IMPROVING DYE-ADSORPTION PERFORMANCE OF KAOLINITE BY MODIFICATION WITH MGAL-LDH

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ABSTRACT

Layered double hydroxides (LDH)-coated kaolinite (LDH-Kao) hybrid material was synthesized by coprecipitation of Mg, Al cations with OH⁻ in presence of suspending kaolinite particle. XRD, FTIR, TGA, TOC and elemental analysis show that, in the prepared materials, the stable and crystallized LDH phase was formed on the surface of kaolinite particles, which changed kaolinite surface morphology. Aqueous methyl orange adsorption experiments show that LDH-Kao is a more efficient adsorbent than unmodified kaolinite. In similar conditions, the adsorption quantities on LDH-coated kaolinite are five times higher than that on pure kaolinite. Langmiur adsorption model fitted well the isothermal data of methyl orange on LDH-coated kaolinite and at pH 8.5 the adsorption capacity exhibited a high value of about 0.227 mmol/g.

1. INTRODUCTION

Synthetic dyestuffs are extensively used in the textile, paper and printing industries, due to their ease of production, fastness and variety of colors compared to natural dyes. Generally reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazine as chromophore. Among the reactive dyes, approximately 66% is unmetallized azo dye[1]. The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali. Today more than 9000 types of dyes have been incorporated in the color index[2]. Dye wastewater is the major source of the pollutants in the textile industry. Effluents from dye-houses contain high concentrations of both inorganic and organic chemicals. Because dyes are almost invariably toxic, their removal from effluent stream is ecologically necessary. Due to their low biodegradability, a conventional biological treatment process is not very effective in treating dye wastewaters, especially for the reactive dyes. Several physicochemical methods have been used for the decolorization and degradation of the organic compounds in dye wastewater, such as coagulation/flocculation[3, 4], adsorption by various adsorbents and oxidation using H_2O_2, ozone, UV[5, 6],etc. In particular, the most commonly used methods for the decolorization of water are based on adsorption. Some of studied adsorbents include activated carbon[7, 8], saw dust[9], some plant shells[10, 11], fly ash[12, 13] chitosan[14], several clays etc. Gupta presented an ample review on non-conventional low-cost adsorbents for dye removal[15].

Kaolinite is one of the most important clay minerals and has wide industrial applications. It is used in the production of ceramics and porcelain and as filler for paint, rubber, and plastics. The clays readily adsorb organic molecules and heavy metal ions. Adsorption of adsorbates from an aqueous solution on kaolintes has been a subject of interest in the environmental research as well as in other research areas. Hitherto, treatment of dye wastewater with the kaolinte have been studied in some aspects, such as applying in treatment of direct dyestuff (direct yellow, direct red 80 and direct blue 71)[10], acid dye[16], cationic dyes (crystal violet and ethyl violet)[17], anionic dyes[18] wastewater.

It is considered that the adsorption of dye ions and molecules on clay minerals occurs as a result of ion exchange, surface complexation, hydrophobic interaction, and electrostatic interaction. For improving the performance of kaolinites in adsorption, some chemical or physical processes were adopted, such as calcination[15], sulfate- and phosphate-modification[19], acid activation, surficial inoculation with organic derivatives[20], etc.

Layered double hydroxide (LDH) compounds belong to a class of anionic clay having a hydrotalcite-like structure, consist of positively charged metal hydroxide layers separated from each other by anions and water molecules, as represented by the formal formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{m-}_{x/m} \cdot nH_2O]$ [21], where M^{II} and M^{III} are divalent and trivalent metal ions, A^{n-} is a compensate n-valent anion, and x can have values between 0.1 and 0.5. Various inorganic or organic anions have been introduced between the hydroxide layers by simple ion-exchange reactions or coprecipitation. LDHs are now well established as excellent anion-exchange materials and their extensive intercalation chemistry has widespread applications in areas such as heterogeneous catalysis, optical materials[22], biomimetic catalysis, separation science[23], and medical science[24]. Recently, LDH has received much scientific attention on their properties as an adsorbent[25, 26].

