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Research paper

Adsorption of Acid Yellow 42 dye on calcined layered double hydroxide: Effect of time, concentration, pH and temperature

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ABSTRACT

The adsorption of textile dyes onto Layered Double Hydroxides (LDH) and their thermally decomposed products is a promising strategy for the treatment of contaminated effluents - combining high removal efficiency with reasonable cost. The main purpose of this paper was to investigate the adsorption of textile azo dye Acid Yellow 42 (AY) onto calcined and uncalcined Mg-Al-CO_3-LDH. A set of analytical techniques was used to characterize the materials, namely X-ray diffraction (XRD), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), thermogravimetric analyses (TGA), N_2 adsorption-desorption isotherms and Scanning Electron Microscopy (SEM). In the study of azo dye adsorption, the following factors were assessed: kinetics, adsorption capacity, effect of temperature, initial pH value, and recyclability of the adsorbent material. The adsorption capacity of calcined LDH (CLDH) was almost four times greater than that of the LDH precursor: 1266 $mg \cdot g^{-1}$ (1.669 $mmol \cdot g^{-1}$) and 330.0 $mg \cdot g^{-1}$ (0.4350 $mmol \cdot g^{-1}$), respectively, at pH equal to 7.0 and 25 °C. The greater adsorption capacity for CLDH is related to the recovery property of these materials in light of the so called "memory effect", which allows an intercalation process of the anionic dye, as demonstrated by XRD data.

1. Introduction

The pollution of rivers and lakes by textile dyes has resulted in a series of environmental problems with serious consequences for fauna and flora. Approximately 100,000 kinds of dyes are available worldwide with annual production exceeding 10,00,000 tons (Robinson et al., 2001; Tan et al., 2015). During dye production and the dyeing process, about 15% of all dyes are disposed of in wastewaters, primarily due to incomplete fixation of the dye onto the fabric (Tan et al., 2015). Adsorption processes have been extensively studied for the removal of dyes from textile wastewaters. High removal efficiency, low cost of installation, and management are key factors in the implementation of adsorption processes on the industrial scale (Gupta and Suhas, 2009; Darmograi et al., 2015).

The Layered Double Hydroxides (LDH), also called hydrotalcite-like compounds, and their thermal decomposition products are receiving greater levels of interest in the removal of various contaminant species such as dyes, surfactants, agrochemicals, and inorganic anions from aqueous solutions (Dos Reis et al., 2004; Santos et al., 2013; Lu et al., 2015; Zhao et al., 2015). LDH can be described by the general formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2] A^{n-}_{x/n} \cdot mH_2O$, abbreviated as [$M^{II}$-$M^{III}$-A], where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is the intercalated anion with n − electrical charge, and *m* denotes the number of interlayer water molecules (Forano et al., 2013). The calcination of LDH at moderate temperatures (400–550 °C) can lead to the formation of metastable mixed oxides. These mixed oxides demonstrate an interesting property known as the "memory effect", which is the recovery of the layered structure of LDH upon contact with water or aqueous solutions containing anions (Forano et al., 2013; Baskaran et al., 2015).

In literature, several studies have described the adsorption of dyes by LDH compounds (Jia et al., 2015; Shan et al., 2015; Koilraj et al., 2016; Yang et al., 2016). El Gaini et al. (2009) showed the efficiency of calcined MgAl-LDH in the removal of Indigo Carmine (IC) dye from aqueous solutions. The adsorbent material calcined at 600 °C showed the highest efficiency of dye removal, with a maximum adsorption capacity of 3.83 $mmol \cdot g^{-1}$. The intercalation of the organic anion, as well as the recovery of the initial layered structure, was clearly evident by the peak dislocation d(003) from 0.76 to 2.13 nm (El Gaini et al., 2009).

In another study, Ni et al. (2007) reported the application of calcined ZnAl-LDH for the Methyl Orange (MO) dye adsorption. The maximum

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adsorption capacity was 0.56 mmol·g^{-1}. The recycling capacity tests of the adsorbent material (calcined LDH) showed, in repeated calcination/adsorption cycles, that the material can be reused in more than three cycles with no significant loss of its adsorption capacity (Ni et al., 2007).

The main objectives of this work were to evaluate the potential for MgAl-LDH materials, in their uncalcined (LDH) and calcined (CLDH) forms, as adsorbents in the removal of Acid Yellow 42 azo dye from aqueous solutions. The effect of various factors such as kinetics, adsorption capacity, temperature, concentration, and initial pH value was studied. Furthermore, the recyclability of CLDH in repeated calcination/adsorption cycles was assessed. The Acid Yellow 42 azo dye was chosen in this study because it is widely used in industry for dyeing wool, silk, polyamide fibers, and leather. Its presence in industrial textile effluents is highly damaging to the environment.

2. Experimental

2.1. Materials

Aluminum nitrate nonahydrate, magnesium nitrate hexahydrate, sodium hydroxide, sodium carbonate and hydrochloric acid were purchased from Sigma-Aldrich®. Acid Yellow 42 dye (abbreviated as AY) was supplied by BASF Company (commercial name Luganil Yellow G®), Porto Alegre-RS, Brazil. The chemical structure and some characteristics of AY are reported in supplementary material (Table S1). The reagents - used as purchased without further purification - were all of analytical grade. All solutions were prepared with high purity deionized water.

