



Separation Science and Engineering

## Effect of interlayer anions on chromium removal using Mg–Al layered double hydroxides: Kinetic, equilibrium and thermodynamic studies

Mohamed Khitous<sup>1,2,\*</sup>, Zineb Salem<sup>1</sup>, Djamilia Halliche<sup>2</sup>

<sup>1</sup> Laboratory of Industrial Process and Engineering LSGPI, Faculty of Mechanical and Process Engineering, University of Sciences and Technology, Houari Boumediene, BP 32 El-Allia, Bab Ezzouar, Algiers 16111, Algeria

<sup>2</sup> Laboratory of Natural Gas Chemistry, Institute of Chemistry, University of Sciences and Technology, Houari Boumediene, BP 32 El-Allia, Bab Ezzouar, Algiers 16111, Algeria

## ARTICLE INFO

## Article history:

Received 5 February 2015

Received in revised form 10 September 2015

Accepted 10 September 2015

Available online 26 November 2015

## Keywords:

Hydrotalcite

Cr(VI)

Sorption

Layered double hydroxide

Kinetic

## ABSTRACT

The influence of interlayer anions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on Mg–Al hydrotalcites for Cr(VI) removal from aqueous solution was studied. The structure of the prepared LDHs was characterized by XRD, SEM, FTIR, TGA, BET surface area and  $\text{pH}_{\text{zpc}}$ . The sorbent ability and sorption mechanisms were also investigated. The LDHs exhibit high removal for Cr(VI), and the sorbed amount depends on the nature of interlayer anion, which decreased in the following order:  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . Nitrate-containing LDH reached a Cr(VI) sorption equilibrium within only 30 min. The effects of operating conditions, including initial concentration, solution pH, agitation time and sorbent amount have been studied in batch mode. The optimum conditions were observed at an initial concentration of  $100 \text{ mg} \cdot \text{L}^{-1}$ ,  $\text{pH} = 6$ , agitation time of 60 min and a sorbent dose of  $2 \text{ g} \cdot \text{L}^{-1}$ . The equilibrium data were fitted to the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The Langmuir model was found to sufficiently describe the sorption process, offering a maximum sorption capacity of  $71.91 \text{ mg} \cdot \text{g}^{-1}$ . The sorption kinetic follows pseudo-second-order reaction with high accuracy. Thermodynamic parameters suggested that the sorption process is spontaneous and endothermic in nature.

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## 1. Introduction

Rapid industrialization and urbanization have resulted in elevated emission of toxic metals entering the biosphere. The release of heavy metals in biologically available forms may damage or alter both natural and man-made ecosystems [1]. One of the most toxic heavy metal contaminants of concern is the hexavalent chromium, which is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and photography industries. It causes severe environmental and public health issues [2]. Cr(VI) is highly mobile and is considered acutely as toxic and mutagenic for most organisms; in humans its main effects are on skin, liver, kidney and respiratory organs, resulting in a variety of diseases such as dermatitis, hepatic and renal tubular necrosis, bronchitis and bronchogenic carcinoma [3, 4]. The tolerance limit for Cr(VI) for discharge into surface water is  $0.1 \text{ mg} \cdot \text{L}^{-1}$  and in drinking water is  $0.05 \text{ mg} \cdot \text{L}^{-1}$  [5]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the concentration of Cr(VI) to acceptable levels.

In this respect, different techniques have been employed to remove Cr(VI) from wastewaters, like chemical precipitation, biological

treatment, membrane filtration and sorption. The physicochemical treatments are commonly used because they are more economical than the electrochemical ones [6]. Among these techniques, sorption is one of the most common and cost-effective physical processes that may be used to remove Cr(VI) from solution. It has been reported that zeolites [7], activated carbon [8], minerals [9], cationic and anionic clays have been used as sorbent materials for Cr(VI) [10,11].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are a class of synthetic two-dimensional nanostructured anionic clays whose structure can be described as containing brucite-like layers, where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been replaced isomorphously by trivalent cations, giving positively charged layers with charge-balancing anions between them. Some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region [12,13]. They may be represented by the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot n\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent and trivalent cations, respectively;  $x$  is the  $\text{M}^{2+}/\text{M}^{3+}$  molar ratio and  $\text{A}^{n-}$  is an anion.

Due to their intercalation ability of anionic species and other physicochemical properties, LDHs represent an inexpensive, versatile and potentially recyclable source of a variety of catalyst supports, catalyst precursors, sorbents, medicine stabilizers and ionic conductors [14–16]. They have attracted attention as low-cost effective sorbents to remove negatively charged contaminants. Their high uptake levels of anionic species can be accounted for by their relatively large surface

\* Corresponding author.

