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Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: A comparative study

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ABSTRACT

The present research discussed the utilization of layered double hydroxides (LDH) materials with different morphologies as adsorbents for Methyl Orange (MO) removal from aqueous solution. The adsorption properties of LDH with flower-like morphology (f-LDH) have been investigated for azo dye, Methyl Orange (MO), and compared to conventional stone-like coprecipitated LDH phases (c-LDH). Flower-like LDH with high specific surface area of 133 m^2/g were synthesized by coprecipitation method in dilute alkaline solution. With relatively high specific surface areas, the as-prepared flower-like LDH, when tested as adsorbents in azo dye removal, showed excellent performance and were better than those of conventional coprecipitated LDH. The adsorption isotherms, kinetics and mechanisms for azo dye MO onto as-prepared flower-like LDH were also investigated. The high uptake capability of the as-prepared flower-like adsorbents 500.6 mg of MO/g of LDH make them potentially attractive adsorbents in water purification avoiding calcination step. Hence, a low cost material will be acquired with much more benefits namely preserving energy.

1. Introduction

One of the most serious environmental problems is the existence of hazardous and toxic pollutants in industrial effluent, especially dyes unloaded into the environment from various industrial processes, such as textile, food, printing, paper, leather, pharmaceutical, cosmetics, and plastic (Robinson et al., 2002; Liu et al., 2014). Among these effluents, Methyl Orange (MO) dye is commonly identified as a hazardous contaminant because of its hazard to the aquatic ecosystem and human beings (Guettaï and Ait Amar, 2005; Ling et al., 2016; Lu et al., 2016). Recently, the possibility of an adsorption process by nanoparticles to remove textile dyes has become a viable option (Patra et al., 2015; Zeng et al., 2016; Chawla et al., 2017). In this way, the application of Layered Double Hydroxides (LDH) as adsorbents of toxic pollutant species has received considerable attention in the last decade (Bu et al., 2016; Lu et al., 2016).

Synthetic LDH consist of brucite-like layers in which a part of divalent cations are replaced by trivalent cations. The general formula of LDH can be expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{n-}_{x/n}]\cdot mH_2O$, where M^{II} and M^{III} are divalent metal cations (Ni^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, etc.) and trivalent metal cations (Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}, etc.), respectively. The metal cations occupy the octahedral positions of brucite-like layers generating excessive positive charge. While, A^{n-} represents an n-valent anion (Cl^-, Br^-, I^-, OH^-, NO_3^-, SO_4^{2-}, etc.) which balances the positive charges on the layers (Miyata and Kumura, 1973; Miyata, 1983; de Roy et al., 2001). Large surface area, high anion exchange capacity and good stability are their most valuable properties (Li et al., 2005), which make them widely used materials for removal of pollutants in aqueous solutions. However, the adsorption capacities of the conventional LDH phases are limited, so the calcination step is required to achieve high capacities (Drici Setti et al., 2010; dos Santos et al., 2013). Nevertheless, the diversity of the morphology of LDH materials has a significant effect on functional diversification and can effluence their potential applications. In this context, many attempts have been focused on controlling the morphology and the particle size of these nanomaterials. Recently, the LDH materials with 3D hierarchical nanostructure have been proved as a potentially attractive adsorbents in water purification. For example, Yu et al. (2012) synthetized 3D hierarchical nanostructure MgAl-LDH by solvothermal method in a mixed solution of ethylene glycol and water and found to have a high specific surface area. The flower-like LDH were tested for their application in water purification as adsorbents in As (V) and Cr (VI) removal, the as-prepared calcined Mg–Al-LDH showed excellent performance. Chen et al. (2014) has obtained the same structure for MgAl-LDH by dispersing the final wet product in an organic solvent using the Aqueous Miscible

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Organic Solvent Treatment (AMOST) method. Although the LDH that are obtained using the AMOST and conventional methods possess the same structural properties, the flower-like LDH possess new physical properties; they have significantly higher surface areas, pore volumes, together with lower density and higher compressibility than conventional LDH phases.

However, this structure is not easily obtained for other types of hydrotaclite-like materials. In this work, a flower-like NiAl-LDH (takovite-like clay) was successfully obtained by a simple coprecipitation in dilute alkaline solution of NaOH. Moreover, the Ni-based Layered structures have higher chemical stability than the Mg-ones. For this reason, they can be effectively used as adsorbents in aggressive environment such as wastewater from dye industry. In order to evaluate the performance of these materials, conventional coprecipated phases were synthetized. The effect of both morphologies obtained for the as-prepared LDH-adsorbents on the removal of azo dye from aqueous solutions, was investigated. The adsorption mechanism of azo dye on both morphology of LDH was discussed.

2. Experimental

2.1. Synthesis of conventional LDH

Aqueous solution (50 mL) of 0.4 M of $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was quickly added to 40 mL of Na_2CO_3 with a concentration of 1 M solution. The addition process was carried out at room temperature. The resulting slurry was aged at 100 °C for 20 h. Then, repeatedly washed into deionized water and filtered. The precipate was dried for 18 h at 65 °C.

