Adsorption of Basic Chromium Sulfate Used in the Tannery Industries by Calcined Hydrotalcite

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Abstract. The sorption behavior of the chemical species of Cr(III) from aqueous solutions by hydrotalcite calcined products was investigated considering the equilibrium pH (5.0 to 8.9) and the chromium concentration in aqueous solution (from 10.6 to 430.0 mmol/L) to obtain the corresponding isotherms. Each solution was prepared from basic Cr(III) sulphate which is a primary tanning agent used in the tannery industries. In this work no previous oxidation treatment was done to form Cr(VI) in order to remove the chromium from aqueous solutions by hydrotalcite. The amount of chromium in the remaining solutions after the sorption processes in a batch system by visible spectroscopy (Vis) was determined. The calcined hydrotalcite before and after the contact with the chromium(III) solutions by X-ray power diffraction (XRD), thermogravimetric analysis (TGA) and Fourier-transformed infrared (FT-IR) spectroscopy, were characterized. The specific area by Brunauer, Emmett and Teller (BET) method of each sample was also evaluated. It was found that under the experimental conditions of this work hydrolyzed species of Cr(III) are precipitated on the surface of the calcined hydrotalcite instead other adsorption mechanism, and the sulfate ions were the responsible to regenerated the crystalline structure of hydrotalcite, therefore the results are discussed in terms of both Cr(III) and sulfate chemical species.
Keywords: Chromium(III); Calcined hydrotalcite; Adsorption; Heavy metal; Freundlich isotherm.

Resumen. En este trabajo, se investigó el comportamiento de sorción de las especies químicas de Cr(III) en soluciones acuosas, en productos de calcinación de la hidrotalcita considerando tanto el pH al equilibrio (5.0 a 8.9) como las concentraciones de cromo en solución acuosa (desde 10.6 a 430.0 mmol/L), para obtener la isoterma correspondiente. Las soluciones se prepararon utilizando sulfato básico de Cr(III), el cual es el agente primario actualmente utilizado en la industria de la tenería. La cuantificación del cromo remanente en la solución, después del proceso de separación en un sistema por "lotes", se realizó por espectroscopia (Vis). La hirotalcita calcinada se caracterizó antes y después del contacto con las soluciones de Cr(III), por medio de difracción de rayos-X (DRX), análisis termogravimétrico (ATG) y espectroscopia infrarroja con transformada de Fourier (FT-IR). También se evaluó el área específica por el método de Brunauer, Emmett y Teller (BET), de cada muestra. Se encontró, que bajo las condiciones experimentales del presente trabajo, el mecanismo de separación es la precipitación de especies hidrolizadas del Cr(III), sobre la superficie de la hidrotalcita calcinada en lugar de otro mecanismo de adsorción, y que por otro lado, los iones sulfato fueron los responsables para regenerar la estructura de la hidrotalcita, por lo tanto los resultados se discuten en términos de las especies químicas de Cr(III) y del sulfato.
Palabras clave: Cromo(III); Hidrotalcita calcinada; Adsorción; Metal pesado, Isoterma de Freundlich.

Introduction

Heavy metals are one of the most dangerous pollutants contained in wastewater due to their permanence and toxicity. Chromium is a heavy metal used in metallurgic, refractory, chemical and tannery industries. Cr(III) is considered to be less toxic than Cr(VI) [1]. Cr(VI) is a carcinogen compound, irritant, and corrosive which can be absorbed by ingestion through the skin and by inhalation [2,3]. Cr(VI) is mobile in aquatic systems and most soil, while Cr(III) is rather immobile due to its limited solubility and it is adsorbed by negatively charged surfaces in soils and sediments and it is bonded with insoluble organic materials, therefore disposal of Cr(III) is considered to be less dangerous than Cr(VI).

Chromium(III) oxidation by manganese oxides has been demonstrated to occur under environmental conditions [4] which depends of the formation Cr(III)—MnO$_2$ complex. Cr(III) has ability to pass easily into the food chain producing noxious effects, for this reason it is important to found alternative methods for the treatment of industrial effluents to remove Cr(III) before they are discharged into receptor water bodies.

The hydrotalcite presents adsorptive characteristics that could be useful for this purpose. Therefore the aim of this work was to determine the influence of the concentration and pH on the chromium and sulfate adsorption by calcined hydrotalcite in order to establish their capacity as an effective sorbent of tanning agent from tannery discharges, in which pH values and Cr(III) concentrations are high (50 mmol/L).

