ADSORPTIVE REMOVAL OF SULFATE, PHOSPHATE AND CHLORIDE BY MG-AL AND ZN-AL LAYERED DOUBLE HYDROXIDES FROM AQUEOUS SOLUTIONS

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Abstract. The wastewater of leather industry contains pollution loads which includes anionic contaminants such as chloride, sulfate and phosphate. Different treatment technologies for tannery wastewater have been investigated. Adsorption is a promising technique due to its greater selectivity, simple operation, faster regeneration kinetics and high uptake capacity even at trace levels. In the present study, Mg-Al and Zn-Al Layered Double Hydroxides were synthesized by the co-precipitation method at variable pH through a semi-batch system. The prepared material was characterized by XRD, BET surface area determination, TG-DTA and FTIR. The chloride, sulfate and phosphate adsorption properties onto Mg-Al and Zn-Al Layered Double Hydroxides from aqueous solutions were evaluated. The adsorption experiments of chloride, sulfate and phosphate were investigated through batch studies at initial concentrations of 100 mg/L of these anions as NaCl, K_2SO_4 and KH_2PO_4, respectively. The experiments were carried out separately for each anionic specie by mixing 10 ml of solution with 1 g/L of adsorbent for 5 h. Mixing was performed on a thermostatic shaker at 200 rpm and at room temperature (25 °C). The effect of co-existing anions on the adsorption capacity was also analyzed. After ion adsorption, chloride, sulfate and phosphate concentrations were measured by ion chromatography. The results showed a removal ratio for Mg-Al Layered Double Hydroxide of 24.4% and 51% for sulfate and phosphate, respectively, while chloride was not removed from the solution. For the adsorbent Zn-Al Layered Double Hydroxide, the removal ratio of sulfate, phosphate and chloride reached 12.8 %, 69.1 % and 6.3%, respectively.

1 Introduction

Leather tanning is a common industry all over the world and represents an important economic field in Mediterranean countries and in developing nations, such as Turkey, China, India, Pakistan, Brazil, and Ethiopia [1-5]. The transformation of raw or wet-blue hides into commercial products for various purposes requires high water consumption and the use of several chemical products. However, these chemicals are not completely fixed by the hides and remain in the effluent [6]. Therefore, leather tanning industry wastewater is characterized by dark brown color, objectionable odour, variable pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), chromium (Cr), sulfate, phosphate, nitrate, and a variety of highly toxic organic chemicals and heavy metals [7, 8].

The high concentrations of pollutants in tannery wastewater represent an environmental and technological challenge [9-11]. If not properly removed in prior treatment plants, anionic contaminants, such as chloride, sulfate and phosphate, can have a significant impact on aquatic environments. High concentrations of chloride in wastewaters cause corrosion of waste pipes or agricultural wreck of crops [12]. Concentrations of sulfate above 250 ppm imparts bitter taste in water and cause corrosion in water pipes which can have a laxative effect, dehydration and gastrointestinal irritation on humans and young livestock. Besides that, high concentrations of sulfate can cause the release of toxic sulfide to water bodies, due to sulfate reduction in sulfide, and damage the environment [13, 14]. Furthermore, the over–abundance of phosphate in water

can result in algal bloom and eutrophication of water sources. The latter causes the degradation of water quality, decreases biological diversity and, consequently, increases the cost of water treatment [15-17]. For these reasons, the adequate wastewater treatment is necessary prior to its discharge in aquatic environments.

A variety of techniques have been investigated regarding tannery wastewater treatment, such as biological treatment [18, 19], chemical processes including coagulation-flocculation [8, 20, 21], ion exchange [22], adsorption [23, 24], electrochemical [25], and combined chemical/biological processes [26-29]. Among these techniques, the main technologies adopted to treat industrial tannery wastewater are chemical and biological methods [5]. The employment of the conventional biological method, which utilizes activated sludge, presents some challenges due to the presence of heavy metals in tannery wastewater that inhibits this technique [30, 31]. However, these challenges can be overcome by combining the aforementioned methods. Adsorption is a promising technique that could be used as a tertiary treatment due to its greater selectivity, simple operation and high uptake capacity even at trace levels [32, 33].

