

## Treatment of Chromium(III) in Tannery Wastewater Using LDH Incorporated With EDTA

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### Abstract

Removing of Chromium(III) from contaminated tannery wastewater by adsorption on Zn/Al layered double hydroxides incorporated with ethylenediaminetetraacetic acid, referred to as Zn/Al-EDTA, has been investigated by batch experiments. The effects of different parameters on the percentage relative adsorption concentration were carried out. The adsorption capacity with the Zn/Al-EDTA, provided almost complete removal of chromium(III) which was accomplished within one hour, while the Zn/Al-EDTA particles were kept in suspension by shaking. The effect of pH on sorption in the range of 2-8 at an optimized temperature of 30°C was studied having 95% removal efficiency. The kinetics of adsorption were evaluated and conformed well with the Langmuir isotherm. The bound Cr(III) ions could be eluted successfully using 0.1 M HCl. The sorption-desorption studies employing that the Zn/Al-EDTA could be regenerated without any major loss in the adsorption capacity. The Zn,Al layered double hydroxides (LDHs) host was intercalated by an anionic ethylenediaminetetraacetate (EDTA) guest. It was prepared by coprecipitation of the EDTA anion with the precursor Zn,Al-NO<sub>3</sub> LDHs in a basic condition. Characterization of Zn/Al-EDTA was done using Powder X-ray diffraction (PXRD), elemental analysis and FTIR spectroscopy indicated that most of the interlayer nitrate anions were displaced by (EDTA) anions to form Zn/Al-EDTA which then used as sorption material for Cr(III) metal ion from tanning wastewater.

**Keywords:** tannery wastewater, layered double hydroxides, sorption, chromium(III), edta.

### Introduction

The indiscriminate discharge of spent wastes of chromium-based industries has created an acute pollution problem especially for drinking water resources (Allen and Hansen, 1996). Leather making is an environmentally challenged process. Tanning is the main process that renders stability to the skin matrix against microbial degradation. Chromium(III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. The toxicity of chromium compounds associated mainly with Cr(VI) that poses a greater health risk, less attention was given to Cr(III) although its toxicity cannot be ignored specially at higher concentrations as the case with tanning wastewaters discharge (ATSDR, 2000). Different methods were employed for the removal of chromium compounds such as precipitation, ion exchange, solvent extraction and voltammetry (Kiptoo *et al.*, 2004; Li and Xue, 2001). Other methods were reported for the removal of metal ions in general using different types of biomass or natural polymers such as cotton, moringa oleifera seeds, cellulose, and chitosan (Juang and Shaiu, 2000; Gonzalez *et al.*, 2006; Sharma *et al.*, 2007). In the last decade, chelating resins from the commercial adsorption resins have been popular (Yan and Viraraghavan, 2001; Hernadi *et al.*, 2001). On the other hand some inorganic materials have been used as exchangers/adsorbents, they are resistant to high temperatures, dissolution, and have high selectivity for specific ions to be removed. A variety of these materials including clays, zeolites, metal phosphates, heteropolyacids, hydrous metal oxides, and layered double hydroxides have been used for the separation of specific ionic and molecular species (Poojary *et al.*, 1996; Jamhour, 2005). Number of these methods has efficiency disadvantages or high operational costs or slow reactivity. Moreover, the application of resins in the treatment of wastewater with a high concentration of heavy metal ions is difficult. Most methods which can be considered to be reasonable for wastewater treatment are based on chemical precipitation technique, and then the remaining ions are treated using chelate resins. To attain a simple method that can function directly as chelate and can rapidly attract the metal ion is desired for the purpose of achieving highly effective treatment for wastewater. The use of EDTA as chelating ligand incorporated between the layers of LDHs is, therefore, of importance.

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds. This layered structures have the potential application as sorbents. The general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot zH_2O$ , where ( $M^{2+}=Mg^{2+}, Zn^{2+}, Ni^{2+}$ , etc.,  $M^{3+}=Al^{3+}, Cr^{3+}, Ga^{3+}$  etc.)  $x$  is the ratio  $M^{2+}/(M^{2+} + M^{3+})$  and a structure

involving positively charged mixed metal hydroxide layers separated by charge-balancing anions ( $A^{n-}$ ) and water molecules (Rives, 2001). The anions are exchangeable, giving rise to rich intercalation chemistry. The use of this layered inorganic solids as frameworks for the creation of inorganic–organic host–guest such as EDTA is of interest to further applications for the use in various chemical reactions like extraction and preconcentration of metal ions from environmental samples (Khan and O'Hare, 2002). In addition, the LDHs host is serving as sorbent for many organic contaminants anions present in environmental samples such as pesticides, phenols, carboxylates and sulfonates which led to the ongoing search for the discovery and design of new materials and further new applications (Newman and Jones, 1998; Rives and Ulibarri, 1999). In continuation to our previous work (Jamhour, 2008), the aim of this paper is to develop an efficient method to evaluate the removal of Cr(III) from tannery wastewater using Zn–Al layered double hydroxides intercalated with EDTA.