E-mail address: [usthbkhitous@yahoo.fr](mailto:usthbkhitous@yahoo.fr) (M. Khitous).

area, high exchange capacities [17], the flexible and large interlayer space containing a significant number of exchangeable anions, which is accessible to polar molecular species as well as harmful anions polluting water and soil. LDHs can take up anion species from solution by three different mechanisms: surface adsorption; interlayer anion-exchange and reconstruction of a calcined LDH precursor by the “memory effect”. The last one takes place when LDHs are calcined to eliminate most of the interlayer anions followed by rehydration; anions are incorporated and the calcined LDHs recover their original layered structure [18]. The memory effect of LDHs is one of their most attractive features as sorbents for anionic species [19]. Calcination allows the recycling and reuse of the sorbent with elimination of organic contaminants as CO<sub>2</sub> and water [20]. Moreover, the calcined LDHs are more effective sorbents than uncalcined LDHs because interlayer carbonate ions of uncalcined LDHs are difficult to displace with other anions [21,22]. However, the use of calcined LDHs presents two shortcomings: (1) a complicated regeneration stage because it needs a recalcination of the samples after sorption and (2) an increase in solution pH [23,24].

The anion-exchange capacity of LDHs is affected by the nature of the interlayer anions initially present and the layer charge density. When the layer charge density is very high, the exchange reaction may become difficult. LDHs have greater affinities for multivalent anions compared with monovalent anions [25,26]. In particular, the favorable lattice stabilization enthalpy associated with carbonate results in these anions being difficult to displace in anion-exchange reaction. Therefore, the anion removal in LDHs by intercalation occurs when the interlayer are intercalated by weak electrostatic interactions with the layers, such as chloride or nitrate.

Previous studies have investigated the ability of LDHs to remove Cr(VI) from solution by both surface sorption and anion-exchange. Lazaridis *et al.* [22] studied the sorption of Cr(VI) over MgAl-CO<sub>3</sub> LDHs. They reported an increase of sorption capacity with agitation speed, at low pH and high Cr(VI) concentration. Detailed kinetic and equilibrium studies were done and they reported 17 mg·(Cr(VI) g)<sup>-1</sup>. Carriazo *et al.* [27] compared the chromate uptake capacity of MgAl-Cl LDH with its carbonate counterpart. The results show that MgAl-Cl samples are better sorbents than calcined MgAl-CO<sub>3</sub> samples. Recently, many studies have been reported on the effect of LDH structure for Cr(VI) removal. Wang *et al.* [28] studied the Cr(VI) uptake using MgAl, NiAl and ZnAl LDHs with molar ratio (M<sup>2+</sup>/M<sup>3+</sup> = 3). The authors found that ZnAl-LDH exhibits excellent sorption capacity (68.07 mg·g<sup>-1</sup>) and good regeneration performance. Zhang *et al.* [29] reported the removal of Cr(VI) onto MgAlFe-NO<sub>3</sub> LDHs synthesized by a mechano-hydrothermal method with varying Mg<sup>2+</sup>/Al<sup>3+</sup> molar ratio. The resulting LDHs have higher removal efficiency of Cr(VI) compared to that prepared by conventional mechanochemical method.

However, few studies have reported the effect of the interlayer anion on the sorption ability of LDHs to remove Cr(VI) [30,31]. Compared to most of the studies focusing on sorption feasibility of LDHs, the sorption mechanism and its kinetics are not yet fully understood. The sorption mechanism was not explained accurately in most of the cases due to the scarcity of reliable methods [32]. Most of the authors focused on the position of the basal reflections to determine the anion-exchange mechanism [30,32]. Moreover, the explanation of the equilibrium isotherms, and the effects of operating and thermodynamic parameters to improve the overall efficiency of contaminants removal were not deeply discussed. Therefore, the objective of this study is to evaluate the sorption ability of MgAl LDHs to remove Cr(VI) from aqueous solution as a function of interlayer anion. The effect of operating conditions on Cr(VI) removal, including dosage of LDHs, solution pH, initial concentration, contact time and temperature, have been examined in batch tests. The explanation of the LDHs structure and sorption mechanism has been supported by X-ray diffraction and FTIR spectra. The sorption kinetic and isotherms are also investigated to determine the sorption mechanism.

