr(III) and 0.05 mg · L⁻¹ for Cr(VI), take into consideration the presence of Cr species [5].

The main sources of water pollution by chromium are mining, leather tanning, cement industry and its use in dyes and corrosive paints. The principal techniques for recovering or removing chromium from wastewater are: i) chemical reduction and precipitation, ii) adsorption and iii) ion exchange. In former times, precipitation was the most common method. Firstly, the hexavalent chromium was reduced to trivalent, and the trivalent chromium was then precipitated as Cr(OH)₃ by addition of an alkaline solution [6]. Several sorbents have been employed to remove chromium from polluted waters, such as activated carbon [7–9], fly ash and wollastonite [10], sphagnum moss peat [11], and pinus sylvestris bark [12].

Bone charcoal is a product obtained from the calcination of bovine bones at high temperatures in the absence of air. The sugar industry uses it essentially to discolor sugar syrup.

Previously a series of studies have been carried out on the use of bone charcoal for the decontamination of tannery effluents. In the laboratory of physical chemistry of Casablanca I, bone charcoal was used for the Cr(III) removal from synthetic solutions [13].

As the most toxic species of chromium Cr(VI) can not be removed directly by precipitation, the main objective of this study was to evaluate the possibility of using bone charcoal as sorbent for the elimination of Cr(VI) from polluted waters by systematic evaluation of the parameters involved, such as pH, bone charcoal mass, chromium concentration and time. The interference of the most common ions present in tannery effluents on the Cr(VI) adsorption was additionally investigated.

Experimental

Apparatus. All atomic absorption measurements were made using a SHIMADZU AA660 V-3 (Kumamoto, Japan) flame atomic absorption spectrometer equipped with a hollow cathode lamp of Cr Unicam (Cambridge, U.K.) at conditions indicated in Table 1.

A Crison-2000 pH meter equipped with a glass electrode and an AgCl/Ag reference electrode was used for measuring the pH of solutions.

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Table 1 Experimental conditions employed for Cr determination

Wavelength nm	357.9
Slit nm	0.25
Lamp current mA	10
Air flow L · min ⁻¹	8
C ₂ H ₂ flow L · min ⁻¹	2.6

An Heraeus Sepatech centrifuge was applied for the centrifugation of the samples.

Reagents. Bone charcoal with an average diameter particle between 0.05 mm and 0.8 mm was used as adsorbant.

All reagents were of analytical grade. Solutions were prepared in deionized water obtained from a Millipore milliQ system (Molsheim, France) with a specific resistivity of 18.2 MΩ.

The stock solution of 100 mg · L⁻¹ Cr(VI) was prepared by dissolution of 0.2827 g of potassium dichromate, Scharlau (Barcelona, Spain), in deionized water and diluted to 1 L. Cr(VI) working solutions were prepared by appropriate dilution of this stock solution.

Standard stock solutions (200 mg · L⁻¹) of V(V), Fe(II), Na(I) and NH₄(I) were prepared by dissolving the following compounds in water: NaVO₃, NaNO₃, NH₄Cl and Fe(NH₄)₂(SO₄)₂ · 6H₂O.

General procedure. Chromium sample solutions were adjusted to pH 1 by adding 10 M NaOH or 15 M HNO₃. 2 g of bone charcoal were added and the mixture stirred in a magnetic stirrer during 30 min, subsequently centrifuged at 4000 rpm for 10 min and the remaining Cr(VI) determined in the solution by AAS.

Results and discussion

Effect of pH

Two series of experiments were carried out to investigate the effect of pH on the adsorption of Cr(VI) by bone charcoal: one using a solution of 25 mg · L⁻¹ Cr(VI) and 0.5 g of bone charcoal and a second one using 10 mg · L⁻¹ Cr(VI)

