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Original Research Paper

Adsorption study of Congo red dye from aqueous solution to Mg–Al–layered double hydroxide

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ABSTRACT

The removal of Congo red (CR), an anionic dye, by adsorption method was investigated using Mg–Al–layered double hydroxide. The Mg–Al–LDH was prepared using method involving coprecipitation with Mg^{2+}/Al^{3+} molar ratio of 2 at constant pH of 9. The solid characterized by X-ray diffraction, IR spectroscopy and was well crystallized. The effects of different parameters on adsorption such as pH, contact time, concentration of dye on the efficiency of CR adsorption onto Mg–Al–LDH were investigated. The adsorption kinetics fit the pseudo-second order kinetic models well and isotherms correspond to Langmuir model strictly. The thermodynamic parameters have been calculated, and the adsorption process was found to be spontaneous, endothermic in nature and the electrostatic attraction was suggested to control CR adsorption on Mg–Al–LDH.

1. Introduction

Nowadays many studies have been devoted to investigating the ability to adsorb oxyanions such as arsenate, chromate, and phosphate from contaminated waters by both surface adsorption and anion exchange of clay. Adsorption is a reliable alternative due to its simplicity, high efficiency, and ease of operation as well as the availability of a wide range of adsorbents. Various kinds of materials including cationic [1] and anionic clay [2] have been found to be capable of removing various pollutants from wastewater. Layered double hydroxides (LDH) or anionic clay are easy to synthesize, not toxic and inexpensive and present a remarkable range of physic–chemical properties which permit the elaboration of monohybrids. Indeed, these properties make the layered doubles hydroxides of excellent matrices of reception of numerous molecules. Layered double hydroxides (LDH) are synthetic solids with positively charged brucite-like layers of mixed metal hydroxides separated by interlayered hydrated anions, defined by the general formula: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot yH_2O]^{x-}$.

Interestingly, a partial and isostructural M^{2+} to M^{3+} substitution would induce a positive charge for these layers, balanced with the negatively charged interlayer region containing anions and water molecules [3]. This remarkable structure feature allows LDHs to have a powerful ability to capture organic and/or inorganic anions in aqueous solutions. To date, the adsorptive removal of various pollutants in water by HDL has been demonstrated [4–7]. Industrial effluents from textile, tanneries or printing the textile effluents contain a large amount of dyes that are non biodegradable and toxic. Due to their toxic effects, dyes have generated much concern regarding its use. It has been informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Therefore focuses on specific methods and technologies to remove dyes from different kinds of wastewater [8]. In this context we undertake in the present work the potentiality of adsorption of dyes by LDHs through Mg–Al–LDH-Congo Red system. The effects of Keys parameters such as pH, contact time, initial dye concentration on the retention of dye will be investigated. The interaction of the dye in the interlayer space and/or on external surfaces of the LDH is studied by XRD, IR SEM and TEM.

2. Experimental

2.1. Chemicals

Aluminum chloride hexahydrate ($AlCl_3\cdot 6H_2O$), magnesium chloride hexahydrate ($MgCl_2\cdot 6H_2O$), sodium hydroxide (NaOH) were purchased from Sigma–Aldrich (Germany).

Congo red, is an anionic azo dye having IUPAC name as 1-napthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo))bis(4-amino

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disodium) salt. Physicochemical properties of the dye are reported in Table 1 and its molecular structure is represented in Fig. 1. Stock solution was prepared in double-distilled water. All the test solutions were prepared by diluting the stock with double-distilled water.

2.2. Preparation of Mg–Al–LDH

The Mg–Al–LDH was synthesized by the co-precipitation method at constant pH [9]. A mixed aqueous solution of $MgCl_2{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$, with Mg^{2+}/Al^{3+} molar ratio of 2 and a total concentration of metallic cations of 1 M, was introduced with a constant flow into a reactor containing distilled water. The pH was maintained constant at a value of 9 for the MgAl phase by the simultaneous addition of a 2 M NaOH solution with vigorous stirring. The synthesis are realized under a nitrogen atmosphere at room temperature 25 °C, the solid is recuperated after several cycles of washing/centrifugation then let dry with the air, at ambient temperature.

2.3. Structural characterization techniques

For the characterization of synthesized clay many techniques have been used. Powder X-ray Diffraction (XRD) patterns were performed on a BRUKER D8 ADVANCE diffractometer using Cu Kα (λ = 0.154060 nm) radiation at 40 kV and 30 mA, and continued scanning mode. The patterns were recorded in a 2θ range from 2 to 70, in steps of 0.02°.

The FTIR analysis was done using a Fourier Transform Spectrophotometer model IRAffinty−1 SHIMADZU. The spectra of the samples before and after adsorption were in a range of 4000–400 cm^{-1}. Samples were pressed into KBr disks. The SEM micrographs were obtained on a scanning electron microscope (Zeiss supra 55-VP) operating at 10 kV. Transmission electron microscopy (TEM) images were taken using a Hitachi 7650 microscope at an acceleration voltage of 80 kV.