Layered Double Hydroxides (LDH), also known as hydrotalcite-like materials or anionic clays, have attracted attention as effective adsorbents [34]. The structure of LDH is based on positive charged brucite–like sheets, where the positive charges are balanced by the intercalation of anions and water molecules in the interlayer regions [35]. LDH are represented by the general formula: $[M^{+2}{}_{1-x}M_x^{+3}(OH)_2]^{x+}A_{x/m}^{m-}.nH_2O$ where M^{+2} and M^{+3} are divalent and trivalent cations, respectively. A^{m-} represents the incorporated anions in the interlayer space and the value of x is equal to the molar ratio of $M^{+3}/(M^{+2} + M^{+3})$. The identities of M^{+2}, M^{+3}, A^{m-} and the value of x may vary in a wide range giving rise to a large class of isostructural LDH with varied physicochemical properties [36]. Due to their large surface area and high anion exchange capacity, LDH have been successfully employed in several studies for removing different anions from aqueous solutions [12-17, 37, 38].

In the present work, Mg-Al and Zn-Al LDH were studied as adsorbents to individually remove chloride, sulfate, and phosphate from aqueous solutions. In addition, the effects of co-existing anions on the removal of chloride, sulfate, and phosphate were investigated. Mg–Al and Zn–Al LDH were prepared containing carbonate anions in the interlayer space. The morphological structure of the materials was examined with X-ray diffractometry (XRD), BET surface area, thermogravimetry coupled with differential thermal analysis (TG-DTA), and Fourier-transform infrared spectra (FTIR).

2 Materials and Methods

2.1 Synthesis of Layered Double Hydroxides

The LDH were synthesized by the co–precipitation method at variable pH through a semi–batch system. Aqueous solutions of the following metal nitrates were used: $Mg(NO_3)_2$ and $Al(NO_3)_3$ for Mg-Al LDH, $Zn(NO_3)_2$ and $Al(NO_3)_3$ for Zn-Al LDH. The atomic ratio of cations M^{2+}/M^{3+} was fixed at 3 and $[M^{2+}] + [M^{3+}] = 1$ mol L^{-1}. A solution of Na_2CO_3 was used as the precipitant agent.

The solutions containing the mixture of bivalents and trivalent metal nitrates were added drop-wise, with constant flow rate into the Na_2CO_3 solution. The co–precipitation was conducted in a glass stirred vessel at room temperature (25 °C). The resulting slurry was kept under stirring for crystallization at room temperature for 24 h, filtered and washed several times with deionized water. The wet solid was dried at 80 °C for 12 h and milled to pass through an 80 mesh sieve.

2.2 Characterization of Layered Double Hydroxides

The materials were characterized by X-ray diffractometry (XRD), surface area measurements, thermogravimetry coupled with differential thermal analysis (TG-DTA) and Fourier-transform infrared spectra (FTIR).

The X-ray diffraction patterns were collected through the powder method in a Shimadzu XRD7000 diffractometer, between 2° and 90° 2θ using Cu–Kα radiation.

The specific surface area measurements were determined by N_2 adsorption/desorption at liquid nitrogen temperature (77 K) on a Quantachrome Nova 1200 surface area analyzer. The samples were pretreated at 250 °C under a He flow rate of 30 mL min^{-1} for 24 h before measurements. The specific surface area (S_{BET}) was calculated according to the multipoint Brunauer–Emmett–Teller (BET) method.

Thermal analysis of the prepared solids was performed by thermogravimetry coupled with differential thermal analysis using a thermobalance (Model SDT600). The samples were heated in the temperature range of 20–900 °C with a heating rate of 10 °C min^{-1}, under a synthetic air flow rate of 100 mL min^{-1}.

FTIR spectra were collected on a Frontier spectrophotometer (PerkinElmer) using the attenuated total reflection (ATR) method. Infrared spectra over the 4000–650 cm^{-1} range were obtained by averaging 32 scans with a resolution of 4 cm^{-1} at room temperature.

2.3 Adsorption studies

For the adsorption experiments, individual stock solutions (100 mg L^{-1}) of sulfate, phosphate and chloride were prepared with ultrapure water (Gehaka) and K_2SO_4, KH_2PO_4, NaCl, respectively. The adsorption experiments were performed in 15 mL centrifuge tubes by mixing 10 mL of each anion aqueous solution with 1 g L^{-1} of Mg–Al or Zn–Al LDH under constant stirring for 5 h. Mixing was performed on a thermostatic shaker (Marconi 832) at 200 rpm and at room temperature (25 °C). The batch studies were conducted without any pH adjustment made to the solutions to avoid the influence of complementary anions.