## 2. Experimental

### 2.1. Materials and Instrumentation.

The starting materials  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ , 50% aqueous NaOH, and aqueous solution of EDTA,  $H_4Y$  or  $H_nY$  (where  $H_nY^{(4-n)-}$  is one of the four possible anions of EDTA depending on the pH) were obtained from commercial sources and used as received. Powder X-ray diffraction (PXRD) data were collected at room-temperature on a Philips X'pert 3065 diffractometer with a curved graphite monochromator (Cu  $K_\alpha$  radiation), in a Bragg–Brentano para-focusing optics configuration. Samples were step-scanned in  $0.02^\circ 2\theta$  steps with a counting time of 1 s per step. FTIR spectra were obtained with KBr pellets using a Mattson Infinity FTIR 60 AR infrared spectrophotometer. pH measurements were recorded by Elico LI-IOT pH meter. A mechanical shaker was used for batch experiments. All the above analyses were carried out at the Institute of Inorganic and Analytical Chemistry, Friedrich-Alexander University, Erlangen-Nurnberg, Germany.

### 2.2. Synthesis of [Zn/Al–EDTA]

All starting chemicals were from Merck (standard analytical grade). Stock solutions of all metals were freshly prepared with deionized water. The buffer solutions of ammonium acetate (0.1 M) were prepared by adding an appropriate amount of acetic acid to ammonium acetate to form solutions of pH 2–6 and ammonium chloride solution with ammonia to form buffer of pH 8–10. The EDTA intercalated LDHs was prepared by CP method following closely a reported procedure by Reichle (1986). Typically, solution of  $Zn(NO_3)_2 \cdot 6H_2O$  (1.97 g) and  $Al(NO_3)_3 \cdot 9H_2O$  (1.12 g) in deionised decarbonated (DD) water (100 mL) was prepared. Another aqueous solution of  $H_4Y$  (0.60 g) was prepared with NaOH (0.5 g) in (50 mL). The NaOH solution was added beforehand to dissolve the EDTA and to adjust the solution to pH ~8. This solution was added drop-wise, with good stirring, to 150 ml of the metal solution, maintaining the pH in the range 8–9. The resulting gel-like slurry was aged overnight at  $70^\circ C$ , filtered and washed several times with DD water and dried in air at  $65^\circ C$  for 12 h.

### 2.3. Adsorption experiments

The adsorption experiments of Cr(III) on Zn/Al-EDTA were carried out suspending duplicate samples of 0.1 g of ZnAl-edta in 50 ml of aqueous solution of chromium chloride salt at various concentrations of 0.1–20 mg shaken in a thermostatic water bath at 20, 30, 40, and  $50^\circ C$  for 15, 30, 60, 120 and 180 min. The pH was varied in the range of 2–8. It was determined for the optimum initial pH, contact time and concentration of metal salts. The supernatants were separated to determine the amount of metal adsorbed by atomic absorption method. This amount was determined from the difference between initial and final concentration of the metal ion in the supernatant solutions. Metal solutions without adsorbent (blank samples) were also shaken under the same experimental conditions.

### 2.4. Analysis of tanning wastewater samples

The wastewater samples were collected from a local tanning industry in clean prewashed polyethylene bottles, filtered, then acidified to 1% with nitric acid and stored in 1 liter polyethylene bottles at  $4^\circ C$  (Soylak and Doggan, 1995). A sample of this water was taken for dilution, and the above adsorption method was applied. The investigated Cr(III) ions concentration in the final solutions were then determined.