2.2. Synthesis of flower-like LDH

A mixed metal nitrates solution of 1 M was obtained by quantitatively dissolving $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in 40 mL. This aqueous solution was added dropwise under vigorous stirring into a reactor initially contains 200 mL of dilute alkaline solution of NaOH (10^{-4} M) and during the co-precipitation process, the pH was kept at around 10 by addition of alkaline solution (0.5 M Na_2CO_3, 2 M NaOH). The dispersion obtained was aged at room temperature 25 ± 2 °C for 18 h under vigorous stirring, repeatedly washed into deionized water and filtered. The gel fractions are dried for 18 h at 80 °C.

2.3. Characterization methods

X-ray diffraction (XRD) was performed at room temperature under ambient air conditions on a Phaser D2 diffractometer, using Cu $K_{\alpha1}$ radiation ($\lambda = 1.54060$ Å) at 10 mA, 30 kV and a 2θ angle ranging from 2° to 90°.

Scanning electron microscopy (SEM) analysis was performed on a Phenom XL scanning electron microscope with an accelerating voltage of 10 kV. LDH powders were spread on carbon tape adhered to an SEM stage. Before imaging, the samples were coated with a thin gold layer to improve the image quality. Transmission electron microscopy (TEM) was performed on a TECNAI G2/FEI instrument operated at 120 kV voltage.

Thermogravimetric (TG/DTG) analysis Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in the temperature range 30–800 °C in flowing air at a heating rate of 10 °C/min using a Setaram TG-DSC-111 instrument.

The Brunauer, Emmett, and Teller (BET) equation was used to obtain the specific surface areas. The samples were measured from the N_2 adsorption and desorption isotherms at 77 K collected from QUADRA ORB SI and Qaudra Win. Before each measurement, LDH samples were first degassed overnight at 110 °C.

Surface functional groups of the sample was determined using Fourier transform infrared spectrometer (FT-IR, Varian 800 Scimitar Series, Australia) through attenuated total reflectance (ATR, GladiATRTM) mode. Spectra were recorded in the range of 400–4000 cm^{-1} with spectral resolution 4 cm^{-1} and 50 times scanning.

2.4. Adsorption experiments

2.4.1. Initial pH effect on dye removal

The effect of pH on the adsorption of MO dye on both adsorbents was studied. The initial dye concentration was 100 mg/L and both adsorbents dose was 1 g/L. The initial range of solution pH was varied from 3 to 11. The initial solution pH was adjusted with HNO_3 (0.1 N or 1 N) and NaOH (0.1 N or 1 N).

2.4.2. Effect of adsorbent dosage

The study was performed at pH 3 and at room temperature 25 ± 2 °C for 10 h. The initial dye concentration was 100 mg/L and the concentration range of both adsorbents (f-LDH and c-LDH) was 0.2–1.0 g/L.

2.4.3. Kinetic adsorption

The kinetics of MO dye retention by both adsorbents were intensely studied for concentrations range 50–250 mg/L. Three kinetics models were applied to fit the experimental data: Lagergren-pseudo-first order, pseudo-second order, and Weber's intraparticle diffusion.

2.4.4. Adsorption isotherms

The dye adsorption isotherms were determined by the batch equilibration method at 25 ± 2 °C. 30 mg were dispersed in 30 mL MO solution at concentration ranging from 50 to 500 mg/L in open beakers. A contact time of 24 h was applied to be sure that the equilibrium is reached for higher concentrations and then the dispersions were centrifuged. The amount of MO dye adsorbed q_e (mg/g) by both adsorbents was determined from the difference between the initial concentration C_i (mg/L) and equilibrium concentration C_e (mg/L) of MO: $q_e = [(C_0 - C_e)/m] \cdot V$, where V (L) and m (g) are the volume and the adsorbent mass, respectively.

2.4.5. Adsorbent recycling

For the regeneration study, a portion of 250 mg f-LDH adsorbent was placed in 250 mL of 100 mg/L Methyl Orange dye solution and shaken for 24 h at room temperature. The adsorbent after adsorption was then filtered, washed with water and separated by filtration with Whatman filter paper. The above washed adsorbent was then subjected to the successive adsorption-desorption cycles.

3. Results and discussion

3.1. Morphological study

The morphological features of f-NiAl, c-NiAl adsorbents and loaded-MO f-NiAl were examined by SEM and TEM techniques. Due to the relatively high surface charge densities ($0.33–0.25 C \cdot m^{-2}$) (Meyn et al., 1990) and the significant hydrophilic character of conventional co-precipitated LDH (Cornejo et al., 2008; Gao et al., 2014), these crystallites are generally found highly aggregated. The SEM image of c-LDH in Fig. 1a shows the c-LDH adsorbent with platelet particles densely stacked on their "ab" face, resulting in the formation of hard stone-like clot with a smooth surface (Ali et al., 2012). On the other hand, the low-magnification SEM image (Fig. 1b) of f-LDH demonstrates that the adsorbent consists of a large quantity of uniform 3D flower-like nanostructures. The flower-like nanostructures have diameters of about 200–500 nm and stack in the c-direction to form loose flower-shape agglomerates, which have a more exposed surface. In order to confirm the result of SEM, Transmission electron microscopic (TEM) observation (Fig. 1c) depicts an image of an individual nanoflower that shows evidently both the dense and the smooth surfaces of the intercrossed nanosheets. These observations were in accordance with other studies that