In order to enhance the adsorption capacity of kaolinite and to improve the separation condition of LDH in aqueous liquid, in this work, we synthesized a novel adsorbent of kaolinte coated with LDH by precipitation of LDH on the surface of kaolinte particles. Then the synthesized material has been studied as an adsorbent for aqueous dye adsorption and methyl orange (MO, the chemical structure formula is shown in Fig. 1) was selected as the adsorbate.
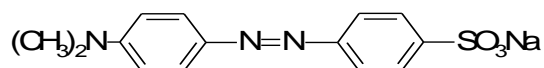
$$(CH_3)_2N \diagdown \diagup \diagdown \diagup - N{=}N - \diagdown \diagup \diagdown \diagup - SO_3Na$$

Fig. 1: Structure of methyl orange (tropeolin D).

2. MATERIALS AND METHODS

$AlCl_3 \cdot 9H_2O$, $MgCl_2 \cdot 6H_2O$ (analytical pure) and methyl orange were supplied by Beijing Chemicals No.1 Plant, China. NaOH, and HCl (analytical pure) were purchased from Xi'an Chemicals Co., China. Kaolinite was obtained from Shanghai Shanpu Chemical Reagent Corporation and chemical composition of kaolinite was determined by XRF method and given in Table 1. All these commercial chemicals and material were used as received without further purification.

Table 1. Chemical element content of pure kaolinite and LDH-Kao (%, w/w)

Component	kaolinite	LDH-Kao
SiO_2	57.62	57.38
Al_2O_3	24.04	23.64
TiO_2	0.45	0.45
Fe_2O_3	0.86	0.83
CaO	0.34	0.32
MgO	0.29	2.54
Na_2O	0.01	0.02
K_2O	0.56	0.55

The obtained materials were characterized by Powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA). XRD were collected on a Rigaku D/Max-2000 diffractometer using Cu Kα source, with a scan step of 0.02° and a scan range between 5° and 80°. FT-IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer in air at room temperature. The sample was pressed into a disc with KBr. The spectrum of each sample was recorded by accumulating 32 scans at 2 cm^{-1} resolution between 400 and 4000 cm^{-1}. Thermal analyses were carried out on a Perkin-Elmer TGA7 thermo-gravimetric analyser in nitrogen, and the measured range

from RT to 850°C. The bulk elemental analysis was performed with with X-ray fluorescence spectrometers (XRF) on a PW2403 Philips instrument. SEM photomicrograph of the samples was obtained using a Quanta 200 scanning electron microscope of Philips-FEI Co. The residual dye solution concentration was determined by the absorbance at 464 nm for MO using UV/Vis calibration curves and UV/vis measurements were performed with a SP2100-UV spectrophotometer (produced by Shanghai Precision & Scientific Instrument Co. Ltd., China).

The MgAl-LDH material was synthesized by coprecipitation at a constant pH of 11.0 and at a temperature of 60 °C. A mixture of 1.000 mol/L $MgCl_2$ 60 mL and 1.000 mol/L $AlCl_3$ 20 mL aqueous solutions ([Mg]/[Al] = 3) was slowly introduced into 200 mL 1M Na_2CO_3 solution in a reactor, where the pH was maintained constant by the simultaneous addition of an 5.0 mol/L NaOH solution. The resulting slurry was aged for 24 h at 60°C and the precipitate was filtered, washed several times with DI water to wash out all the dissolved salt, and then dried at 65 °C for 24h. The LDH-coated kaolinite (LDH-Kao) was prepared by the coprecipitation method too. First, the quantitative 25.00 g kaolinite powder was dispersed in 500 ml DI water with treatment of 2 hours ultrasonic under 40 kHz. With vigorous stirring, a mixed liquid of 0.100 mol/L $MgCl_2$ 60 mL and 0.100 mol/L $AlCl_3$ 20 mL aqueous solutions was slowly introduced into a 200 mL 1 M Na_2CO_3 solution suspended 10.00 g kaolinite, which was simultaneously kept about pH11 by adjusting with 1.0 mol/L NaOH solution. After the reaction, the same processes were followed as that of MgAl-LDH synthesis.

