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Different dye removal mechanisms between monodispersed and uniform hexagonal thin plate-like MgAl–CO_3^{2-}-LDH and its calcined product in efficient removal of Congo red from water

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A B S T R A C T

Monodispersed and uniform hexagonal thin plate-like magnesium-aluminum layered double hydroxide intercalated with CO_3^{2-} (MgAl–CO_3^{2-}-LDH) is synthesized by an ethanol–water mediated solvothermal method. The maximum adsorption capacities of the as-synthesized and calcined MgAl – $CO_3{}^{2-}$ – LDH are 129.9 and 143.27 mg g^{-1}, respectively, which are higher than those of the other metal oxide nanostructures reported to date. More importantly, although N_2 adsorption–desorption analysis indicates that the BET surface area changed from 24.74 m^2 g^{-1} for the as-synthesized MgAl – $CO_3{}^{2-}$ – LDH to 165.07 m^2 g^{-1} for the calcined MgAl – $CO_3{}^{2-}$ – LDH, the as-synthesized and calcined hexagonal thin plate-like MgAl – $CO_3{}^{2-}$ – LDH structures show similar adsorption capacity of Congo red (CR) from aqueous solution. The adsorption mechanism for the as-prepared LDH is anion exchange while adsorption mechanism for the calcined LDH is reconstruction. Our study opens a new insight for understanding and preparing high-performance adsorbents for organic dye removal.

1. Introduction

Organic pollutants in the drinking water are a current worldwide and serious environmental issue due to their high carcinogenicity and toxicity. Azo dyes, such as Congo red (CR) and methyl orange (MO), are an abundant class of synthetic colored organic compounds used in most of the textile dyestuffs. They also have caused water pollution and provided a more serious threat to human health. It is an important and significant subject to find an effective way of removing aqueous pollutants from environment using new materials and techniques. Various methods have been used to eliminate the organic pollutants from water, such as adsorption, [1–3] photocatalysis, [4,5] electrochemical method, [6] membrane separation, [7,8] *etc*. Due to validity and simplicity, the adsorption is considered to be the most attractive method for organic pollution purification. A wide variety of materials are used as adsorbents [9–13]. Among them, layered double hydroxides (LDHs) have attracted more and more interesting not only because their excellent adsorption performance but the low-cost, as well as other potential applications, such as catalysts, ion exchange host, decolorizing agents and so on [14–16]. As anionic clay, hydrotalcite type LDHs are composed of positively charged hydroxide layers, and anions together with water molecules existing between the layers, where interlayer anions can be exchanged. Considering the unique structure and properties of LDHs, many groups have developed varied routes to synthesis LDHs, for example coprecipitation, calcination rehydration, sol–gel method, induced hydrolysis method, mechanochemical approach etc. [17–20]. Most recently, ethanol, as an environmentally benign organic additive, has been widely used, and received more and more attention in inorganic synthetic procedures. Various nanostructured materials, such as pyramid-like SnO_2, [21] polymorphic Ni/Al LDHs, [22] disk and thread-ball-like sodalite particles, [23] Bi_2WO_6 hollow nanospheres, [24] three-dimension flowerlike β-In_2S_3 microspheres, [25] broom-like or straw bundle-like β-$Co(OH)_2$, [26] hierarchical

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nanostructure $LaPO_4$ [27] have been formed in mixed ethanol-water solvents. However, it still remains a challenge to develop a facile and environmentally friendly method for obtaining monodispersed and uniform hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$.

Another important issue is if the adsorbents with bigger specific surface area show higher adsorption capacity? As we all know, the type of LDH materials can greatly increase their specific surface area when the calcination treat is applied. The question is very important for preparing high-performance adsorbents because it decides if the calcination is necessary.

In this paper, an ethanol–water mediated solvothermal method is used to synthesis monodispersed and uniform hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$. This method is low-cost and environment-friendly. At the same time, the calcined $MgAl–CO_3^{2-}LDH$ is investigated for comparison. The as-synthesized and calcined hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$ structures shows high efficiency for the adsorption of Congo red (CR) from aqueous solution. In addition, the difference of adsorption mechanism has been investigated by using organic dyes removal and adsorption kinetics in detail.

2. Experimental

2.1. Synthesis of $MgAl - CO_3{}^{2-} - LDH$

$Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Ethanol and Urea were analytical reagent grade and used without further purification. The products were synthesized by a low temperature ethanol–water mediated solvothermal method. The typical synthesis details are as follows: $Mg\,(NO_3)_2 \cdot 6H_2O$ (1.75 g), $Al(NO_3)_3 \cdot 9H_2O$ (1.25 g) and Urea (3 g) were dissolved and stirred in 42 mL mixed solvents of deionized water and ethanol (volume ratio 1:1) at room temperature. Then, the resulting solution was transferred into a 60 ml Teflon-skinned autoclave and heated at 190 °C for 1 h. After the reaction was complete, a translucent colloidal suspension was obtained. The translucent colloidal suspension was filtered, washed, and dried under air atmosphere for characterization. In our experiment, the success rate for preparation of the monodispersed and uniform hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$ is about 90%. We have also calcined the as-synthesized $MgAl - CO_3{}^{2-} - LDH$ under 700 °C for 3.5 h to further ensure that the weight losing of as-synthesized $MgAl - CO_3{}^{2-} - LDH$ finishes completely.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained in the 2ɵ range of 5–70° using a Philips X'Pert Pro X-ray diffractometer with Cu Kα radiation (1.5418 Å). Transmission electron microscopy (TEM, EM-2010, operated at 200 kV) and field emission scanning electron microscope (FE-SEM, Quanta 200FEG, operated at 10 kV) were used to characterize the morphology. Fourier-transform infrared (FT–IR) spectrum was recorded with a Nicolet-iS10 spectrophotometer using a standard KBr pellet technique. Thermogravimetry analysis (TGA) was carried out by heating the dry powder products at a rate of 10 °C/min using STA-449F3 (Netzsch, Germany) instrument. Surface area determination, pore volume and size analysis were performed using an ASAP 2020 M + C accelerated surface area and porosimetry system.

