

Retention of chromium by modified Al-Bentonite

(Retenção de cromo por Al-bentonita modificada)

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Abstract

Retention of chromium (III) from a tanning wastewater by modified Al-bentonites was studied. One bentonite from San Juan province, Argentina, was used. Al-bentonite was prepared by contact of bentonite with hydrolyzed OH-Al solutions (0.10 M in Al) for 24 hours. The modified Al-bentonites were obtained by: a) treatment with 0.5 M sodium chloride; b) with 0.5 M sodium chloride adjusted at pH 8; and c) treatment with an hexametaphosphate solution after sodium addition. Then, the samples were dried at 100 °C and heated at 500 °C. The chromium (III) retention by samples was carried out in batch system putting in contact the material with a 2000 ppm Cr tannery waste at different times. The retained chromium was characterized by analyzing the supernatant using UV-visible spectroscopy. The different chromium retention was correlated with structural characteristics of the solids.

Keywords: chromium retention, Al-bentonite, tanning wastewater.

Resumo

Foi estudada a retenção de cromo (III) de águas residuais por meio de Al-bentonitas modificadas. Foi usada uma bentonita da província de San Juan, Argentina. As bentonitas-Al forma preparadas colocando-as em contato com soluções (0,10 M Al) hidrolizadas de OH-Al durante 24 horas. As bentonitas-Al modificadas foram obtidas por meio de: a) tratamento com cloreto de sódio 0,5 M; b) com cloreto de sódio 0,5 M sódio com pH ajustado para 8; e c) tratamento com uma solução de hexametáfosfato após a adição de sódio. As amostras foram então secas a 100 °C e aquecidas a 500 °C. A retenção do cromo (III) pelas amostras foi feita em lotes colocando o material em contato em diferentes tempos com um resíduo contendo 2000 ppm de cromo. O cromo retido foi caracterizado por meio de análise do sobrenadante usando espectroscopia UV-visível. As diferentes retenções de cromo foram correlacionadas com características estruturais dos sólidos.

Palavras-chave: retenção de cromo, Al-bentonita, águas residuais.

INTRODUCTION

Many industrial wastewater contain heavy metals (e.g. Pb, Cr, Hg, Cd, etc.). Previous works indicate that natural clays retain chromium from solution. The amount of retained Cr is mainly a function of the clay types and the polymerization states of the chromium species in solution [1, 2].

The reaction of Al₁₃ interlayered smectite with inorganic and organic anions was previously summarized [3, 4]. The Al polymers in the interlayer are positively charged, the net positive charge decrease with increasing pH, and form Al-OH anion complexes or basic salts with counteranions [3, 4]. Thus, depending on the anion charge, the Al-OH anion complexes will have a positive charge density lower than that of the intercalated Al species [4]. Therefore, the use of this material as adsorbent for cations from aqueous environments is possible.

In this work, the adsorption properties of a modified Al interlayered bentonite were examined. Several materials were prepared after treatment of an hydroxi-Al bentonite with NaCl, NaCl at pH 8 and Na-hexametaphosphate solution. The removal of Cr from a tanning wastewater solution by using

modified Al-bentonites were determined and related with adsorbent structural properties.

MATERIALS AND METHODS

The sample used in this study was a bentonite from San Juan province, Argentine (C). It is constituted by dioctahedral smectite and small amount of quartz as impurity. The smectitic species present in this sample were Cheto montmorillonite and beidellite [5]. The bentonite sample was dispersed in distilled water (10 wt %) and the OH-Al-solution was added slowly with stirring. Hydroxy-Aluminum solution (0.10 M in Al) was prepared by dilution of the commercial concentrate solution (6.0 M) and aged seven days at room temperature. The amount of Al added was 1000 meq Al per 100 gram of bentonite. After 24 hours in contact the solids were separated and washed several times in order to remove the electrolyte excess (Al-C). The intercalated OH-Al bentonite previous washing was separated in different portions and treated as follow: a) with 0.5 M NaCl and after washing by distilled water (Al-CNa); b) similar to a) but 0.5 M NaCl was adjusted at pH 8 (Al-CNa8); c) similar to

a) with further addition of HMP solution (Al-CNaH). All prepared samples were washed, dried at 100 °C and calcined at 500 °C previous to retention chromium analysis.

The natural and modified samples were characterized by X-ray diffraction (XRD), using a Phillips 3020 diffractometer at 40 kW and 20 mA. The diffractograms were performed on the total samples from 3° to 70° at 1°/min.

