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Research paper

Joint synthesis of Zeolite A-LDH from mineral industry waste

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ABSTRACT

This study evaluated the use of waste from the copper concentration process and kaolin processing for the combined synthesis of Zeolite A and layered double hydroxide (LDH). The synthesis occurred in two stages: synthesis of LDH by coprecipitation and submersion in a hydrothermal bath and then the addition of metakaolin for the synthesis of Zeolite A. The synthesized ZA-LDH sample was characterized by X-ray diffraction (XRD), scanning electron microscopy coupled with X-ray energy dispersive spectroscopy (SEM-EDS), N_2 physisorption and point of zero charge (PZC). X-ray diffraction detected phases of high structural order, quantified by the Rietveld method in 90.57 Zeolite A, 9.21 pyroaurite and 0.22 anatase (% mass). In adsorption tests, the ZA-LDH showed greater efficiency in dye removal than commercial zeolite.

1. Introduction

The Amazon region has major mineral deposits, particularly in the Pará state, the second largest national producer, with greater production of waste from ore processing (IBRAM, 2016).

In Brazil, this type of waste is inadequately disposed over large regions, causing serious environmental problems. Its use minimizes these impacts, and one of the proposed approaches to this end is the synthesis of zeolites and layered double hydroxides (LDH), which has been receiving attention from researchers because it allows low-cost production (Belviso et al., 2015; Cunha and Corrêa, 2011; Maia et al., 2007, 2011, 2015; Moisés et al., 2013; Rebelo et al., 2012; Yusof et al., 2010).

Zeolites are characterized by the presence of pores, cages, and cavities of molecular dimensions that are occupied by charge-compensating cations and water molecules. These ions are non-covalently bonded to the structure, which makes zeolites excellent cation exchangers (Braga and Morgon, 2007; Guisnet et al., 2004; Melo and Riella, 2010).

LDH are anionic clays with positive layers of di- and trivalent metal ions and anions in the interlayer region to neutralize this charge. The freedom of these interlayer anions makes LDH good anion exchangers (Cavani et al., 1991; Gomes et al., 2011).

Yamada et al. (2006) coated Zeolite A with LDH (Mg-Al-CO_3, Mg/Al = 3), proposing the preparation of a composite with simultaneous adsorption properties of cations and anions. The synthesis occurred in two stages, first with the production of the hydrotalcite from reagents with an analytical purity grade, and then the coating with commercial Zeolite A.

Othman et al. (2006) coated commercial Zeolite A with LDH and used it in the adsorption of CO_2 from a mixture of CO_2 and N_2. They verified that the zeolite covered with LDH had a higher yield in the analysed system.

These and other studies have shown that zeolites and LDH have many applications, especially in the environmental field, for the removal of dyes in water (Ahmed et al., 2017; Rahmani et al., 2018; Rida et al., 2013; dos Santos et al., 2017). They are considered pollutants due to their toxicity to aquatic organisms and groundwater (Muthukumaran et al., 2016; Rida et al., 2013).

The objective of this study is to use mineral industry waste (processes of copper concentration and kaolin processing) as a precursor for the joint synthesis of Zeolite A-LDH, for application in dye removal.

2. Materials and methods

2.1. Materials

Two types of industrial waste were used in the synthesis of Zeolite A-LDH, one from the production of copper concentrate from the Sossego mine, Carajás region, southeast of Pará state (called Rcopper); the other one was from the processing of kaolin from the Rio Capim region, northeast of the state of Pará (called Rkaolin). The other reagents, $MgCl_2.6H_2O$, NaOH (Sigma Aldrich) and HCl (Vetec) were of analytical grade purity.

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Before the synthesis, the wastes were pre-treated as follows: Rcopper was leached with concentrated HCl under heating (300 °C) for solubilization of the Fe^{3+} ions of the structure. The obtained acidic solution was denoted AS, and the leached solid residue was thereafter denoted RRcopper; Rkaolin was calcined at 700 °C for 2 h to produce metakaolin and then called Mkaolin (Maia et al., 2014).

2.2. Synthesis process

The process was performed in a single batch, in a glass reactor with mechanical stirring and heating at 95 °C (± 2 °C), according to the steps: 1) LDH synthesis and 2) Zeolite A synthesis.

In the LDH synthesis, 0.57 g of $MgCl_2.6H_2O$ was dissolved in 2.5 mL of acid solution (AS) and then diluted with deionized water to 10 mL (Mg/Fe molar ratio = 3/1). This solution was dripped under constant stirring into 50 mL of NaOH (3 mol L^{-1}). The dispersion formed was placed in a hydrothermal bath (95 °C) for 2 h. After this time, 1.5 g of metakaolin was added to the reactor for the synthesis of Zeolite A. The theoretical Zeolite A: LDH ratio was 87.5:12.5% m/m. The total hydrothermal bath time was 6 h, maintaining a pH between 13 and 14 throughout the process. The final product was filtered, washed with deionized water, dried at 100 °C for 24 h, and stored in a desiccator for characterization. The synthesized material was named ZA-LDH.

2.3. Characterization of samples

The samples (Rcopper, RRcopper, Rkaolin, Mkaolin and ZA-LDH) had their structures characterized by X-ray powder diffraction (XRD) on a Bruker D8 Advance diffractometer using a LynxEye detector with Cu radiation (Kα = 1.5406 Å) at 40 kV tension and 40 mA current, a step size of 0.02° 0.2 s^{-1} and a divergence slit of 0.6 mm. The phases of the synthesized product were quantified by the Rietveld method using the general structure analysis system (GSAS) program (Larson and Von Dreele, 2004) with the EXPGUI interface. The diffraction patterns for refinement were obtained from the inorganic crystal structure database (ICSD). The reflection profiles, scale factor, background polynomial parameters, network parameters and the half-height width of all reflections were refined as proposed by Azároff (1968). LaB_6 was used as the standard material to obtain the instrumental function parameters.