Results and discussion

Sorption isotherms

The sorption of the calcined hydrotalcite was 26.5 ± 0.8 mmol Cr(III)/g (1.38 ± 0.04 g Cr(III)/g), this value suggests that the sorption could be not the unique processes involved in the separation of chromium from water as will be discussed later.

Studies on the sorption of chromium by calcined hydrotalcite have shown that the concentration of chromium in solution diminishes from 0.92×10^{-3} to 0.15×10^{-5} mmol/L when the chromium(III) is previously oxidizing with sodium
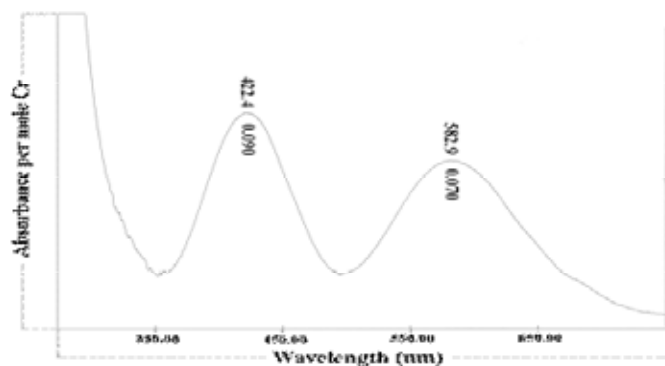
Figure 1. UV-Vis spectra of Cr(III) in solution after contact with CHT.

hypochlorite solution and then in contact with calcined hydrotalcite which initial crystalline structure is regenerated [5]. By the other hand it was observed that the chromium equilibrium experiments fitted well to Freundlich isotherm. Hydrotalcite presented a sorption capacity of approximately 17 mg Cr/g under their studied conditions [6].

Cr(III) chemical speciation

The variation of the pH values of chromium solutions before and after contact with calcined hydrotalcite (Table 1) were the reason to consider the pH influence on the Cr(III) chemical speciation. As it can be observed on Table 1, at pH from 2 to 3 no changes were observed when the chromium concentration vary in solution (samples from 1 to 10), however Cr(III) species were changed after the contact with calcined hydrotalcite (samples from HT1 to HT10), i.e., solutions at pH 5.5 had greenish blue color, suggesting the presence of dimeric ion

$[Cr_2(OH)_2]_{(aq)}$ which was confirmed later by its UV-Vis spectra (Figure 1). This dimeric specie shows two bands at 422.4 and 582.9 nm. Although they are similar to those for the monomer and trimmer [7], the dimmer was undoubtedly identified through the ratio between the extinction coefficients of these two maximum bands (1.2 ± 0.01) corresponding precisely to that previously reported [8-10] for the Cr(III) dimeric specie.

The conventional Cr wastewater treatment consists in the reduction of Cr(VI) to Cr(III) and precipitation of Cr(III) as $Cr_2O_3 \cdot xH_2O$ [11]. The chromium (III) precipitation starts at pH >6 forming a hydrous oxide. In this study it was found that the pH which a precipitation is observed also depends of the chromium concentration in the solutions as can be seen in Table 1.

According with the chromium chemical speciation found in the solutions at different pH values it is reasonable to propose that there are two chromium species involved in the sorption processes by calcined hydrotalcite which are $[Cr_2(OH)_2]^{4+}_{(aq)}$ and $Cr_2O_3 \cdot xH_2O$. The first of them probably interact with the anions from the surface of the HT because this specie could not participate in the regeneration of the structure of the HTC after the contact with the chromium solutions because it is cationic in nature. The point of zero charge (pzc) [12] of the hydrotalcite is nearly pH 5.7. This pzc and the initial pH of the different chromium(III) solutions indicate that the surface charge is mainly negative. The negative surface charge could be compensated by chromium cationic species. The pH values at equilibrium (Table 1) changed from 5.5 to 8.9. In the CHT, pH increase was still higher, probably because of the consumption of protons in the reconstruction of the layered HT structure [13]. By the other hand the second chromium specie precipitates on the surface of the HT due to the pH conditions and the chromium concentration in the solutions.

Characterization

Specific area (BET)

The specific surface areas of HT and CHT were 70.33 and 210.7 m²/g, respectively. When the HT is thermally treated then the material undergoes dehydroxylation and decarbonation which increase its exchange capacity, specific area and pore volume [14].