The chromium (III) retention by the samples were carried out in batch system putting the material into contact with a 2000 ppm Cr tannery wastewater. The ratio of solid/liquid was of 5.0 wt/vol %. The retained chromium by the solid was calculated by the difference between the chromium of the original solution and the chromium of the supernatant using a Hewlett Packard Model 8453 spectrophotometer. The absorbance at 419 nm was measured.

RESULTS AND DISCUSSION

Characteristics of samples and the tanning wastewater solution.

Fig. 1 shows the X-ray diffraction patterns of the original sample, Al-bentonite (Al-C) and modified Al-bentonites. The DRX pattern of the Al-C sample shows a high and well-defined 001 reflexion at 19.1 Å. Both Al-CNa and Al-CNa8 samples showed high d(001) peaks with a similar basal spacing to that of Al-bentonite. HMP treatment (Al-CNaH) produced a basal spacing reduction from 19.1 to 15.0 Å and broadening of the peak (Fig. 1) indicating high degree of structural disorder probably due to Al extraction and partial replacement of Al in the interlayer by Na.

The DRX pattern of Al-C also exhibited a small 4.85 Å peak, which was attributed to the presence of gibbsite [6]. The relative intensity of the 4.85 Å peak varied with the treatments.

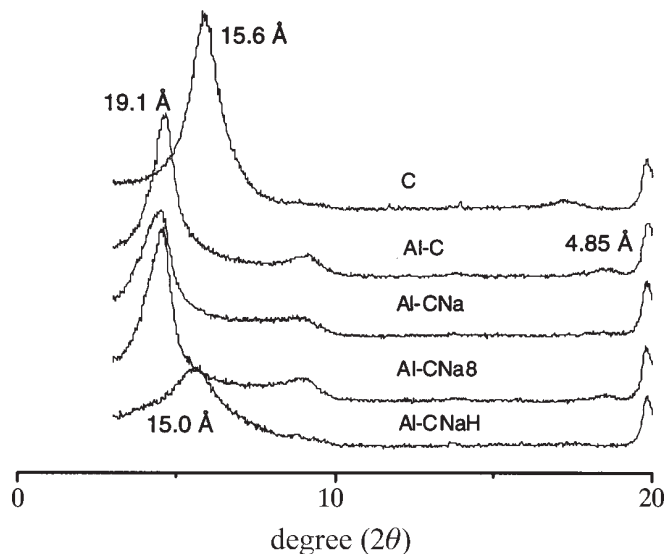


Figure 1: DRX patterns of powdered original, Al-bentonite and modified Al-bentonites.

[Figura 1: Difratogramas de raios X de pós da bentonita-Al e da bentonita-Al modificada.]

It was absent after the NaCl treatment (Al-CNa) and after HMP addition (Al-CNa-H). The treatment with NaCl at pH 8 (Al-CNa8) produced a slight decrease in intensity compared to that of the Al-bentonite.

Fig. 2 shows the X-ray diffraction patterns of the original bentonite, Al-bentonite and modified Al-bentonites after heating at 500 °C. The interlayer spacing of the original bentonite, 15.6 Å, (Fig. 1) collapsed to 9.5 Å after heating (Fig. 2). A slight decrease in intensity and broadening of d(001) peak regarding to the uncalcined samples were observed for Al-bentonite (Al-C) and modified Al-bentonites, due to dehydroxylation of the pillar

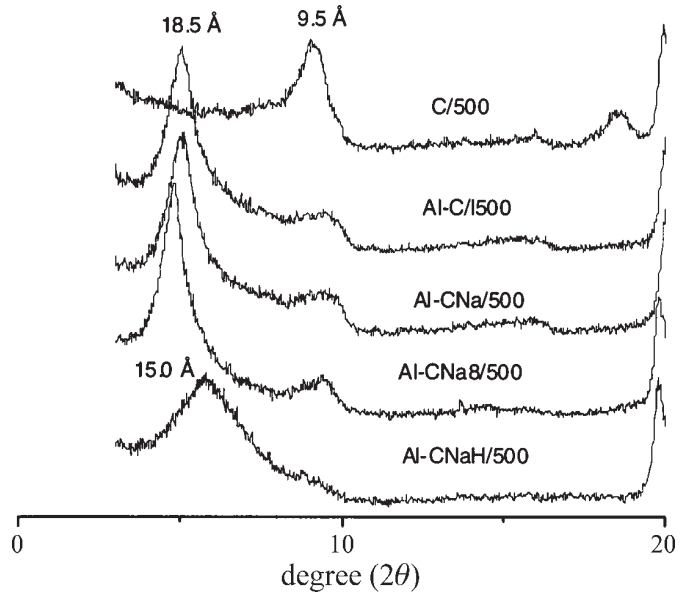


Figure 2: DRX patterns of powdered original, Al-bentonite and modified Al-bentonites heated at 500 °C.