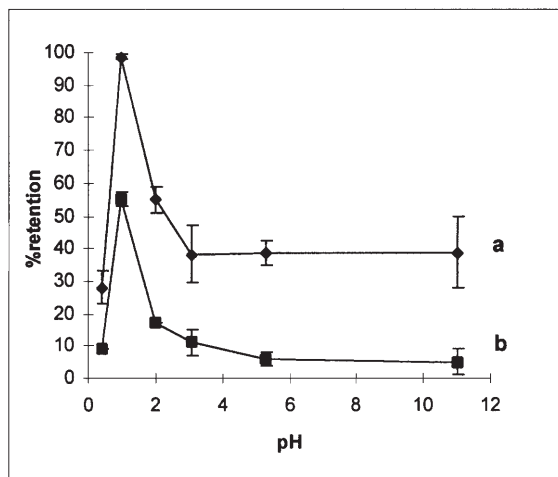


Fig. 1 Effect of pH on Cr(VI) adsorption by bone charcoal. *a* 50 mL of 10 mg · L⁻¹ Cr(VI) treated with 2 g of bone charcoal during 30 min with continuous magnetic stirring; *b* 50 mL of 25 mg · L⁻¹ Cr(VI) treated with 0.5 g of bone charcoal during 30 min with continuous magnetic stirring. Bars indicate the variability of 2 independent assays carried out on each condition

and a bone charcoal mass of 2 g. In both cases a fixed volume of 50 mL and a stirring time of 30 min were employed. The pH of the Cr(VI) solutions was adjusted by adding appropriated volumes of 15 M HNO₃ and 10 M NaOH to the chosen value before the introduction of bone charcoal.

Figure 1 depicting the dependence of the Cr(VI) retention as a function of pH shows that independent from the level of retention, which extremely depended on the proportion between Cr(VI) and bone charcoal, the increase of pH from 0 to 1 tremendously increased the Cr(VI) adsorption, which diminished when increasing the pH to values higher than 1 to reach a poor adsorption between pH 3 and 11. This effect was accompanied by a change of the color of solutions which became green in alkaline medium, thus indicating a probable reduction of Cr(VI) to Cr(III) favored in the presence of bone charcoal.

A working pH of 1 was therefore selected to improve the quantitative recovery of Cr(VI) from aqueous solutions.

Effect of the mass of bone charcoal

The effect of the mass of bone charcoal on the retention of Cr(VI) was studied using 50 mL of 10 mg · L⁻¹ Cr(VI) solutions at pH = 1 treated with bone charcoal masses from 0.5 to 2 g during 30 min. The Cr(VI) retention increases gradually on increasing the bone charcoal mass until a quantitative retention for an adsorbent mass of 2 g was reached.

Effect of Cr(VI) concentration

50 mL of solutions with different concentrations of Cr(VI) were treated at pH = 1 with 2 g of bone charcoal during 1 h with magnetic stirring in order to evaluate the

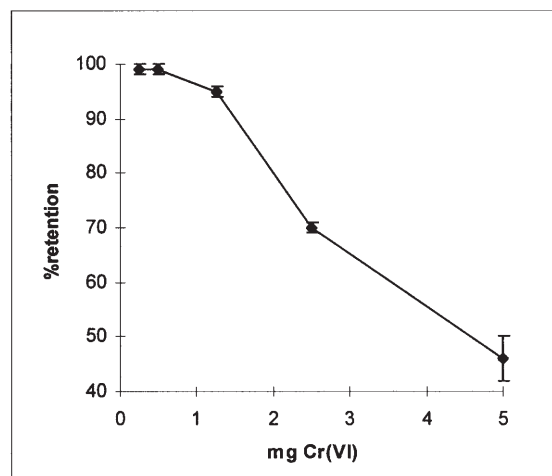


Fig. 2 Effect of Cr(VI) mass on Cr(VI) retention on bone charcoal. Experimental conditions: 50 mL of Cr(VI) solutions containing different amounts of Cr(VI) were treated at pH = 1 with 2 g bone during 1 h

Table 2 Effect of the volume of a 0.5 mg Cr (VI) solution on the retention of CR (VI) by a fixed mass of 2 g bone charcoal^a

Volume mL	Retention %
50	99 ± 1
75	75 ± 0
100	32 ± 4
125	28 ± 12
150	24 ± 16

^aResults reported are the average ± the corresponding standard deviation of 2 independent assay solutions containing 0.5 mg Cr (VI) treated at pH = 1 with 2 g of bone charcoal under magnetic stirring for 30 min

influence of the proportion Cr(VI) to charcoal on the retention process.

Figure 2 indicates a drastic reduction of the Cr(VI) retention by bone charcoal with increasing Cr(VI) amounts using fixed masses of bone charcoal, thus indicating the strong dependence of the process on the relation Cr(VI)/bone charcoal. However it can not be concluded that a relationship of 0.5 mg of Cr(VI) for 2 g bone charcoal can assure the quantitative recovery of chromium, because the process is dependent not only on the mass relation of Cr to bone charcoal but also on the volume of solution. This can be seen from Table 2, in which the results are given obtained for 0.5 mg Cr(VI) diluted to different volumes with distilled water and treated with 2 g of bone charcoal during 30 min. The increase of solution volume for a fixed amount of Cr(VI) and bone charcoal mass reduces the percentage of retention of Cr(VI) and also the repeatability of the process.