### 2.5. Sorption isotherms

The adsorption capacity of Zn/Al-EDTA for the Cr(III) ions was determined by the known isotherm model of Langmuir:

$$q_e = q_{\max} \frac{bC_{eq}}{1 + bC_{eq}}.$$

Where  $q_e$  and  $q_{max}$  are the observed uptake capacity at equilibrium and maximum uptake capacities (mg/g ZnAl-edta),  $C_{eq}$  is the equilibrium concentration (mg/L solution);  $b$  is the equilibrium constant (L/mg). The percent uptake for the sorption capacities of Cr(III) were calculated using the following Equation:

Percent uptake (%) = conc. of  $Cr^{+3}$  in the solid phase / conc. of  $Cr^{+3}$  in aqueous phase  $\times$  100. Effect of initial metal concentration was investigated using initial Cr(III) concentration varied from 0.1 to 20 mg/100 ml. In experiments concerning the effect of adsorbent dose, a range of solid material samples (0.5, 1, 2, and 5 g) were used. For contact time experiments, the same procedure above was followed, with the difference that the phases were separated after a determined period of contact time. The temperature was optimized at 35°C for all adsorption experiments.

### 2.6. Desorption studies

In order to study the reuse of the material different concentrations of stripping acid were tested. A 0.05-0.1M hydrochloric acid was of choice for further experiments. The regeneration process was carried out by transferring the sample material used in the adsorption experiment into a 100 ml flask and shaken with 50 ml of the acid. The filtrate was decanted and analyzed for desorbed Cr(III) content.

## 3. Results and discussion

PXRD pattern of Zn/Al-EDTA is represented in Figure 1. The prepared intercalated compound in (b) is different from that of the precursor sample with nitrate anion in the interlayer (a), but both are characteristic of a layered phase with the basal diffractions mainly due to planes of (003) and (006). These patterns also indicate that the intercalation of edta in Zn/Al-NO<sub>3</sub> gives rise to an increase in basal spacing from  $d=7.2$  Å to  $d=14.4$  Å. The subtraction of 4.8 Å as the hydroxalcite-layer thickness, from the  $d=14.4$  Å gives 9.6 Å as interlayer space occupied by EDTA. On the other hand, the values for Zn/Al-NO<sub>3</sub> decrease slightly from Zn/Al-EDTA which agrees with the reported classical values for Zn/Al-edta (Perez *et al.*, 2006). This suggests that the ligand is probably accommodated in the interlayer space of the LDHs. To confirm the chelation of metal cations in the interlayer, the PXRD patterns of the products Zn/Al-edta-M were obtained, but no much change in the basal spacing of the adsorbent material was observed (PXRD not shown). In addition, the basal spacing is very similar to that found in previous reports (Li *et al.*, 2004). The results suggest that the M-edta complexes are formed and accommodated into the interlayer without apparent deformations. The preparation of hybrid Zn<sub>n</sub>Al layered materials containing intercalated EDTA anions was achieved by aqueous coprecipitation of two different precursor in nitrate form at constant pH= 8, by addition of a mixed Zn/Al nitrate solution to an NaOH/NaNO<sub>3</sub> solution, followed by aging overnight at 70 °C. Elemental analysis indicated that the Zn/Al ratio in the final materials was close to 2. The following compositions of the intercalation compound is given as:  $[Zn_{0.66}Al_{0.34}(OH)_2](H_2Y)_{0.28} \cdot 0.4H_2O$ .

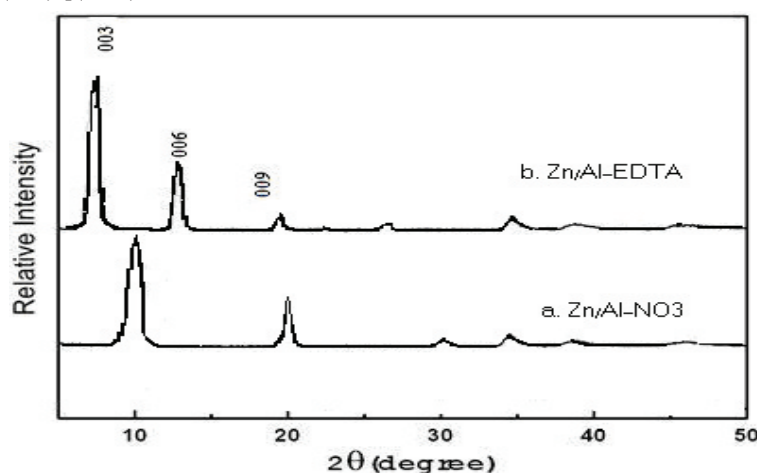


Figure 1. The PXRD pattern of: (a) Zn/Al-NO<sub>3</sub> and (b) Zn/Al-EDTA.

A portion of the carboxylic acid groups were deprotonated upon co-precipitation with almost complete exchange of the nitrate ions by EDTA. The hybrid material exhibited similar FTIR spectra to that of the precursor host reported earlier by Perez *et al.* (2006).