[Figura 2: Difratogramas de raios X de pós da bentonita-Al original e bentonita-Al modificada aquecidas a 500 °C.]

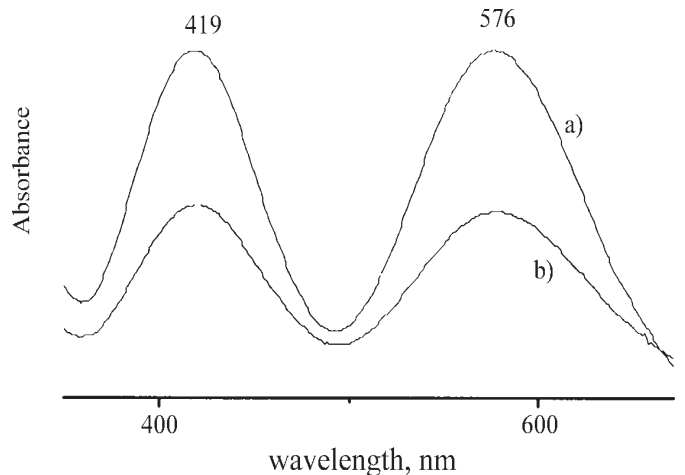


Figure 3: Adsorption spectra: (a) 2000 ppm Cr tanning wastewater solution; (b) supernatant after using Al-CNaH bentonite as adsorbent of chromium.

[Figura 3: Espectros de adsorção: (a) solução de água residual com 2000 ppm de cromo; (b) sobrenadante após uso de bentonita-Al-CNaH como meio adsorvente de cromo.]

Fig. 3a shows the visible spectrum of tanning wastewater containing 2000 ppm Cr. The spectrum showed two bands at 419 and 576 nm. The peak intensities ratio and position of the two bands depend of the exhaustion degree of the original agent salt for tanning (basic chromium sulfate), which has two bands situated at 410 and 575 nm.

These two bands appeared in the spectra of the supernatant solutions using the modified Al-bentonites as adsorbents. For a comparison, Fig. 3b shows the spectrum of the supernatant after contacting the modified Al-bentonite with the tanning wastewater.

Retention of Cr by untreated, Al-bentonite and modified Al bentonites dried at 100 °C.

Fig. 4 a) shows the Cr retention by C bentonite after drying at 100 °C. About 6.5 mg Cr/g was adsorbed after 1 day and the amount of Cr retained increased to 7.8 mg Cr/g after 14 days in contact. Cr ions may be retained by a cation exchange mechanism due the high cation exchange capacity (CEC) of the bentonite. The same Figure also shows that the amount of retained Cr on Al-bentonite was lower than that on the untreated clay. Fig. 1 shows that basal spacing expanded to 19.1 Å after intercalation. However, Al intercalation generally reduced the CEC of the bentonite as Al complexes in the interlayer remained positively charged. Therefore, high electrostatic repulsion

between positively charged Al-OH groups at the surface and Cr ions in solution prevented high Cr retention.

The curve of Cr retention as a function of time (Fig. 4) shows that the amount of retained Cr by the modified Al-bentonite with NaCl treatment (Al-CNa) was significantly enhanced. XRD pattern of this sample was similar to that of Al-C bentonite indicating that the amount of Al interlayered complexes was nearly the same. In addition, the 4.85 Å reflexion of the gibbsite was absent.

The NaCl treatment displaced most of exchangeable Al monomers and small polymers [7] and consequently low amount of Al hydroxide was formed during washings.

Less gibbsite formation favored chromium retention. Treatment of Al bentonite with NaCl solution at pH 8 slightly improved Cr adsorption capacity (Fig. 4a). The DRX pattern of the Al-CNa8 sample showed a high d(001) peak with a basal spacing similar to that of sample Al-CNa. However, the relative intensity of the 4.85 Å peak increased probably due to high pH reduced the exchangeability of Al species that may control the formation of Al hydroxides. For the Al-CNa8 sample, the amount of retained Cr slightly increased with respect to that for the Al-CNa sample. Low electrostatic repulsion resulting from the additional negative charge neutralization of the retained Al species, improving the Cr retention capacity by this sample.

