Applied Clay Science 80–81 (2013) 189–195

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Removal of *Acid Green 68:1* from aqueous solutions by calcined and uncalcined layered double hydroxides

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ARTICLE INFO

Article history:
Received 27 April 2012
Received in revised form 8 April 2013
Accepted 18 April 2013
Available online 17 May 2013

Keywords:
Layered double hydroxides
Hydrotalcite
Adsorption
Dyes
Acid Green 68:1
Colorants

ABSTRACT

Magnesium aluminum layered double hydroxide (LDH) was synthesized by the co-precipitation method followed by calcination. The resulting materials were characterized by X-ray diffraction (PXRD) and attenuated total reflectance with Fourier transform infrared spectroscopy (FTIR/ATR) and simultaneous thermogravimetric analysis/differential scanning calorimetry coupled to mass spectrometry (TGA–DSC–MS). Calcined and non-calcined LDHs were used as adsorbents to remove azo dye *Acid Green 68:1* in an aqueous solution. Adsorption experiment results indicated that calcined LDH possesses greater adsorption capacity (154.8 mg g^{-1}) than non-calcined LDH (99.1 mg g^{-1}). Isotherms showed that adsorption of the dye was more consistent with the Langmuir model. Kinetic experiments of calcined LDH adsorption showed that for low concentration (50, 100 and 200 mg L^{-1}), the system reached the adsorption equilibrium in 1, 2, and 4 h, and for higher concentration after 10 h. The best kinetic model was the pseudo-second order. Adsorption studies also showed that the capacity for adsorption of the dye by calcinated LDH does not significantly diminish with pH level variation.

1. Introduction

In recent years, environmental problems related to water contamination have increased (Schwarzenbach et al., 2006). Synthetic dyes used in many industrial processes, such as dying of paper, plastics and fiber are frequently found in groundwater, and this is becoming a serious environmental and public health problem (Caritá and Marin-Morales, 2008; Lima et al., 2007). Many processes for the removal of dyes from wastewater have been studied including adsorption, chemical oxidation, ion exchange, coagulation and flocculation (Jamil et al., 2011; Rocha et al., 2012; Liu et al., 2010; Verma et al., 2012). Among these processes, adsorption is the most effective physiochemical process in dye removal. Many materials, such as charcoal, clay minerals and molecular sieves, have been used as adsorbents (Gok et al., 2010; Meyer et al., 1992; Yeh and Thomas, 1995).

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, have been used as adsorbents or anion-exchangers for the removal of various anionic species in aqueous solutions, especially in the treatment of industrial effluents (Crepaldi et al., 2002; Kim et al., 2011; Seida and Nakano, 2002; Silvério et al., 2008). These compounds present properties such as a layered structure, high porosity, high surface area, and interlayer anion mobility (Forano et al., 2006). To better understand LDH structure, it is convenient to begin with the structure of brucite. In brucite, a mineral of $Mg(OH)_2$, magnesium cations are located in the center of octahedrons with hydroxyl anions at their vertices. These octahedrons share their edges forming planar and neutral layers, which are held together by hydrogen bonds. When bivalent cations of this type of structure are isomorphically substituted by trivalent cations, the lamella begins to show a positive residual charge. For the system to reach electroneutrality, the presence of anions between the layers is necessary, which together with water molecules promotes the stacking of the double hydroxide layers within a second order interlayer domain. Therefore, this substitution results in a hydrotalcite type of structure. LDHs can be represented by the following general formula: $[M_{1-x}^{2+}M_x^{3+}(OH)_2A_{x/m}^{m}nH_2O]$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation, and A^{m-} represents the intercalated anion with the m − charge. The calcination process of magnesium aluminum LDHs may lead to the formation of mixed oxides; these materials exhibit the so-called "memory effect", which is the reconstruction of the lamellar structure of LDH when its calcined derivative is placed into contact with an aqueous solution (Cavani et al., 1991; Forano et al., 2006). Due to these properties, LDHs can be applied in different areas, such as adsorption, catalysis, anion exchange, medicine, functional packaging

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http://dx.doi.org/10.1016/j.clay.2013.04.006

systems etc. (Bouraada et al., 2009; Cavani et al., 1991; Costantino et al, 2009; Cunha et al., 2010; Darder et al., 2007; Gao et al., 2010; Kwak et al., 2002; Leroux and Besse, 2001; Li et al., 2009; Ni et al., 2007).

LDHs can remove anions from aqueous solutions through adsorption processes, intercalation by anion exchange, and intercalation by the reconstruction of a calcined precursor. The adsorption process occurs on the surface of the LDHs. Examples of anion adsorption in LDHs include adsorption of colorants, surfactants, pesticides, etc (Barbosa et al., 2005; Chaara et al., 2011; Ni et al., 2007; Pavan et al., 1998; Setti et al., 2010; Zhu et al., 2005). During intercalation via anion exchange the anion intercalated in the LDH precursor should have a weak electrostatic interaction with the lamellas (examples of exchangeable anions include Cl^- and NO_3^- ions). The level of exchange depends on the substituent anions and the anions to be intercalated, which is determined by the charge density of each anion. A reconstruction of the calcined precursor is based on the "memory effect", normally an Mg–Al–LDH containing CO_3^{2-} anions in the interlayer is calcined at high temperatures to eliminate the majority of interlamellar anions (Cavani et al., 1991; Forano et al., 2006). The calcined material is then placed in water or in a solution containing anions of interest. The mixed oxide obtained after calcination is rehydrated, regaining the original lamellar structure. The reconstruction of the lamellar structure in water gives origin to the intercalation of hydroxide anions (OH^-) or it can occur with the intercalation of other anions, since these are present in the solution (Kooli et al., 1997).