Figure 2 compares the FTIR spectra of the host Zn/Al-NO<sub>3</sub> (a) and its anion exchange product with EDTA, Zn/Al-EDTA (b). The FT-IR spectrum of ZnAl-NO<sub>3</sub> is similar to that reported by Cavani *et al.* (1991). The intercalated EDTA anion was confirmed by the presence of the FTIR bands at 1493, 1271 and 900 cm<sup>-1</sup> for the C=C, and C-O stretching vibrations. New FTIR bands at 1530 and 1383 cm<sup>-1</sup> for the hybrid material are ascribed to  $\nu_{as}(\text{OCO})$  and  $\nu_s(\text{OCO})$  of deprotonated carboxylate groups, respectively (Cavani *et al.*, 1991). The wide band at 3500 and 2933 cm<sup>-1</sup> are attributed to the C-H, H-bonding stretching vibrations of OH-groups in the brucitelike layers and water molecules. Water bending vibration observed at 1620 cm<sup>-1</sup>. The very sharp peak at 1383 cm<sup>-1</sup> and a broad band at 600 cm<sup>-1</sup> is attributed to C-N stretching vibration of NO<sub>3</sub><sup>-</sup> group, and it is not registered in the spectrum of the product.

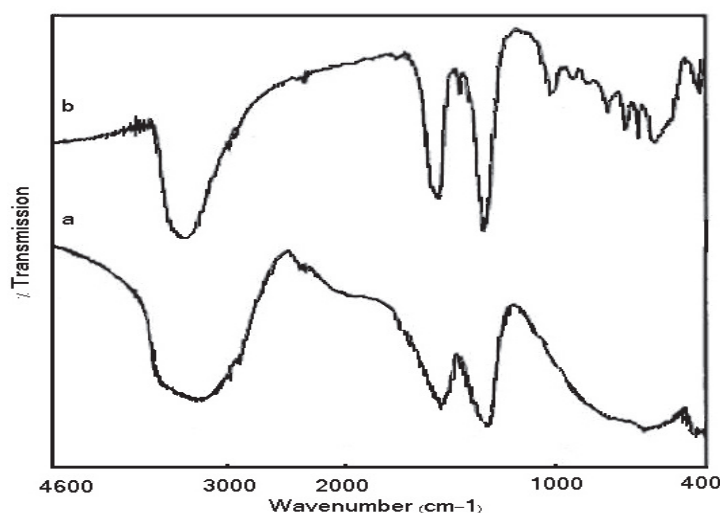


Figure 2. The FTIR spectra of: (a) Zn/Al-NO<sub>3</sub> and (b) Zn/Al-EDTA.

The effect of pH is probably the major factor influencing metal sorption process (Velkova *et al.*, 2012). The pH of the solution influence both metal binding sites on the cell surface and the chemistry of metal complex formation in solution. In order to demonstrate the effect of pH on sorption capacity, uptake of Cr(III) ions onto Zn/Al-EDTA as a function of pH was studied in the pH ranges of 2 to 8 and showed in Figure 3.

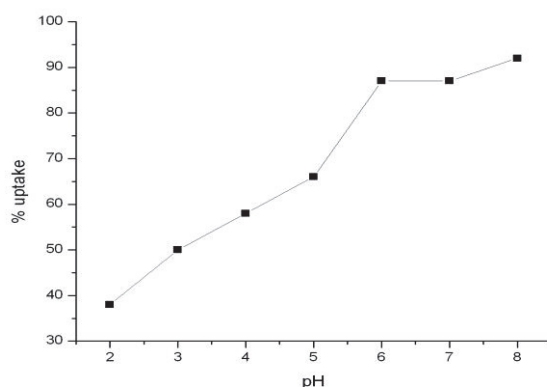


Figure 3. Effect of pH on the percent uptake of Cr(III) ions from wastewater.

The Cr(III) ion uptake was affected by pH of the solution as the pH increases the uptake increases reaching a maximum of 92% and 87%, respectively at pH 8.0 and pH 6.5. The sorption capacities of metal ions at the optimal temperature of 35°C are 0.45, 0.58, 0.63, 0.72, 0.74 and 0.75 mmol/g, at pH 2, 3, 4, 5, 6 and 7,

respectively. The capacity is relatively constant for pH 6-7. Thus, the optimum pH was chosen to be 6.5 to avoid any false uptake at pH 8 or above due to the formation of metal hydroxides. This order of uptake is clearly show the pH dependant and the sorption increases with increasing pH value of solution as expected trend for heavy metal ions. The effect of contact time between adsorbent and a Cr(III) solution with an initial concentration of 100 mg/L, 1g of solid material and pH 6.5 at 30°C is presented in Figure 4.