## 2. Materials and Methods

### 2.1. Sorbent synthesis

Co-precipitation method was adapted to synthesis MgAl LDHs with NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> as interlayer anion. All chemical reagents used were analytically pure reagents and obtained from Merck and Sigma-Aldrich. The solutions were prepared with deionized water.

MgAl-NO<sub>3</sub> and MgAl-SO<sub>4</sub> LDHs were synthesized by adding Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution drop wise into a NaNO<sub>3</sub> or NaSO<sub>4</sub> solution, respectively. MgAl-Cl LDH was prepared by adding MgCl<sub>2</sub> and AlCl<sub>3</sub> solution into NaCl solution. For all the above syntheses, 50 ml of Mg-Al precursor solution containing 0.025 mol of Mg<sup>2+</sup> and 0.0125 mol of Al<sup>3+</sup> to give Mg<sup>2+</sup>/Al<sup>3+</sup> molar ratio,  $R = 2$  and 50 ml of anion precursor solution containing 0.025 mol of anions were used. Aqueous solution of NaOH at 3.4 mol·L<sup>-1</sup> was then added to the mixture drop wise, with vigorous stirring at room temperature and the pH of precipitation was adjusted to 10. The precipitate formed was aged at 60 °C in an oil bath shaker for 24 h, cooled and filtered. The obtained precipitate was washed repeatedly with distilled water to reach a neutral pH and then dried at 80 °C in an oven for 24 h. Finally, the resulting solids were ground and sieved into powder of 50–100 μm in diameter, and kept in sample bottles for further use and characterization. The calcined MgAl-NO<sub>3</sub> LDH was prepared by heating its dried sample at 500 °C in air for 4 h, with a heating rate of 4 °C·min<sup>-1</sup>. In this study, sulfate-containing LDH was selected because of the abundance and relatively low toxicity of sulfate ions. Moreover, as discussed by Y. Mitsuo [33], sulfate-containing LDH is effective for the removal of Cr(VI) *via* anion-exchange compared to CO<sub>3</sub><sup>2-</sup>-type MgAl LDH for which the anion-exchange is very difficult to occur. On the other hand, sulfate ions in wastewater can be reduced during the feeding process of plants, algae and bacteria.

### 2.2. Sorbent characterization

Powder X-ray diffraction (XRD) analyses were carried out to identify the phase of Mg-Al LDHs using an XPERT-PR diffractometer with CuK<sub>α</sub> radiation ( $\lambda = 0.154060$  nm) at 45 kV and 40 mA. Scanning diffraction angle is set at the speed of 0.06 (°)·s<sup>-1</sup>. The BET specific surface area and average pore diameter of the prepared MgAl-NO<sub>3</sub> LDH and its calcined product were measured from the N<sub>2</sub> adsorption/desorption isotherms at 77 K by using Tri-Star II 3020V1.03 Micromeritics surface area and pore size analyzer. The thermogravimetric analysis (TGA) was carried out using a thermal gravimetric analyzer (Perkin Elmer STA 6000). The samples were heated in air from 30 to 900 °C with a ramping rate of 5 °C·min<sup>-1</sup>. The morphology of samples before and after sorption of Cr(VI) was viewed by scanning electron microscopy (SEM) using an XL30 ESEM at accelerating voltage of 20 kV.

Elemental chemical analysis was performed using an inductivity coupled plasma (ICP) emission spectrometer for metal ions in the samples to determine the Mg/Al molar ratio of the prepared materials. 0.04 g of each sample was dissolved in solution containing 15 ml of concentrated HNO<sub>3</sub> and 5 ml of HCl.

FTIR spectra of LDHs materials and their samples after sorption of Cr(VI) were recorded using an Alpha Bruker FTIR spectrometer over the 4000–400 cm<sup>-1</sup> wave number range.

The pH at the point of zero charge (pH<sub>zpc</sub>) of the prepared MgAl-NO<sub>3</sub> LDH was determined by different concentrations of NaCl at 0.1 mol·L<sup>-1</sup> and 0.05 mol·L<sup>-1</sup> as inert electrolytes. The initial pH was adjusted from 2 to 13 by addition of 0.1 mol·L<sup>-1</sup> HNO<sub>3</sub> and NaOH solutions. The experiments were carried out in a thermostatic shaker at 200 r·min<sup>-1</sup> and 20 °C for 2 h, by adding suspension of the same solid to solution ratio (1 g·(5 L)<sup>-1</sup>) for all experiments. Then the suspensions were filtered and the final pH values were measured. The pH<sub>zpc</sub> was obtained through the plots of pH<sub>final</sub> versus pH<sub>initial</sub> [34].

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