After adsorption, the samples were filtered through a 0.45 µm cellulose nitrate membrane filter. The effect of competitive anions on sulfate, phosphate and chloride adsorption was also evaluated. 1 g L^{-1} of each adsorbent was introduced in a multi anion solution, containing 100 mg L^{-1} of each of the following anions: chloride, bromide, nitrate, sulfate and phosphate. The mixtures were shaken for 5 h.

The residual sulfate, phosphate and chloride concentrations were analyzed by ion chromatography (IC) (Metrohm Professional IC 850–AnCat). The IC separation was performed on a Metrosep A Supp 5 analytical column (250 × 4.0 mm) using a standard carbonate eluent (sodium hydrogen carbonate: 1.0 mmol L^{-1} and sodium carbonate: 3.2 mmol L^{-1}) at a flow rate of 0.7 mL min^{-1}. Each run was carried out in duplicate.

The removal ratio R(%) of sulfate, phosphate and chloride (Eq. 1) was obtained from the following relation:

$$\mathrm{R}(\%) = \frac{(C_0 - C_e)}{C_0} 100 \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium concentration of each anionic specie in solution (mg L^{-1}).

3 Results and Discussion

3.1 Characterization

The XRD patterns of the synthetized materials are illustrated in Figure 1. Mg–Al and Zn–Al LDH exhibited the characteristic reflections of the layered structures. Both samples presented reflections at angles 11.8°, 23°, 34.7°, 60.5° and 61.8° corresponding to the crystalline planes of (003), (006), (012), (110) and (113), respectively, which are related to the hytrotalcite structure [39, 40].

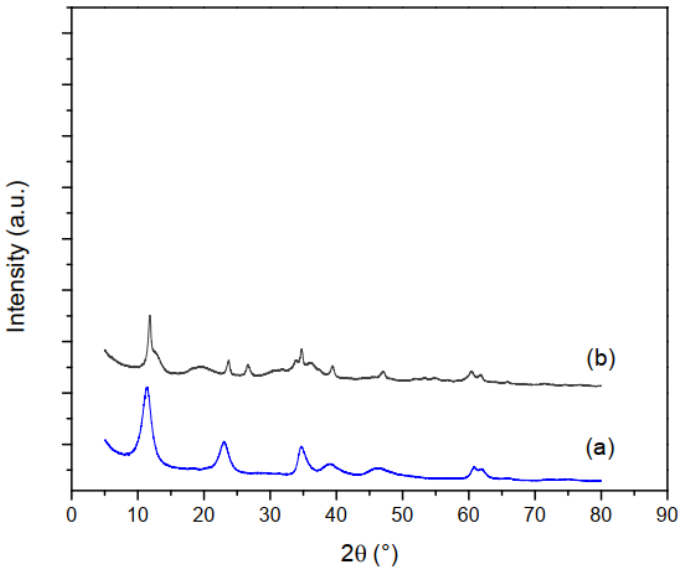

Fig. 1. XRD patterns of Mg–Al (a) and Zn–Al (b) LDH.

The BET surface area of Mg–Al and Zn–Al LDH were 93.7 and 133.2 $m^2\ g^{-1}$, respectively. For adsorbents, a large surface area can offer more available adsorption sites. Furthermore, The TG–DTA profiles are depicted in Figure 2. It was observed that Mg–Al and Zn–Al LDH showed endothermic decomposition in two stages, in agreement with typical results for hydrotalcites [41, 42]. The first step in the range of 25-200 °C had a weight loss of approximately 23% and 12% for Mg-Al and Zn-Al samples, respectively, which can be attributed to the elimination of the surface and interlayer water. The second thermal decomposition occurred at a temperature range between 200 and 400 °C. The weight loss in this stage is due to the loss of OH groups and anion carbonate decomposition. At higher temperatures, the weight loss corresponds to the formation of the mixed oxide and the collapse of the LDH structure [43].