The pH at the point of zero chare (pH_{PZC}) was measured using the mass titration method [10].

2.4. Adsorption experiments

Batch adsorption experiments were carried out in a set of 50 mL erlenmeyer flasks containing 50 mg adsorbent and 25 mL dye solutions with initial concentrations of 20, 40, 80, 120 and 160 mg/L. The flasks were agitated in a water-bath shaker with shaking speed of 220 rpm for 24 h and at temperature 25 °C. The dye concentration in aqueous phase was analyzed using a double beam UV–vis spectrophotometer (UV-1601 Shimadzu, Japan) at 498 nm. All samples were filtered through filter papers prior to analysis. Each experiment was carried out in triplicate under identical conditions and an average value was determined. CR uptake at equilibrium, q_e (mg/g), was calculated by:

$$q_t = (C_i - C_t)\frac{V}{W} \quad (1)$$

Table 1
Physicochemical properties of the dye Congo red.

Parameter	Values
Molecular weight	696.68
Molecular formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Solubility in water	Soluble (1 g/30 mL)
Absorption maxima	498 nm
Synonyms	Direct red 28, C.I 22120

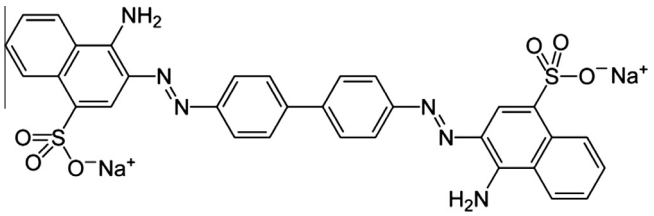

Fig. 1. Molecular structure of CR.

where C_i and C_t are the initial and at time t CR concentration respectively (mg/L), V is the volume of dye solution (L), and W is the weight of the adsorbent used (g).

3. Results and discussion

3.1. Characterization of Mg–Al–LDH

The X-ray diffraction patterns of the LDH samples are shown in Fig. 2. Mg–Al–LDH illustrates the 003, 006, 009, 110 and 113 reflections in the spectrum. The results suggest that the synthesized LDH was crystallized with well-ordered layered structures [11,12]. The X-ray diffraction patterns of Mg–Al–LDH-CR show no shifting of rays confirming the surface adsorption and no intercalation of CR. The FT-IR spectra of Mg–Al–LDH and Mg–Al–LDH-CR are shown in Fig. 3. The spectra show absorption bands due to hydroxyl groups, water molecules and MII-O, MIII-O and MII-O-MIII stretching vibrations which are typical of LDH materials and have already been reported in the literature [13,14]. The FTIR spectrum of the Mg–Al–LDH exhibited characteristic absorption bands; the intense and broad band at approximately 3200–3700 cm^{-1} region (max. at 3462 cm^{-1}) was related to the asymmetric and symmetric stretching mode of hydrogen-bonded OH groups in the hydroxyl layers (Mg/Al–OH or Al–OH) of Mg–Al–LDH and the lattice water or interlayer water molecules; the small shoulder, at approximately 3076 cm^{-1}, was assigned to hydroxyl interactions with carbonate ions impurities in the interlayer, and was attributed to the bridging mode H_2O–CO_3^{2-}. The broad band observed at 3462 cm^{-1} is attributed to the interlayer water molecules. The weak band at 1624 cm^{-1} is due to the bending vibration (deformation mode of H–O–H (δ H–O–H) of interlayer water molecules in LDH [15,16]. The weak peak at 1367 cm^{-1} is due to the stretching vibration of CO_3^{2-} that is converted from CO_2 captured from air during washing

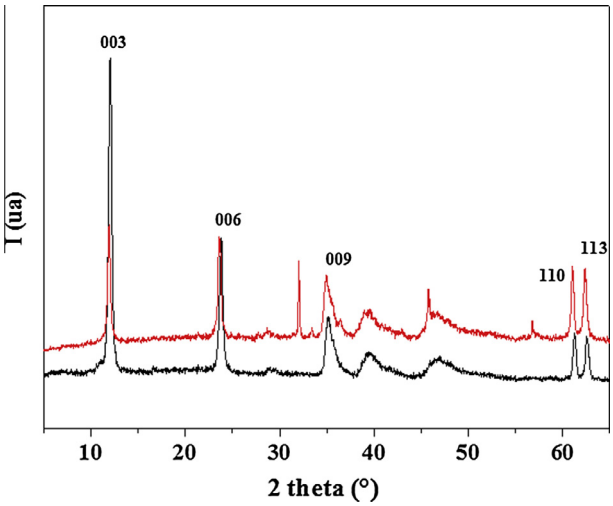

Fig. 2. The X-ray diffraction of Mg–Al–LDH and Mg–Al–LDH-CR.