X-ray diffraction

The synthesized HT showed a similar XRD pattern in comparison with that of the HT reference (JCPDS card-22-700). The XRD pattern showed a different reflexions corresponding to a mixture of Al and Mg oxides after the HT was calcined (JCPDS card-4-829). When CHT was in contact with the solution of 50 mmol Cr(III) /L, the lamellar HT structure is regenerated and the characteristics reflexions appear (Figure 2). It is important to note that the (006) reflexion increased after the contact of CHT with the basic sulfate chromium solution and it is prob-

Table 1. pH variability after the contact of Cr(III) solutions with calcined hydrotalcite.

Sample	Cr(III) initial concentration (mmol/L)	pH values		
		pH_0	pH_{eq}	pH_p
Cr(III)-HT1	10.6	3	8.9	6.5
Cr(III)-HT2	27.0	2.9	7.5	6.5
Cr(III)-HT3	53.0	2.8	7.0	6.5
Cr(III)-HT4	106.0	2.7	6.5	6.3
Cr(III)-HT5	160.0	2.6	6.3	5.3
Cr(III)-HT6	210.0	2.5	6.0	5.2
Cr(III)-HT7	270.0	2.4	5.5	5.0
Cr(III)-HT8	320.0	2.2	5.4	4.5
Cr(III)-HT9	370.0	2.1	5.0	4.2
Cr(III)-HT10	430.0	2.1	5.0	4.0

pH_o : initial pH
pH_{eq} : equilibrium pH
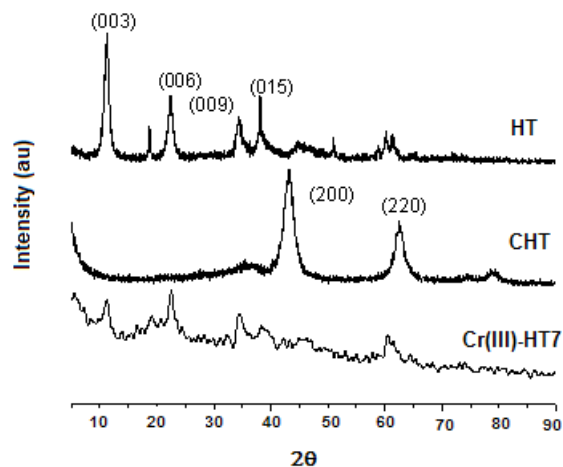pH_p : initial precipitation pH

Figure 2. X-ray diffraction patterns of HT, CHT and Cr(III)-HT7.

ably due to the SO_4^{2-} anion incorporated to the HT crystalline network during the lamellar reconstruction.

Thermogravimetric analysis (TGA)

Figure 3 shows the HT thermal degradation pattern after contact with $Cr(OH)SO_4$ solution. The weight loss at 210.7 °C (23.15%) corresponds to the elimination of chemically bounded water, giving an intermediate trihydrate compound, $Cr_2O_3 \cdot nH_2O$ [15], that agrees with the CrOOH structure ($2CrOOH \approx Cr_2O_3 \cdot 3H_2O$). The second weight loss at 404.81 °C (9.61%), probably is due to dehydroxylation and decarbonatation of Cr(III)-HT7 sample. The third weight loss at 619.35 °C (8.74%) is compatible with the thermal degradation of hidroxo complexes of chromium [16, 17]. The fourth weight lost, between 600 and 800 °C, shows the thermal decomposition of the sulfate phase. It is important to mention that the chromium samples
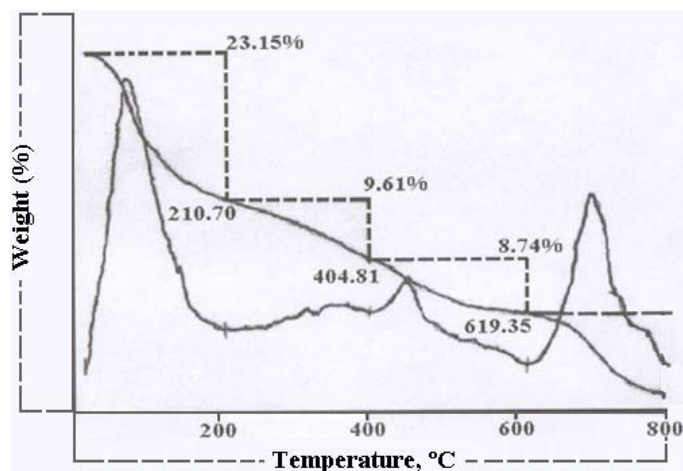
consist in a mixture of Cr_2O_3 and $Cr_2(SO_4)_3$, therefore it is reasonable to consider that the sorption of Cr(III) by CHT is not by the incorporation of Cr(III) in the HT lamellar structure regeneration processes instead a surface interaction or precipitation mechanisms seems to be the most convenient as was mentioned before. This explanation could be supported through a metal hydroxo complexation [18, 19].