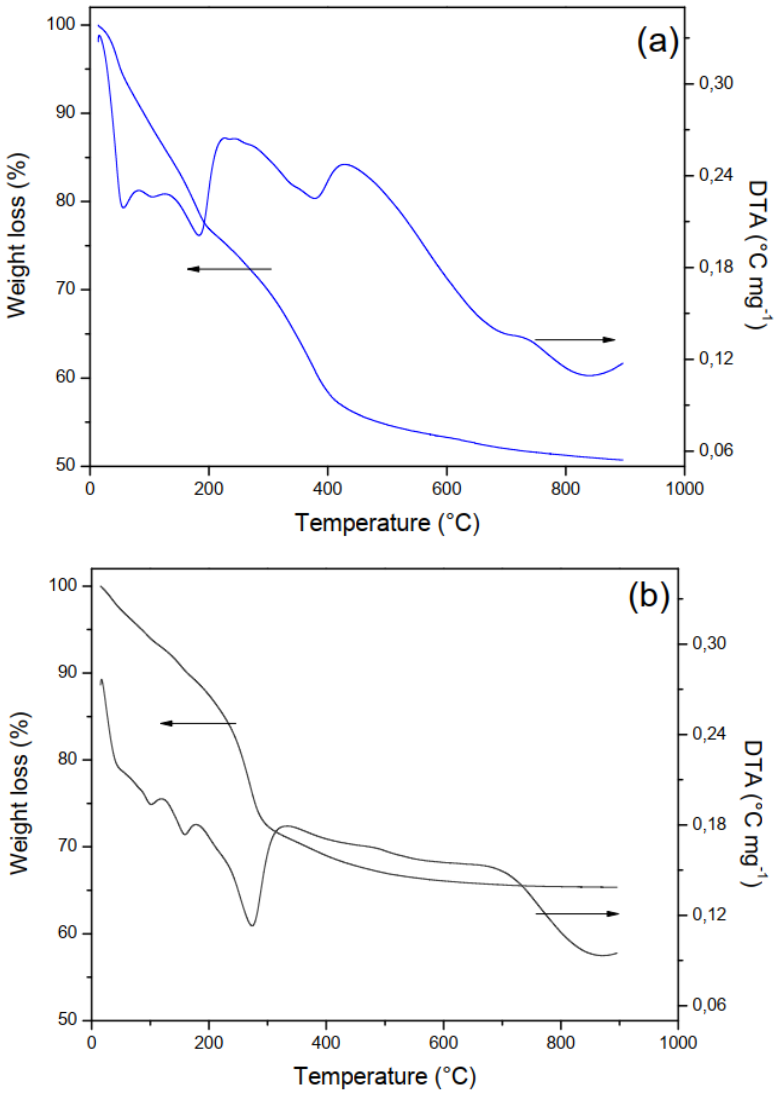

Fig. 2. Thermogravimetric profile (TG–DTA) of Mg–Al (a) and Zn–Al (b) LDH.

Based on the vibrational bands and its respective assignments (FTIR) for Mg-Al and Zn-Al LDH, as presented in Table 1, it can be inferred the presence of O-H stretching vibrations from structural hydroxyl groups and interlayer water molecules; O-H bending mode of water molecules and the indication of the existence of CO_3^{2-} species in the interlayer space [32, 44].

Table 1. FTIR bands and respective assignments for Mg-Al and Zn-Al LDH.

Bands (cm^{-1})		Assignment
Mg-Al LDH	Zn-Al LDH	
3350.6	3308.7	O-H stretching
1634.9	1427.9	O-H bending
1359.2	834.1	CO_3^{2-}

3.2 Adsorption studies

Adsorption experiments were performed to verify the removal potential of chloride, sulfate and phosphate by Mg-Al and Zn-Al LDH. Chloride, sulfate and phosphate removal were individually evaluated at initial concentration of 100 mg L^{-1} and contact time of 5 h. The obtained results are illustrated in Figure 3. It was observed that the anion phosphate achieved highest removal values of 51% and 69.1% for Mg-Al and Zn-Al LDH, respectively. Chloride was not adsorbed by Mg-Al LDH and reached a removal value of only 6.3% for Zn-Al LDH. Moreover, the polyvalent anion sulfate had removal values of 24.4% and 12.8% for Mg-Al and Zn-Al LDH, respectively. Previous studies by Novillo et al. (2014) and Lv et al. (2008) showed that LDH have a significant selectivity towards multivalent inorganic anions when compared with monovalent inorganic anions [45, 46].