Chemical analyses of the Rkaolin and Rcopper waste samples were performed by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) in PANalytical Axios Minerals sequential equipment. The determination of Fe^{3+} ions in the AS, for the stoichiometric calculation of the theoretical Mg/Fe molar ratio for LDH synthesis, was performed using a colorimetric method, based on the formed ortho-phenanthroline ferrous complex (ABNT NBR:13934, 1997).

The morphology and chemical composition of the ZA-LDH were obtained using scanning electron microscopy (SEM) coupled with X-ray energy dispersion spectrometry (EDS) in Tescan equipment, model VEGA3. For imaging, the sample was metallised with gold and an operating voltage of 20 kV was used in high-vacuum mode.

The specific surface area and pore volume were determined on physisorption equipment Quantachrome Instruments Nova 2200e. The obtained data were plotted by the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Helenda) methods, respectively. The particle size distribution of the samples was obtained using the laser method in a SHIMADZU Sald 2201 particle analyser.

The point of zero charge (PZC) was determined with the 11-point method, using a solid-liquid ratio of 1:1000. In the analysis, 20 mg of sample was added to 20 mL of 0.1 M aqueous NaCl solution under 12 different initial pH conditions (1, 2, 3, 4, 5, 6, 7, 8, 10, 11, and 12), adjusted with HCl or NaOH (0.1 mol L^{-1}) solutions when necessary (Robles and Regalbuto, 2004).

2.4. Dye adsorption test

Adsorption experiments were done for the removal of both dyes, crystal violet, CV (Dynamic), and methylene blue, MB (Synth) on ZA-LDH. Commercial Zeolite A (CAS 1318-02-1, SigmaAldrich) was used as adsorption comparison standard because it is a commonly used material in this type of treatment (Fardjaoui et al., 2017; Rahmani et al., 2018).

The tests were performed in solutions of MB and CV dyes under stirring (240 rpm), at pH values of 4, 6 and 9, and initial concentrations of 5, 10 and 20 mg L^{-1}. The pH adjustment was done with HCl and NaOH (0.1 mol L^{-1}). All experiments were conducted at 25 °C.

The adsorption process was prepared by the addition of 10 mg of adsorbent to a 10 mL solution of the dyes. After 14 h of contact, the samples were centrifuged at 3000 rpm for 1 min. The supernatant was analysed using a Varian Cary 50 Probe UV visible spectrophotometer at wavelength λ = 665 nm for the methylene blue solutions and λ = 582 nm for crystal violet solutions. All experiments were performed in triplicate and only the means are shown in the results. The removal of the dyes (%) was determined using Eq. (1):

$$\%\text{Removal} = \frac{C_i - C_f}{C_i} * 100 \tag{1}$$

where C_i and C_f are the initial and final concentrations of the dyes in the solution (mg L^{-1}), respectively.

3. Results and discussion

3.1. Characterization of waste

The mineralogical composition of the waste samples is shown in Fig. 1. Rcopper had the following minerals: chlorite, biotite, actinolite, albite, quartz, and magnetite. After processing with HCl, some minerals remained unaltered (quartz, actinolite, albite) due to their insolubility in the acidic medium (Leinz and Campos, 1976). In the Rkaolin, the presence of three reflections with basal distances of 7.13, 3.57 and 2.38 Å, characteristic of the clay mineral kaolinite (Santos et al., 2013), was observed. After thermal treatment, Rkaolin became amorphous, indicating the collapse of the kaolinite structure and the production of metakaolinite (Maia et al., 2014).

The chemical compositions of the wastes are shown in Table 1. The high concentration of Si and Al in the Rkaolin sample confirms the kaolinite phase detected in the XRD (approximately 83% of the total mass), with an Si/Al molar ratio close to 1, ideal for Zeolite A synthesis (Heller-Kallai and Lapides, 2007). The AS solution, resulting from the leaching of Rcopper, had a 0.37 mol L^{-1} concentration of Fe.

3.2. Characterization of the synthesis product

Fig. 2 shows the calculated and experimental X-ray diffraction patterns of the synthesized ZA-LDH blend and difference between the experimental and the calculated patterns. The diffraction reflection profiles were refined using the Thompson-Cox-Hastings pseudo-Voigt (axial divergence asymmetry) function and the background function was of the shifted Chebyshev type. The final Rietveld analysis result presented a Rwp index of 5.69% and Gof (defined as Rwp/Rexp) of 2.39, which are considered satisfactory for the refinement (Larson and Von Dreele, 2004).

The obtained diffractogram showed well-defined reflections regarding the expected phases of Zeolite A (ICSD 88329) and pyroaurite (ICSD 6295), as well as a small amount of anatase (ICSD 63711), a remnant from the kaolin (Maia et al., 2007). The refinement showed Zeolite A with a high degree of structural order, characterized by the presence of sharp and narrow reflections, belonging to the cubic crystalline system and space group Fm3c, with unit cell parameters a = b = c = 2.456 nm. Pyroaurite is an LDH of the Mg-Fe-CO_3 system, belonging to the hexagonal crystalline system and to space group R-