Effect of time of contact

For a fixed concentration of Cr(VI) and bone charcoal mass, the retention of Cr(VI) increases with increasing

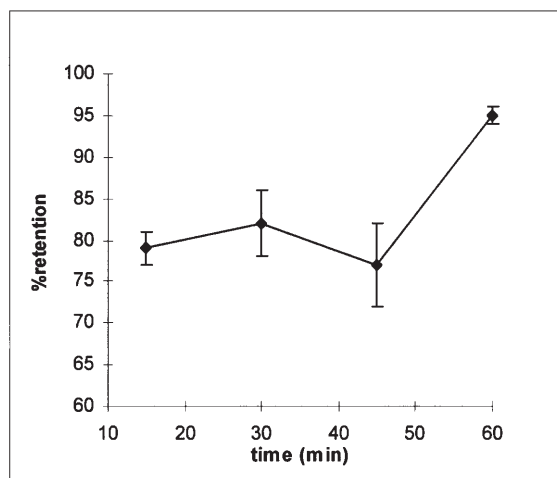


Fig. 3 Effect of stirring time on the retention Cr(VI) by bone charcoal. Experimental conditions: 50 mL of 25 mg · L⁻¹ Cr(VI) were treated at pH = 1 with 2 g of bone charcoal during different times of magnetic stirring

contact times. From Fig. 3 it can be concluded that the treatment of 50 mL of 25 mg · L⁻¹ Cr(VI) with 2 g bone charcoal at pH = 1 can assure the quantitative removal of Cr(VI) within 60 min stirring.

Comparing these results with those reported before for the treatment of 10 mg · L⁻¹ Cr(VI) for 30 and 60 min shows that the increase of the Cr(VI) concentration involves the need of increasing times of contact with bone charcoal to provide the same level of retention.

Effect of bone charcoal activation

Two pretreatments were employed, a first one consisting of an acid treatment of 25 g bone charcoal with 50 mL 0.1 M HNO₃ for 48 h, followed by washing with ultrapure water and drying at 50 °C for 2 h, and a second one based on the same treatment with 0.1 M NaOH.

Non-pretreated charcoal resulted in retentions of 46 ± 4%, acid-pretreated in recoveries of 48 ± 3% and alkaline-pretreated in 48 ± 2% thus evidencing that the pretreatment of bone charcoal had no influence on its capacity against Cr(VI).

Study of interferences

A study of the interferences of vanadium, sodium, ammonium and iron on the Cr(VI) adsorption by bone charcoal was made. Solutions of 10 mg · L⁻¹ Cr(VI) were treated with 2 g of bone charcoal in presence of increasing concentrations of interfering ions from 0 to 100 mg · L⁻¹ and results obtained were evaluated in terms of Cr retention. No obvious influence of these ions on the sorption process of Cr(VI) was observed.

Cr retention in tannery waste waters

A real tanning bath containing 5296 ± 200 mg · L⁻¹ total chromium was diluted 500 times and treated with 2 g bone charcoal for 30 min. A retention percentage of total chromium in the order of 47 ± 5% was obtained. This small retention is probably due to the fact that in the tannery waste water Cr(III) instead of Cr(VI) is the main species.

In order to evaluate the influence of the tannery wastes matrix components on the retention of Cr(VI) by bone charcoal, additional studies were carried out by spiking waste waters with known amounts of Cr(VI) from 2 to 10 mg · L⁻¹. The recovery now varies from 122 to 107% thus indicating that Cr(VI) was totally recovered whereas being the retention of Cr(III) was less favorable.

Conclusions

Bone charcoal is an appropriate adsorbent for the Cr(VI) removal from aqueous solutions, the process being dependent on pH, time of contact, mass of bone charcoal and Cr

concentration additional to the volume of effluent treated. pH 1 and a bone charcoal mass of 2 g seems appropriate for the quantitative removal of Cr(VI) concentrations in order of $10 \text{ mg} \cdot \text{L}^{-1}$ in only 30 min and in the presence of other ions or matrix components of real tannery effluents.

The high efficiency of bone charcoal for the removal of Cr(VI) from complex mixtures opens also the possibility for using this material to clean analytical wastes.

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