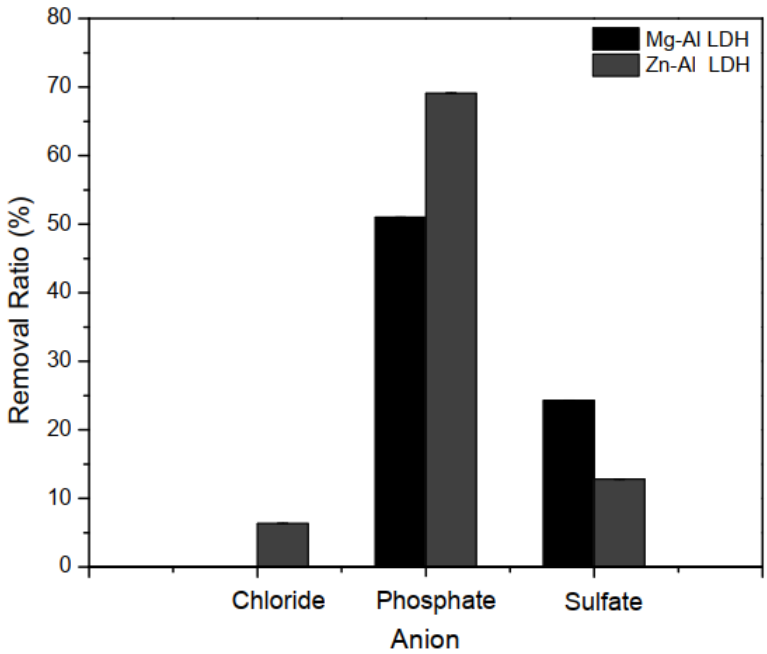

Fig. 3. Chloride, phosphate and sulfate removal from aqueous solutions utilizing Mg-Al and Zn-Al LDH.

3.2.1 Effect of competitive anions

Wastewater usually contains many anionic species such as nitrate, sulfate, bromide, phosphate and chloride. These anions are expected to interfere in the adsorption process of desired anions. The effects of co-existing anions on the removal of chloride, sulfate and phosphate were studied by using a multi-anion solution containing equal concentrations of chloride, bromide, nitrate, phosphate and sulfate of 100 mg.L^{-1}.

The results presented in Table 2 showed a selective adsorption for the phosphate anion also in the multi-anion experiment. It demonstrates that the active adsorption sites preferred the higher effective charge anion. The World Health Organization (WHO) has set a maximum discharge limit of phosphorus of 0.5 – 1 mg L^{-1} as a guideline. Since biological and chemical processes display fluctuating and unsteady results for phosphate removal, the adsorption technique could be incorporated as a complementary treatment based on the results obtained in this current work [47].

There was a decrease in the removal of chloride, sulfate and phosphate when compared with their individual removal values. Phosphate adsorption by Mg-Al LDH is practically unaffected by the presence of other anions in solution. For the adsorption experiment with Zn-Al LDH, phosphate removal is decreased by almost 15% due to interfering anions. In addition, sulfate adsorption efficiency onto Mg-Al LDH is strongly reduced in the presence of other anionic species. Chloride was

not removed by neither Mg-Al nor Zn-Al LDH. This fact showed that Mg-Al and Zn-Al LDH had in fact greater affinities for multivalent anions. Similar results were obtained by Das et al. (2006) who showed that phosphate removal ratio decreased approximately 25% in the presence of sulfate but only 15% in the presence of monovalent anions [48].

Table 2. Effects of competitive anions on the adsorption of chloride, sulfate and phosphate by Mg-Al and Zn-Al LDH.

Anion	Mg-Al LDH		Zn-Al LDH	
	Individual solution Removal (%)	Co-existing anions Removal (%)	Individual solution Removal (%)	Co-existing anions Removal (%)
Chloride	0.0	0.0	6.3	0.0
Phosphate	51.0	50.8	69.1	54.6
Sulfate	24.3	6.8	12.8	8.4

4 Conclusions

In this study, Mg–Al and Zn-Al LDH were prepared and used to remove chloride, phosphate, and sulfate from aqueous solutions. Characterization analysis showed that both adsorbents formed the structure of hydrotalcite-like materials. The BET surface area of Zn-Al LDH was larger than Mg-Al LDH. Both LDH did not show remarkable selectivity towards the monovalent anion chloride and it was not effectively removed from the solution. Although sulfate achieved a removal of 24.3% when utilizing Mg-Al LDH, the presence of several competitive anions decreased its removal value. In the individual and multi-anion adsorption studies, Mg-Al and Zn-Al LDH exhibited high selectivity for phosphate ions, achieving removal values higher than 50%. Due to the significantly higher removal values, Mg-Al and Zn-Al could be used as effective adsorbents in a tertiary treatment for phosphate removal.

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