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

Beatriz Eugenia López Muñoz,* Roberto Rivera Robles, José Luis Iturbe García, and María Teresa Olguín Gutiérrez

Instituto Nacional de Investigaciones Nucleares, Departamento de Química. Carretera México Toluca S/N, La Marquesa, Ocoyoacac, México, C.P. 52750, México
beatriz.lopez@inin.gob.mx, Tel.:+52 5553297200, fax: +52 5553297301

Received August 25, 2010; accepted February 17, 2011

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 of 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.

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)—MnO₂ complex. Cr(III) has ability to pass easily into the food chain producing noxious effects, for this reason it is important to find 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.
hypochlorite solution and then in contact with calcined hydro
talcite 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) spe-
cies 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

\[ \text{[Cr(OH)}_2]^{4+}(\text{aq}) \]

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 mono-
mer and trimer [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
\( \text{Cr}_2\text{O}_3\cdot x\text{H}_2\text{O} \) [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

\[ \text{[Cr}_2\text{(OH)}_2](\text{aq}) \]

and \( \text{Cr}_2\text{O}_3\cdot x\text{H}_2\text{O} \). 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 consump-
tion of protons in the reconstruction of the layered HT structure
[13]. By the other hand the second chromium specie precipi-
tates 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 decarbona-
tion which increase its exchange capacity, specific area and pore
volume [14].

**X-ray diffraction**

The synthesized HT showed a similar XRD pattern in compar-
ison 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-
Adsorption of Basic Chromium Sulfate Used in the Tannery Industries by Calcined Hydrotalcite

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 bound water, giving an intermediate trihydrate compound, Cr$_2$O$_3$.nH$_2$O [15], that agrees with the CrOOH structure (2CrOOH ≈ Cr$_2$O$_3$.3H$_2$O). 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$_2$O$_3$ 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 $\nu_1$, $\nu_3$ and $\nu_4$ 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 $\alpha$-Cr$_2$O$_3$ were assigned.

The FT-IR spectra of basic chromium sulfate solution [23] shows an absorption at 1100 cm$^{-1}$ corresponding to the
α-Cr₂O₃ 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 SO₄²⁻. The observation of these bands is compatible with the thermal behavior of both, α-Cr₂O₃ is formed in an inert atmosphere at nearly 600 °C [16, 17] whereas the sulfate phase remains. However, the ν₃ and ν₄ 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 ν₄ 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 SO₄²⁻ 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 SO₄²⁻ 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)SO₄₃H₂O) which is the primary tanning agent actually used in the tannery industry. In this product 25% of Cr as Cr₂O₃ 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 shaken 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% NH₃ 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 Cr³⁺(aq) and 7.7% of the first hydrolysis product [Cr(OH)⁺](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 MINTÉQA2 [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 Cr₂O₃ [33], were determined.

**Characterization**

**Specific Area (BET)**

BET measurements in a Gemini III 237 surface area analyzer using a He/N₂ (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 N₂ 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**

The authors acknowledge to Cristino Rodríguez Flores and Elvia Morales Moreno for their technical support.

**References**