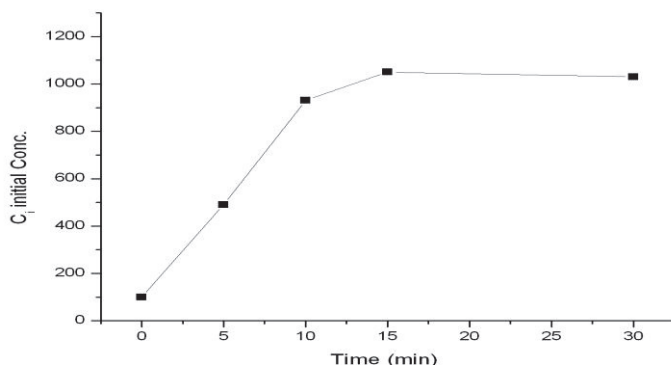


Figure 4. Effect of contact time on Cr(III) adsorption by Zn/Al-EDTA.

The sorption process can be divided into two phases. The first phase passed in a short period of time, 10-15 min, followed by second slower phase until the equilibrium was reached at 30 min. The rapid phase might be due to the complex formation of the edta ligand with Cr(III) ions and the availability of enough free active metal binding sites on the layered surface. A second slow phase might be attributed to the decrease in number of free binding sites. Figure 5 shows the isotherm of Langmuir model.

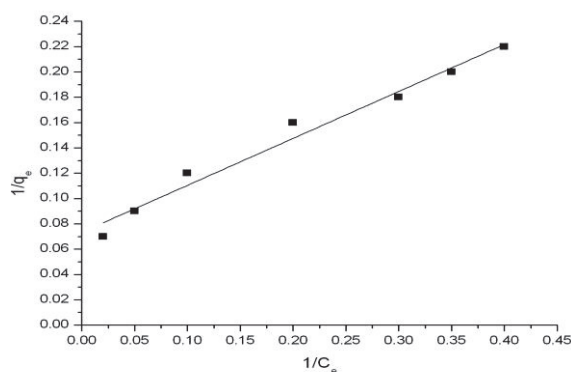


Figure 5. Langmuir Isotherm model for sorption of Cr(III) on Zn/Al-EDTA.

As it can be seen, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient  $R^2 = 0.97$ ). The fact that the Langmuir isotherm fits the experimental data may be due to the homogeneous distribution of active sites in the presence of EDTA ligand between layers. The good performance of the Langmuir model can also be found in other studies (El-Hassouni *et al.*, 2013). The experimental data were applied to the equation, the data fit well with this model and clearly show that the Langmuir isotherm model is suitable for describing the equilibrium sorption of the metal by Zn/Al-EDTA in the given concentration range.

In order to estimate the accuracy and the effectiveness of Zn/Al-EDTA to remove Cr(III) ions from tannery wastewater effluent, different amounts of Cr(III) ions 1, 5, 10, 20, and 50 mg Cr were added to 500 ml of diluted effluent samples. The procedure in the experimental section was followed with a 10 ml final sample volume. The results in Table 1 show a very good agreement between the added and measured Cr amounts. The recovery values were higher than 95% which conform the accuracy of the proposed procedure.

Table 1. Recovery of Cr(III) From Tannery Wastewater Samples

Wastewater Samples		
Amount Added (ppm)	Found (ppm)*	Recovery (%)
0	0.9	-
1	1.8 ± 0.04	95%
0	1.4	-
5	6.1 ± 0.35	95%
0	19.7	-
10	28.5 ± 0.81	96%
0	185	-
20	197 ± 0.85	96%
0	384	-
50	400 ± 3.2	92%

\*Average of five determinations, ± standard deviation.

#### 4. Conclusion

Layered double hydroxides intercalated by EDTA ligand of the type Zn/Al-EDTA have successfully been prepared by ion-exchange. The materials may have applications in the field of tannery wastewater treatment in the removal of Cr(III). This procedure was successfully carried out at different contact time, pH and metal concentrations. The shape of the adsorption isotherms suggests in this case specific interaction and high affinity of Cr(III) toward the intercalated composite material. From these results it is concluded that the adsorption of Cr(III) on Zn/Al-EDTA was high with sorption capacity of 0.75 mmol/g at pH 6.5 and percent uptake of 95%.

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