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Research paper

Chemically modified kaolinite nanolayers for the removal of organic pollutants

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ABSTRACT

Modified kaolinite nanolayers were prepared from two-dimensional (2D) raw kaolin through a combination of calcination, acid leaching, and ultrasonic dispersion. The obtained nanolayers were subjected to effective modification with amino functional groups through grafting with (3-aminopropyl) triethoxysilane (APTES). The resultant materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS), scanning transmission electron microscopy (STEM), Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). The results revealed that the chemically modified materials exhibited increased specific surface area and pore structures, and chemical treatments showed obvious effects on the adsorption performance of kaolin. Owing to the protonation of the amino groups, the organic modified material exhibited excellent adsorption performance for Congo red and efficient regeneration. The chemically modified kaolinite nanolayers show significant potential applications in the fields of adsorption, separation, catalysis, and other environmental remediation.

1. Introduction

Industrial pollution in many countries is largely associated with the contamination of wastewater with dyes. The advances in the world economy and the technology in the dyestuff industry over the last decades were accompanied by increased production levels. These advances, however, resulted also in dramatically increased environmental pollution. Congo red is a benzidine-based anionic diazo dye, which is typically used in rubber, leather, coatings, inks, and many other applications (Afkhami and Moosavi, 2010). Human exposure to Congo red can cause significant eye and skin irritation in mere minutes. Additionally, ingestion of Congo red can result in stomach irritation, accompanied by nausea, vomiting, and diarrhea (Foroughi-Dahr et al., 2015). Further, Congo red is believed to be carcinogenic, and prolonged exposure might induce tumor formation in humans (Datta et al., 2016).

Most dyes are robust organic molecules, which are resistant to aerobic digestion and stable to light, heat, and oxidants. As a consequence, dye molecules are extremely challenging to remove from wastewater (Vasu, 2008; Rong et al., 2017). In the past, electrolysis, biochemical, and adsorption methods were usually used to treat dye-contaminated wastewater (Sadettin and Dönmez, 2006; Chen et al., 2013; Kong et al., 2014; Zhao et al., 2017). The electrolysis method, however, is associated with high consumption of electricity and electrode damage, while the biochemical method requires very demanding temperature control. In addition, the advances in dyestuff production methods are making the wastewater increasingly more difficult to decompose, with a rise in the resistance to biological degradation (Lucas et al., 2006). Compared to the above methods, adsorption is not only economical and efficient, but also possesses the advantage of limited production of toxic by-products (Crini, 2006; Mittal et al., 2012).

Clay minerals can adsorb molecules, thus adsorbing and removing pollutants from wastewater (Ghosh and Bhattacharyya, 2002; Nandi et al., 2009). Also, clay minerals could be chemically modified to prepare high-performance materials (Hou et al., 2017a, 2017b; Liu et al., 2017a, 2017b; Long et al., 2017a, 2017b; Peng and Yang, 2017; Yan et al., 2017a, 2017b, 2018a, 2018b). To date, kaolinite was established as a mineral with excellent adsorption properties, large specific surface area, and good physical and chemical stability (Hu and Yang, 2013; Li et al., 2015; Long et al., 2017a, 2017b; Zuo et al., 2017). However, the adsorption capacity of raw kaolin is still insufficient for the treatment of dye wastewater. The objective of this work is to investigate the adsorption performance of chemically modified kaolinite for Congo red dye in wastewater under different experimental conditions.

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Table 1
The chemical composition of RK, CK and AK (wt.%).

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	P_2O_5	K_2O	LOI[a]
RK	44.53	37.32	0.35	1.04	0.25	0.23	0.42	0.35	15.51
CK	52.21	42.25	0.93	1.41	0.35	0.35	0.61	0.55	1.34
AK	83.25	1.23	0.46	0.52	0.05	0.04	0.07	0.01	14.37

[a] Loss on ignition.

2. Experimental

2.1. Materials

Raw kaolin (denoted as RK) was obtained from Zhangjiakou, China, and the major chemical composition was detected by X-ray Fluorescence analysis (Table 1). X-ray diffraction (XRD) analysis of RK indicated the presence of 91 wt.% of kaolinite and 9 wt.% of quartz. Analytically pure Congo red ($C_{32}H_{33}N_6Na_2O_6S_2$) and (3-aminopropyl) triethoxysilane ($C_9H_{23}NO_3Si$, APTES) were supplied by Shanghai Aladdin Industrial Corporation Co. Ltd., China.

2.2. Chemical modification of kaolinite nanolayers

In order to obtain the modified kaolin, RK was treated thermally at a heating rate of 5 °C/min to 750 °C and held at this temperature for 2 h to obtain the calcined kaolin (denoted as CK). Specifically, 4 g of CK were added to 200 mL of HCl aqueous solution (4 mg/L), and the mixture was treated thermally at 85 °C for 8 h, cooled to room temperature naturally, dispersed through ultrasonic irradiation and washed several times with distilled water to ensure the removal of free Cl^- and Al^{3+}, then resulted in the formation of acid-leached kaolin (denoted as AK). Finally, solid AK was obtained by centrifugation. Distilled water and ethanol were mixed in a 1:1 ratio by volume and added to AK and then the mixture was sonicated for 2 h to improve the dispersibility of the sample. The resulting mixture was washed sequentially with distilled water, ethanol, and methanol several times. Once these steps were completed, AK was mixed with methanol in a solid-to-liquid ratio of 20 mg per 1 mL. Subsequently, 20 mL of the mixed liquor were added to 40 mL of toluene (analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The boiling points of methanol and toluene are 64.7 and 110 °C, respectively, and therefore the mixed liquor was heated at 75 °C for 30 min in a three-necked, round-bottom flask to remove methanol. Once removed, 3 mL of APTES were added into the flask and the solution was left to react for 90 min under nitrogen atmosphere in order to prevent the oxidization of APTES. The reaction can be described using the following equations (Eqs. (1) & (2)):