Adsorption was carried out using the batch method to evaluate the performance of the new prepared materials. We adopted aqueous MO as the adsorbates. Typically, in a 100 mL glass conical beaker, LDH-Kao (0.0500 g) was added to the given concentration adsorbate aqueous solution (50 ml) adjusted with pH by 0.1 mmol/L NaOH or HCl solutions. The suspended mixture was shaken at a steady temperature for 24 h using a reciprocating shaker. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in about 12 h. After this period solutions were centrifuged (3600 rpm, 15min) and the remaining concentrations of MO in the solutions were determined and the MO concentrations retained in the adsorbent phase were calculated by mass balance equation.
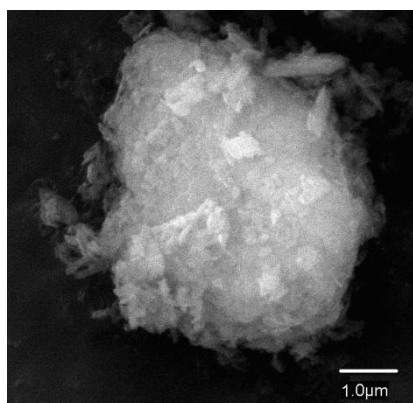
3. RESULTS AND DISCUSSION
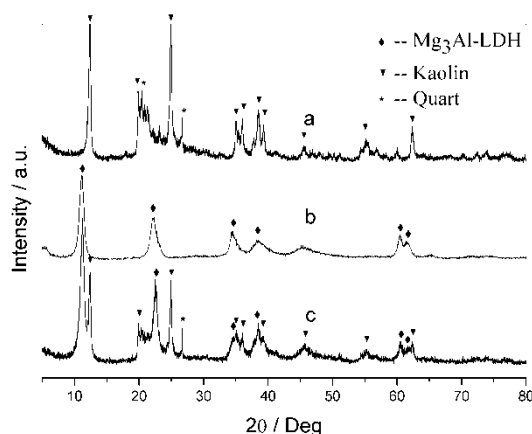

Fig. 2: SEM image of a particle of LDH-Kao

Fig. 3: XRD patterns of (a) Kaolin, (b) MgAl-LDH and (c) LDH-modified Kaolin.

The prepared material, LDH-Kao is gray powder. The elemental content in the surface of LDH-Kao and pure kaolinite (Table. 1) revealed that, the content of MgO is much higher in LDH-Kao than that in pure kaolinite as a result of LDH precipitation on the surface of kaolinite, which was also exhibited in a SEM micrograph (Fig. 2) distinctly. The generation of MgAl-LDH changed kaolinite surface morphology with a lightly heterogeneous covering of imbricate particles. The crystal morphology was very similar to that of typical LDH. XRD patterns of LDH-Kao, Kaolinite and MgAl-LDHs are shown in Fig. 3. In that of LDHs (Fig. 3. b), the three strong peaks at 2theta values of about 11.7°, 23.4 ° and

34.5^o are characteristic of a layered structure and correspond to the basal spacing and higher order reflections. The diffraction peak near 61.0^o corresponds to the (110) crystal plane. It can be seen in Fig. 3 that the diffraction peaks are sharp, indicative of relatively wellformed crystalline layered structures. It was found that the starting kaolin material consisted primarily of kaolin and a little amorphous component, but the crystallinity of LDH-modified product was relatively low and some new lines observed that can be attributed to LDH-coated structure formed respect to the original kaolinite.
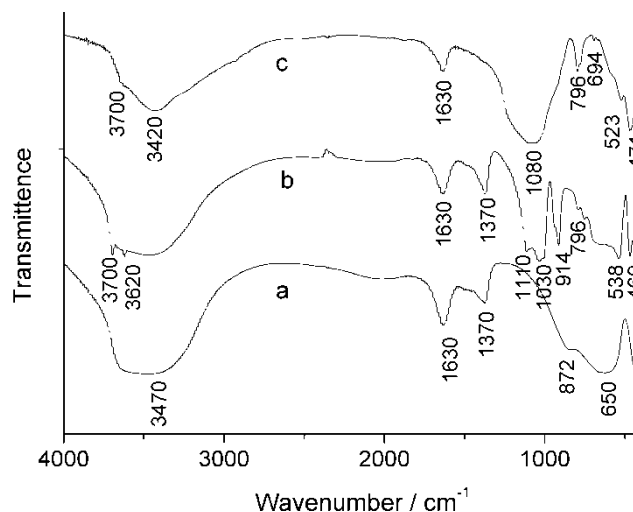