Fourier-transformed infrared spectroscopy

The Fourier-transformed infrared spectra (FT-IR) of Cr(III)-HT7 was similar to those of HT and CHT reported in the literature [13, 20-22] as can be seen in Figure 4. However, four additional vibration bands were also observed at 1122, 609, 556 and 443 cm^{-1}. The FT-IR spectra of HT sample (Figure 4a) shows a broad band at 3444 cm^{-1} resulting as an overlapping of hydrogen vibration: stretching vibrations of structural -OH, adsorbed water, and -OH vibrations of hydroxide bonded with carbonate ions in Mg and Al environment. The low intensity band at 1637 cm^{-1} is assigned to bending vibrations of strongly adsorbed water (solvatation water for compensating anion vibrations) and carbonate vibrations (CO_3^{2-}) at 1482-1422 cm^{-1}. Figure 4b shows the FT-IR spectra of CHT and a considerable decrease of the carbonate bands was observed as a consequence of the HT calcination. Figure 4c shows the FT-IR spectra of Cr(III)-HT7. The broad band at 3431 cm^{-1} corresponds to the overlap of hydrogen vibrations, as was mentioned previously for HT spectra. The ν_1, ν_3 and ν_4 frequencies of carbonate were not clearly observed. The four additional vibration bands were assigned as follows: the vibration observed at 1122 cm^{-1} was assigned to sulphate groups and the vibrations observed at 609, 556 and 443 cm^{-1} for α-Cr_2O_3 were assigned.

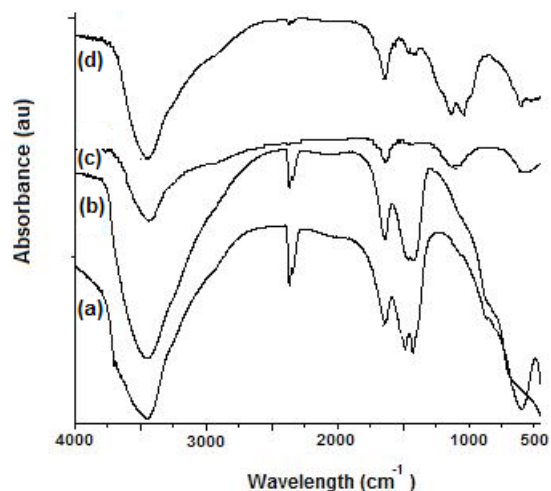The FT-IR spectra of basic chromium sulfate solution [23] shows an absorption at 1100 cm^{-1} corresponding to the

Figure 3. Thermal degradation pattern of Cr(III)-HT7.

Figure 4. Fourier-transformed infrared spectroscopy of (a) HT, (b) CHT, (c) Cr(III)-HT and (d) $Cr_2(SO_4)_3$.

α-Cr_2O_3 component. This vibration would indicate surfaces which are indeed highly oxidized. Moreover, it has been reported that the formation of those species is a general tendency of oxygen-rich metal oxide surfaces [24]. These spectra also shows three bands in 609 cm^{-1}, 556 cm^{-1} and 443 cm^{-1}, which can be attributed to absorptions due to strongly overlapping vibrations between Cr-O and SO_4^{2-}. The observation of these bands is compatible with the thermal behavior of both, α-Cr_2O_3 is formed in an inert atmosphere at nearly 600 °C [16, 17] whereas the sulfate phase remains. However, the v_3 and v_4 modes at 1122 and 556 cm^{-1}, respectively, are related to the tetrahedral sulfate ion [25,26]. In these spectra the band at 609 cm^{-1} could be associated with v_4 sulfate mode, but owing to the background absorbance of the CHT structure, the splitting of this mode can not be observed; hence, the broad maximum band at 609 cm^{-1} is attributable to the vibration of Cr-O (Figure 4d). Within this context, the FT-IR results indicate vibrational overlapping about the characteristics bands. Therefore, it is possible that SO_4^{2-} interacts through a metal cation-sulfate bound formation.