2.2. Preparation of the adsorbent materials

LDH was prepared by a coprecipitation method at constant pH value as follows: a solution containing $Mg(NO_3)_2{\cdot}6H_2O$ (54.0 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (18.0 mmol) in water (250 mL) was added dropwise under vigorous stirring to a solution containing Na_2CO_3 (73.0 mmol) in water (1000 mL). A NaOH solution (2.00 mol·L^{-1}) was added dropwise to keep the pH value constant at 10.0. The resulting slurry was aged at 65 °C for 24 h. After synthesis, the solid in suspension was washed with deionized water by centrifugation/resuspension cycles until the pH was 7. The material was subsequently dried at reduced pressure in the presence of silica gel. To prepare the calcined LDH (abbreviated as CLDH), LDH was heated in a tubular furnace at 550 °C for 4 h under atmospheric air with a flow of 50 mL·min^{-1} and heating rate of 10 °C·min^{-1}.

2.3. Synthesis of azo dye-intercalated LDH

AY-intercalated LDH (abbreviated as LDH-AY) was prepared by coprecipitation at a constant pH value of 10.0 under nitrogen atmosphere, avoiding the formation of carbonate-intercalated LDH. The properties of this material were compared with those of the LDH and CLDH submitted to adsorption tests. For this synthesis, a solution containing $Mg(NO_3)_2{\cdot}6H_2O$ (5.40 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (1.80 mmol) in water (25.0 mL) was added dropwise under vigorous stirring to a solution containing AY (4.50 mmol) in water (100 mL). The resulting slurry was washed with deionized water by centrifugation/resuspension cycles until the pH value was 7. The solid material obtained was hydrothermally treated at 65 °C for 24 h. The material was then dried at reduced pressure in the presence of silica gel.

2.4. Characterization methods

The elemental analysis was carried out using a ContrAA 300 high-resolution continuum source flame atomic absorption spectrometer (Analytik Jena). X-ray diffraction (XRD) was performed using a Shimadzu XRD-6000 diffractometer with graphite crystal as monochromator to select Cu-Kα_1 radiation ($\lambda = 1.5406$ Å), with a scanning rate of 0.02°·s^{-1}. Thermogravimetric analyses (TGA) were carried out under synthetic air atmosphere at 10 °C·min^{-1}, using TGA/DSC 490 PC Luxx. Attenuated Total Reflectance with Fourier Infrared Spectroscopy (ATR-FTIR) spectra were recorded on a Jasco FTIR 4100 spectrophotometer. The specific surface area and pore distribution of the material were analyzed by N_2 adsorption-desorption isotherms at −196 °C on a Micromeritics ASAP 2000 instrument. SEM analysis was accomplished on a scanning electron microscope provided with a field emission gun (FEG-SEM, JEOL-7500F). The samples were supported in the sample chamber by dispersing the powder upon conductive double-sided carbon tape.

2.5. Batch adsorption tests

2.5.1. Analysis of the azo dye concentration

The concentration of AY in the supernatant - determined eventually by comparison with a previously obtained standard curve - was obtained using a UV–vis spectrophotometer (Evolution 300, Thermo) with the absorbance being measured at $\lambda = 410$ nm in quartz cuvettes with an optical path length of 10 mm.

2.5.2. Effect of initial pH value

As the dye adsorption capacity of the CLDH was much greater than that of LDH, the effect of pH value, temperature and the adsorption kinetics were studied only for CLDH. Suspensions were stirred in a thermostatic bath at 25 °C for 420 min. The tested initial pH values - adjusted by NaOH or HCl solution addition - were 4.0, 7.0, and 12.0. The dye concentration of these solutions ranged from 50 to 2000 mg·L^{-1}.

2.5.3. Adsorption kinetics

The suspensions were prepared by adding CLDH (10 mg) to 20 mL AY solutions (250, 500, 1000 and 2000 mg·L^{-1}) at a pH of 7.0. The suspensions were placed in a thermostatic bath at 25 °C under stirring for different times (0–420 min) and the solid material was then separated by centrifugation. The kinetic models of pseudo-first order (Eq. (1)), pseudo-second order (Eq. (2)) and intraparticle diffusion (Eq. (3)) were tested.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \quad (2)$$

$$q_t = k_i t^{1/2} + C \quad (3)$$

where q_e and q_t are the adsorbed amounts (mg·g^{-1}) of AY per gram of adsorbent at equilibrium and at time t (min), respectively; k_1 and k_2 are the velocity constants of pseudo first-order and pseudo second-order, respectively; k_i is the constant representing the intraparticle diffusion rate, and C is the intercept.

2.5.4. Adsorption isotherms and thermodynamic study

Adsorption isotherms were determined from the adsorption equilibrium of the kinetic experiments (420 min). The dye concentration of these solutions ranged from 50 to 2000 mg·L^{-1}. The suspensions were stirred in a thermostatic reciprocating shaking bath at 25, 30, 35 and 40 °C. The amount of AY adsorbed at equilibrium (q_e, mg·g^{-1}) was calculated using the following equation:

$$q_e = V{\cdot}\frac{(C_0 - C_e)}{m} \quad (4)$$

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