Fig. 4. FT-IR spectra of (a) MgAl-LDH, (b) LDH-Kao and (c) kaolinite.

FT-IR spectra of the samples are shown in Fig. 4. The FT–IR spectrums of LDH (Fig. 4a) and LDH-Kao (Fig. 4b) are characteristic of a hydrotalcite-like solid. The broad peak around 3470 cm^{-1} can be ascribed to the stretching of OH groups attached to Al and Mg in the layers and of interlayer water molecules, which have the bending vibration at 1630 cm^{-1}. The peaks around 650, 872 cm^{-1} are attributed to the Mg-O, Al-O stretching vibrations, respectively. The main IR functional bands of the kaolinite sample were given in Fig. 4c. The peak at 3420 cm^{-1} has been assigned to inner-hydroxyl group, the 3700 cm^{-1} corresponds to the inner-surface O–H group, the 1080 cm^{-1} (and 1110, 1030 cm^{-1} in Fig. 4b) belong to Si–O stretching, the peaks at 796 cm^{-1} assign to ν_s(Si-O-Si) and finally, 471 cm^{-1} (or 469 cm^{-1} in Fig. 4b) peaks are adapted to the deformation vibration of Si–O.
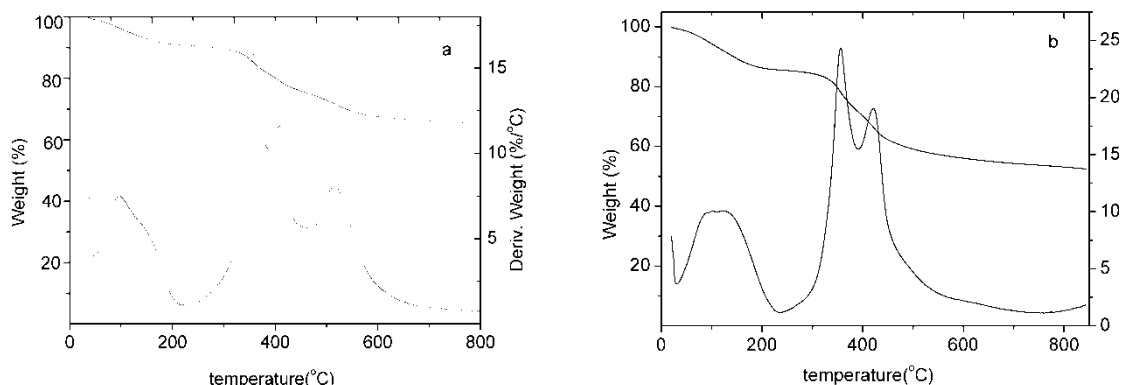

Fig. 5: TG–DTA curves of (a) LDH-Kao and (b) LDH.

Furthermore, the thermal stabilities of LDH-Kao and LDH were investigated. Fig. 5 displays the TGA thermograms of weight as a function of temperature in an environment of nitrogen. For LDH (shown in Fig. 5b) three major mass losses of 15.5% around 123 °C, 12.9% around 356 °C and 19.0% around 421 °C can be observed. These three weight losses correspond to the loss of interlayer water, the elimination of OH$^-$ and Cl$^-$ loss[27], respectively. For LDH-Kao (shown in Fig. 5a) four major mass losses of 9.3% around 101 °C, 17.5% around 358 °C, 25.1% around 408 °C and 35.0% around