The sulfate anion onto Cr(III)-HT7 founded by FT-IR spectroscopy could be explained considering the memory effect of the CHT because the regeneration of the HT structure is reversible if the calcinations temperature does not exceed 500-600 °C. The CHT can rehydrate and incorporate anions, sulfate$^-$ in this case, in order to rebuild the initial hydrotalcite lamellar structure. In the other hand the ion exchange equilibrium constant for hydrotalcite-like compounds is greater for divalent anions than for monovalent anions.

Conclusions

The final pH of the chromium sulfate solutions in contact with the CHT in combination with the concentration that promote different chromium(III) chemical species play and important role for the chromium(III) sorption by the HT.

The maximum sorption of CHT to sorbs Cr(III) is 26.5 mmol/g and the SO_4^{2-} is incorporated into the lamellar crystalline structure of HT during the regeneration processes as a consequence of the memory effect.

The removal of Cr(III) from wastewater using CHT is a good alternative because the oxidation of Cr(III) to Cr(VI) it is not necessary due to the characteristics of the processes.

Experimental

Calcined hydrotalcite

Hydrotalcite (HT) according with the technique reported in the literature was synthesized with Mg/Al molar ratio of 2.9 [27]. Then the HT was calcined in air at 500 °C for 12 h to obtain a mixture of magnesium aluminum oxides (CHT). The structural changes of the HT and CHT by X-ray diffraction (XRD) were determined as was mentioned above.

Chromium stock solution

Cr(III) stock solution of 500 mmol/L and dilutions were prepared from basic chromium sulfate (Cr(OH)SO_4.nH_2O) which is the primary tanning agent actually used in the tannery industry. In this product 25% of Cr as Cr_2O_3 is contained with basicity ranges from 33 to 58%.

Sorption isotherms

Aliquots of 10 mL of chromium solutions (from 10.6 to 430 mmol/L) were in contact with 0.1 g of CHT into polyethylene tubes of 50 mL. Suspensions were mechanically shacked at 30 rpm during 2 h, subsequently the mixtures were filtrated using filters with aperture of 0.22 μm and pretreated [28]. The pH values were immediately determined in the remaining solutions. It is important to mention that the sorption equilibrium was reach into 2 h as was previously determined. The CHT samples after the contact with the different chromium solutions in this work as Cr(III)-HT from 1 to 10 were named.

pH of Cr(III) aqueous systems

The pH where the Cr(III) species were precipitated in the different aqueous systems (1-10) was determined by the addition of 10% NH_4OH solution until a green turbidity was observed in the solutions. For the pH measured a potentiometer Hanna Instruments pH meter was utilized.

Cr(III) chemical speciation

The chemical species of chromium present in the aqueous solution were 92.3% of the monomer $Cr^{3+}_{(aq)}$ and 7.7% of the first hydrolysis product $[Cr(OH)]^{2+}_{(aq)}$ at pH 3. However, at pH 5, the largest fraction of Cr(III) is present as $[Cr(OH)]^{2+}_{(aq)}$, according with the chemical equilibrium program MINTEQA2 [29-32].

Cr(III) determinations

Cr(III) concentrations in each filtered solution using a UV-Vis spectrophotometer (Shimadzu UV 265FW) at the maximum absorbance wavelength (λ) of 349.8 nm corresponding to Cr_2O_3 [33], were determined.

Characterization

Specific Area (BET)

BET measurements in a Gemini III 237 surface area analyzer using a He/N_2 (30:70) mixture were obtained. Before analysis, samples of HT and CHT (300 mg) approximately 2 h at 200 °C were degassed. Surface areas were determined from the application of the BET multipoint method, considering

the N_2 sorption isotherms at relative pressures between 0.05 and 0.3.

X-ray diffraction

Powder diffractograms of HT and CHT samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the CHT compounds.

Thermogravimetric analysis (TGA)

TGA experiments were carried on in a TGA 51 Thermogravimetric Analyzer T.A. Instruments, using approximately 15 mg of the CHT sample with a particle size between 100 and 500 μm. The temperature was increased 10 °C/min from 20 °C to 800 °C under nitrogen atmosphere maintaining the flow at 50 mL/min.

Fourier-transformed infrared spectroscopy

Samples of HT and CHT were characterized by FT-IR spectroscopy with a Nicolet Fourier transform infrared spectrometer model 550 and IR spectra were recorded from 4000 to 300 cm^{-1}.

Acknowledgements

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