The objective of this study was to assess the efficiency of hydrotalcite compounds (calcined and non-calcined) in the adsorption of the anionic dye (3Z)-5-amino-3-[[4-[[4-[(2Z)-2-(2-hydroxy-4-oxocyclohexa-2,5-dien-1-ylidene)hydrazinyl]phenyl]sulfamoyl]phenyl] hydrazinylidene]-6-[(4-nitrophenyl)diazenyl]-4-oxonaphthalene-2,7-disulfonic acid, known as *Acid Green 68:1* and distributed by BASF as Luganil Dark Green N. The isolated inorganic adsorbent materials were characterized by X-ray diffraction (PXRD), attenuated total reflectance with Fourier transform infrared spectroscopy (FTIR/ATR) and simultaneous thermogravimetric analysis/differential scanning calorimetry coupled to mass spectrometry (TGA–DSC–MS).

2. Experimental

2.1. Preparation of adsorbent material based on LDH

Mg-Al-CO_3-LDH, referred simply as LDH in this study, was prepared by co-precipitation following the method described by Reichle (1986). A solution containing 1.50 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.50 mol of $Al(NO_3)_3 \cdot 9H_2O$ in 700 mL of water was added one drop at a time to a vigorously stirred solution of 3.50 mol of NaOH and 0.943 mol of Na_2CO_3 in 1000 mL of H_2O. The resulting gel was shaken for 18 h at 65 °C. The resulting material was washed and separated by filtration, dried under reduced pressure in the presence of silica gel.

2.2. Preparation of calcined LDH

Calcined Mg–Al–CO_3–LDH, referred in this study as CLDH, was prepared in an atmosphere of molecular oxygen with a flow velocity of 150 mL min^{-1} at 550 °C for 4 h. The heating rate was 10 °C min^{-1}. The calcination temperature was previously determined by TGA–DSC–MS analysis.

2.3. Adsorbate

To study adsorption on LDHs, the anionic dye *Acid Green 68:1* (manufactured for dye leather) was provided by BASF (Porto Alegre/RS, Brazil). The chemical structure of the dye *Acid Green 68:1* is presented in Fig. 1. Solutions containing the dye were prepared by dissolving a known quantity of the dye in distilled water (1.00 g L^{-1}) followed by serial dilutions to reach the necessary concentrations.

2.4. Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption on *Acid Green 68:1* on CLDH was studied. This study was conducted at pH 7 and 25 °C for 10 h. The dye concentration in the studied solutions was 300 mg L^{-1} and the concentration range of CLDH was 0.1–1.0 g L^{-1}.

2.5. Initial pH effect on dye removal

The effect of pH on adsorption on *Acid Green 68:1* on CLDH was studied. This study was conducted under an initial range of solution pH that varied from 3 to 13. The dye concentration in the studied solutions was 200 mg L^{-1} and the quantity of CLDH was 100 mg. All studies were conducted by stirring the mixtures at 25 °C. NaOH and HNO_3 solutions were used to adjust the initial pH.

2.6. Adsorption kinetic

A suspension was prepared by the addition of 100 mg of LDH in 50 mL of dye solution at pH 7. The range of studied concentrations varied from 50 to 600 mg L^{-1}. The suspensions were shaken at different time intervals (15 min to 16 h) at 25 °C. The dye concentrations were analyzed as previously described.

2.7. Adsorption isotherms

The adsorption isotherms were produced by the batch method at 25 °C. A constant mass of 100 mg of LDH (calcined or non-calcined) was added to 50 mL of solution containing the *Acid Green 68:1* dye. The range of solution concentrations containing the dye varied from 50 to 600 mg L^{-1}. The pH of these solutions was corrected to a value of 7.00 with the addition of NaOH or HNO_3. The suspensions were then placed into a Dubnoff type bath and shaken for 72 h. After this time, solid material was separated by centrifugation. The concentration of the *Acid Green 68:1* dye in the supernatant was determined by UV–Vis spectrophotometry along a calibration curve ($\lambda = 660$ nm).

The amount of the adsorbed dye (q_e, mg g^{-1}) during the adsorption phase was quantified according to Eq. (1):

$$q_e = V \cdot \frac{(C_0 - C_e)}{m} \tag{1}$$

where C_0 is the initial dye concentration (mg L^{-1}), C_e is the final dye concentration (mg L^{-1}), V is the volume of the dye solution (L), and m is the mass (g) of LDH or CLDH.

2.8. Sorbent recycling

The recycling of the sorbent was evaluated by repeating cycles of adsorption/calcination, using the same CLDH sample. The calcined solid was prepared following the same method as described above (*i.e.*, 550 °C for 4 h). A portion of 250 mg of the CLDH was placed in 500 mL of a 100 mg L^{-1} *Acid Green 68:1* solution (1st cycle). The resulting material was calcined again and a portion of 125 mg was placed in 250 mL of an *Acid Green 68:1* solution (2st cycle). This procedure was repeated 3 more times, resulting in five cycles; the last one was carried out by the addition of 25 mg of the calcined material to 50 mL of an *Acid Green 68:1* solution.