2.3. Adsorption experiments

The adsorption experiments were carried out in a serial of 15 mL glass vials, equipped with aluminum foil-lined teflon screw caps. Adsorbents and CR aqueous solution were added to the glass vial. Products were shaken for 24 h in order to achieve adsorption equilibrium. After the adsorption, adsorbents were separated using centrifugation. Then, the concentration of CR in the solution was determined using a Shimadzu UV-2550 spectrophotometer. The adsorption capacity of the adsorbents was measured by the difference between the initial and remaining concentrations of CR. The equilibrium adsorption capacity, q_e ($mg\ g^{-1}$), was calculated by $q_e = \frac{V(C_o - C_e)}{W}$, where C_o is the initial concentration of CR ($mg\ L^{-1}$); C_e is the equilibrium concentration ($mg\ L^{-1}$); V is the volume of the solution used (L); and W is the weight of the adsorbents (g). The adsorption capacity of the adsorbents at time t, q_t ($mg\ g^{-1}$), was also calculated: $q_t = \frac{V(C_o - C_t)}{W}$, where C_t is the concentration of CR at contact time t ($mg\ L^{-1}$).

3. Results and discussion

The goal for preparation of monodispersed and uniform hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$ and its calcined product is to efficient removal of the organic dye CR from water. Two important issues will be discussed. One is to demonstrate that the as-prepared monodispersed and uniform hexagonal thin plate-like $MgAl - CO_3{}^{2-} - LDH$ and its calcined product show high adsorption capacity. Another one is to discuss the different the adsorption mechanism of the $MgAl - CO_3{}^{2-} - LDH$ and its calcined product. Series of experiments are carried out for demonstrating this issue, including the structural and morphological characteristics, BET evaluation and organic dye removal from water.

3.1. Preparation of $MgAl - CO_3{}^{2-} - LDH$ and its calcined product

Fig. 1(a) displays the XRD pattern of the as-synthesized product, which represents a typical XRD pattern of $MgAl - CO_3{}^{2-} - LDH$. The XRD pattern can be indexed to the JCPDS file (No. 89-5434). Compared with the standard diffraction patterns, no characteristic peaks are from impurities. The as-synthesized $MgAl - CO_3{}^{2-} - LDH$ will convert to Mg–Al oxides after applying the thermal treat. As shown in Fig. 1(b), the XRD pattern illustrates that all the diffraction peaks belong to Mg–Al oxides for the calcined product. [28]. The blue curve of Fig. 1(c) shows the FT-IR spectrum of the as-synthesized $MgAl - CO_3{}^{2-} - LDH$. An intense and broad peak appears at around 3423 cm^{-1}, which is attributed to the stretching vibration of the hydroxyl group from both the hydroxide layers and the interlayer water. [29]. The two bands around 783 and 1354 cm^{-1} corresponds to the ν_2 (out of plane defomation) and ν_3 (symmetric stretching) vibrations of interlayter CO_3^{2-} anion. [30]. Other absorptions near 557 and 447 cm^{-1} are associated with M–O stretching and M–OH bending vibrations (M = Mg and Al) in the octahedral host layers. [31,32]. The red curve of Fig. 1(c) shows the FT-IR spectrum of the calcined $MgAl - CO_3{}^{2-} - LDH$. All the absorption bands are weakened. Especially, compared to the as-synthesized $MgAl - CO_3{}^{2-} - LDH$, the peak intensity of CO_3^{2-} ions at 1357.64 cm^{-1} become relatively weaker. This indicates that more CO_3^{2-} ions in the interlayer are removed. Fig. 1(d) shows the thermogravimetry analysis (TGA) curve of as-synthesized $MgAl - CO_3{}^{2-} - LDH$, which depicts the weight losing that occurs essentially in two steps. [33]. The first one, between 40 and 240 °C, can ascribe to the removal of physisorbed water as well as water intercalated in the interlayer gallery. And it corresponds to about 15% of the total weight. The second one, between 240 and 600 °C, is due to dehydroxylation of the layers as well as the removal of volatile species arising from the interlayer CO_3^{2-} anions. [34].

Fig. 2(a) and (b) show the SEM image of the as-synthesized $MgAl - CO_3{}^{2-} - LDH$, from which it can be clearly seen that the product is composed of many nearly monodispersed hexagonal