515 °C can be observed. The first three mass losses are similar to that of LDH, and the fourth is due to the kaolinite crystal lattice dehydroxylation with formation of meta-kaolinite.
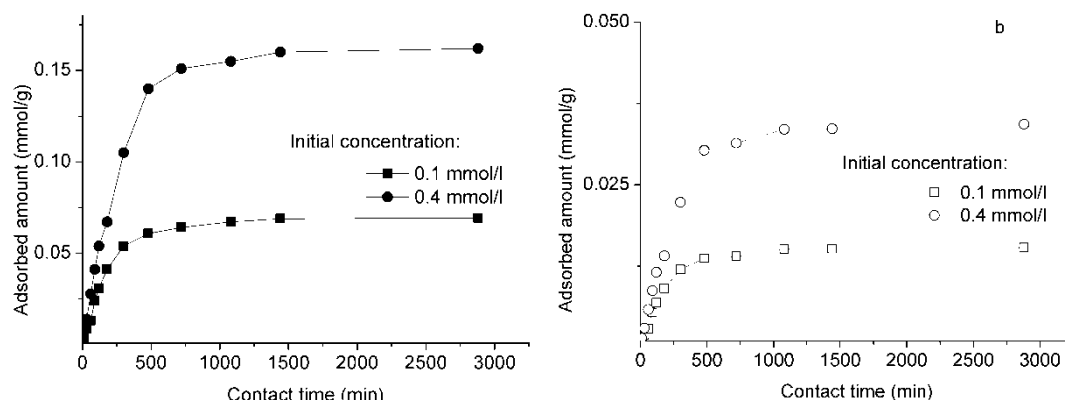

Fig. 6: Adsorption kinetic curves of methyl orange (MO) on (a) LDH-Kao, (b) kaolinite; adsorbent dose
w/V = 1.0 g/l, pH 8.5 and T = 30 °C.

The most important parameters, which affect the efficiency of an adsorbent, are time, pH and initial concentration of the solution. Fig. 6a shows the amount of MO removal at various initial solute concentrations and different contact time by LDH-Kao. The plot show adsorption was completed in the first 1500 min and the equilibrium was reached. With an increase in the initial MO concentration from 0.1 to 0.4 mmol/L, the sorption capacity at equilibrium increases from 0.069 to 0.162 mg/g. It is evident that the amount of MO adsorbed onto LDH-Kao hybrid materials increased with increased concentration of the solution. Higher concentration resulted in higher driving force of the concentration gradient and this driving force accelerated the diffusion of MO from the solution into the adsorbent[28]. Additionally, these curves indicate that higher the contact time between dye and adsorbent, higher is the removal efficiency till the equilibrium time is reached. The adsorption kinetics of aqueous MO on pure kaolinite was showed in Fig. 6b, which give similar processes to that of LDH-Kao, besides of the markedly low adsorption quantities.

Table 2. Effect of various anions on the adsorption quantity of MO on LDH-Kao (dose (w/V) = 1.0 g/l,
MO initial conc. = 0.4 mmol/L, pH 8.5, contact time = 24 h and T = 30 °C.)

Anion added	Adsorption quantity (mmol/g)
None	0.165
0.001M NO_3^-	0.161
0.001M Cl^-	0.153
0.001M SO_4^{2-}	0.145
0.01M NO_3^-	0.152
0.01M Cl^-	0.138
0.01M SO_4^{2-}	0.103