Fig. 4 shows that the amount of retained Cr by the AlCNaH

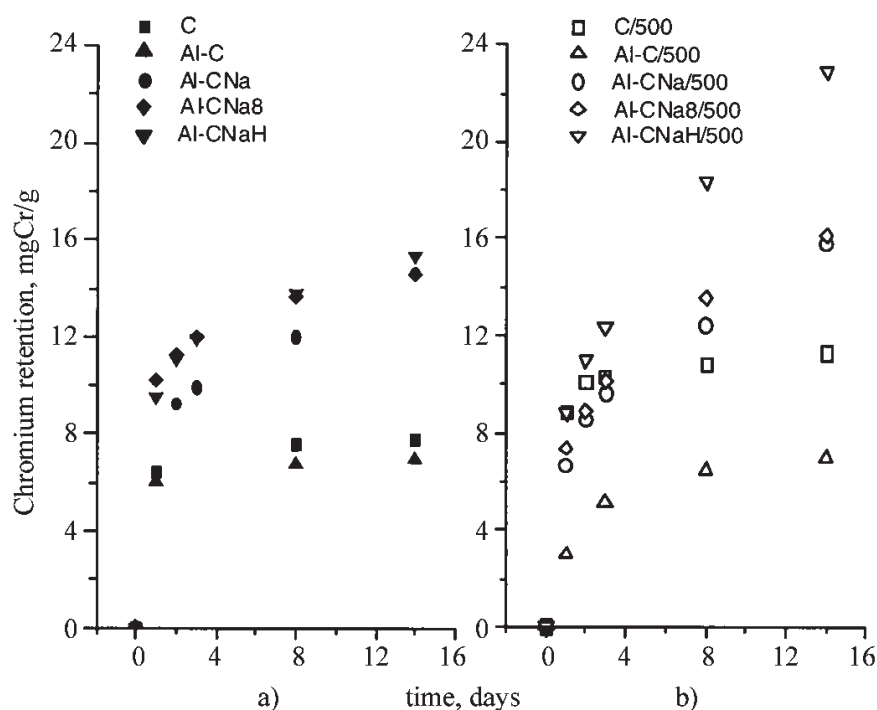


Figure 4: Amount of retained Cr as a function of time for untreated bentonite, Al-bentonite and modified Al-bentonites. Retention using samples: a) dried at 100 °C; b) after heated at 500 °C.

[Figura 4: Quantidade de cromo retido em função do tempo para as bentonitas não tratada, bentonita-Al e bentonita-Al modificada. Retenção usando amostras: a) seca a 100 °C; b) após aquecimento a 500 °C.]

sample is similar to that of Al-CNa8. HMP addition produced some structural modifications in the Al-CNa sample. Low basal spacing and broadening indicated less amount and poor ordered Al-OH complexes in the interlayer than that present in well ordered Al-CNa bentonite. As the structural disorder increased more Al-OH groups developed on the surface [4]. These groups were available for reaction with HMP. Modified Al bentonite with HMP probably became less positively charged at low pH and consequently was better adsorbent for chromium than modified Al bentonite with NaCl. Also, the improvement in Cr retention may possibly related to the formation of aluminum-phosphate compound.

Retention of Cr by untreated, Al-bentonite and modified Al bentonites heated at 500 °C

Fig. 4b shows that Cr retention for Al-CNaH, was significantly affected by heating at 500 °C. After heating, the amount of retained Cr increased from 15 to 23 mgCr/g after 14 days in contact.

Structural properties were similar to those corresponding to the unheated samples (Figs. 1 and 2). However, removal of adsorbed and interlayered water; and dehydration of Al-phosphate compounds favored the availability of active sites for Cr retention.

CONCLUSIONS

The amount of retained Cr by dried samples increased in the following order Al-C < Al-CNa < Al-CNa8 = Al-CNaH. Adsorption capacity increased due to the combined effect of the reduction in the Al exchangeable content and subsequent

neutralization of retained Al by alkalization or by HMP addition.

The retention of Cr by modified Al-bentonite with HMP after heating at 500 °C increased 3 times with respect to the original bentonite.

Like other complexing agents, HMP anion promoted structural disorder in Al-bentonite. Therefore, more Al-OH groups developed on the surface than that present in well ordered Al bentonite. These groups were available for reaction with HMP. After heating at 500 °C structural properties remained unchanged but dehydration of an external Al phosphate possibly occurred. High amount of retained Cr may be related to the presence of surface phosphate groups.

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