Since the dyestuff industrial effluents are always contaminated with various ions, it is therefore important to study the effect of these ions on the adsorption property of dye wastewater. As competitive anions are expected to interfere in the adsorption process of desired anions, therefore the adsorption experiments were carried out in the presence of various competing anions. The concentrations of all these ions in solution were kept at 1×10^{-3} and 1×10^{-2} M in each case. The results are shown in Table 2. It can be seen that adsorption of the dye decreased substantially in the presence of sulfate and chloride anions, especially, high concentration SO_4^{2-} will markedly decrease the adsorption of MO on prepared LDH-Kao.
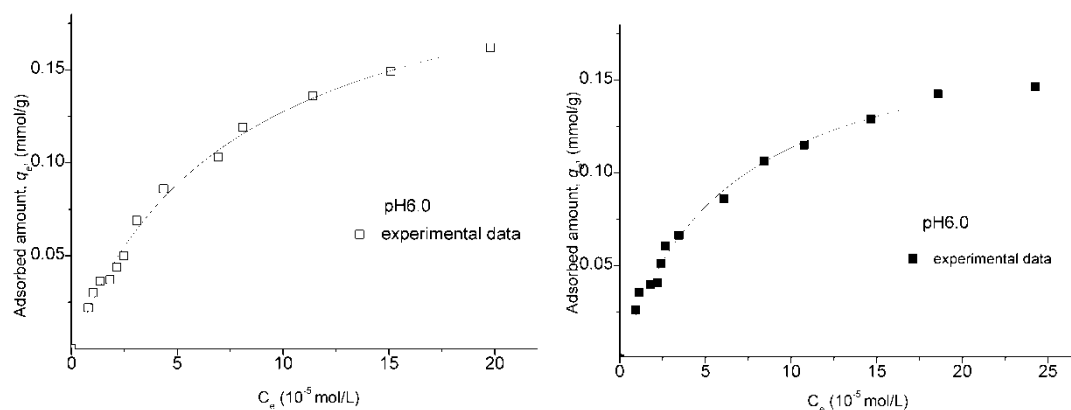
Fig. 7: The variation of the amount adsorbed vs. equilibrium concentration at temperature of 30 °C.

The purpose of equilibrium adsorption experiments were to investigate the effectiveness of removal MO from an aqueous solution using prepared LDH-coated kaolinite materials, and the high adsorption of MO may be expected and explained by the form of stable MO-intercalated LDH structure. It was found that the isotherms of MO adsorption essentially showed a Langmuir character. The equilibrium adsorption isotherms of MO on LDH-Kao at 30°C are shown in Fig. 7. The results were interpreted in terms of Langmuir isotherm models equations perfectly, with the correlation coefficients R=0.994, 0.993 for the case of pH8.5 and pH6.0, respectively. Langmuir equation is:

$$q_e = q_m \frac{K_L c_e}{1 + K_L c_e}$$

Where the variables c_e and q_e are the adsorbate equilibrium concentrations in the liquid and solid phases, K_L is constants and q_m is the maximum adsorption capacity according to the Langmuir model. For the case of MO as adsorbate, q_m were about 0.227, 0.185 mmol/g and K_L 7.84×10^{-5}, 6.34×10^{-5} L·mol^{-1} at pH 8.5 and 6.0, respectively. Higher adsorption of MO occurred at pH 8.5 than at pH 6.0, which is attributed to the fact that, when the pH is such that dyes are in ionized form (such as aquatic MO in high pH), the anion methyl orange will intercalated into the interlayer space via ion-exchange. Otherwise, adjacent molecules of the dyes on the hybrid adsorbent surface will repel each other to a significant degree, because of their equal electrical charge. The later process is distinctly weaker than the former. The result instructed the LDH modification will improve the adsorption performance of kaolinite at high pH.

4. CONCLUSIONS

An LDH-coated kaolinite hybrid material was synthesized by using coprecipitation methods. LDH-coated kaolinite hybrid material was synthesized. XRD, FTIR, TGA, TOC and elemental analysis showed that, in the prepared materials, the stable and crystallized LDH phase was formed on the surface of kaolinite particles, which changed kaolinite surface morphology. Adsorption experiments showed that LDH-coated kaolinite is more efficient for removing methyl orange from artificial aqueous solutions than original kaolinite. In similar conditions, the adsorption quantities on LDH-coated kaolinite are just five times higher than that on pure kaolinite. Langmiur adsorption model fitted well the isothermal data of methyl orange on LDH-coated kaolinite and at pH8.5, the adsorption capacity exhibited a high value of about 0.227 mmol/g.

5. ACKNOWLEDGEMENTS

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