$$\mathrm{Si-OH + (C_2H_5O)_3-Si-CH_2CH_2CH_2NH_2 \rightarrow Si-O-Si(C_2H_5O)_2 - CH_2CH_2CH_2NH_2 + C_2H_5OH} \quad (1)$$

$$\mathrm{Si-OH + Si-O-Si(C_2H_5O)_2 - CH_2CH_2CH_2NH_2 \rightarrow Si-O-Si(C_2H_5O)_2 - CH_2CH_2CH_2NH_3^+ + Si-O^-} \quad (2)$$

The resulting material was centrifuged and washed with toluene and methanol several times to remove any remaining APTES and toluene. After drying at 60 °C for 12 h, the sample was ground to a fine powder to give the organic modified kaolinite (denoted as OMK).

2.3. Characterization

RK, CK, AK and OMK were characterized by X-ray diffraction (XRD, DX-2700, Haoyuan, Dandong, China) with Cu Kα-radiation (λ_1 = 1.5405983 Å), performed on the samples with a step width of 0.02° in the range of 3–80°. The composition of the samples was determined by means of PANalytical Axios mAX wavelength dispersive X-ray fluorescence (XRF) spectrometer. The scanning electron microscopy (SEM) combined with EDS analysis were obtained using a Mira3 LMU, Tescan, Czech Republic SEM. Scanning transmission electron microscopy (STEM) combined with EDS analysis were performed using a Titan G2 60-300 microscope operated at an accelerating voltage of 300 kV. Fourier transform infrared spectra (FTIR) were recorded using a Shimadzu FTIR 8120 spectrometer over the range of 400 cm^{-1} to 4000 cm^{-1} under the following conditions: KBr and the sample powder (concentration in KBr of around 1%), diffuse reflectance, resolution of 4 cm^{-1}, number of scans = 64. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Escalab 250Xi spectrometer equipped with an Al Kα monochromated X-ray source; the obtained binding energies were calibrated with respect to the C 1 s peak (284.6 eV). Nitrogen adsorption measurements were performed at a temperature of 77 K using a Micromeritics ASAP 2020 gas adsorption instrument; the specific surface areas were calculated using the multipoint Brunauer–Emmett–Teller (BET) method, and the total pore volumes (V_{tot}) were estimated from the adsorbed volumes at a relative pressure (P/P_0) of 0.995. The pore size distributions were determined from the adsorption branches of the obtained isotherms using the Barrett–Joyner–Halenda (BJH) method.

2.4. Adsorption experiments

A stock solution of the dye at 400 mg/L was first prepared by dissolving the required amount of dye in distilled water (pH = 7.6). Solutions for the adsorption experiments were prepared from the main stock solution at different concentrations (20, 50, 100, 150, 200, 250, 300, 350 and 400 mg/L), times (1, 2, 5, 10, 20, 30, 60, 120 and 360 min), and pH (3, 4, 5, 6, 7.6, 9, 10, 11, 12). Before each experiment, a blank sample in the form of a Congo red solution in the same concentration range (as used in the adsorption experiments) was examined in beakers containing the adsorbents. Firstly, the walls of the beaker didn't adsorb Congo red. The adsorption experiments were carried out in the same beakers by mixing 25 mg of adsorbents with 50 mL of the aqueous dye solution at different concentration and pH. Once mixed, the mixture was agitated in a thermostatic water bath for a different amount of time. Finally, the mixture was centrifuged for 5 min and any remaining unadsorbed Congo red in the supernatant liquid was determined spectrophotometrically at λ_{max} = 497.0 nm using a Unico UV-2600 UV–Vis spectrophotometer. All samples were examined in triplicate to minimize experimental error and the error rates of the experimental measurements were under 5%.

3. Results and discussion

3.1. Chemical treatment of kaolinite nanolayers

Fig. 1 illustrates the preparation method employed in the synthesis of the organic OMK. The typical SEM image of RK revealed the hexagonal flakes (Fig. 1a), similar to those reported previously, with edges that could be observed clearly (Bu et al., 2017). Compared with the SEM image of RK, the edges of plates in CK were fuzzier after the thermal treatment at 750 °C (Fig. 1b). The SEM images of AK showed that the nanolayers were stacked on top of each other and formed a larger lamellar structure than that observed in the original kaolin (Fig. 1c), which could increase the contact area and thus have a beneficial effect on the grafting of APTES onto AK surface. From the SEM image of OMK (Fig. 1d), it was apparent that even after grafting with APTES, the nanolayer morphology remained, indicating that the grafting of APTES had little influence on the surface morphology of AK.

The TEM image of OMK (Fig. 2a) showed the porous nanolayer structure. The EDS spectrum (inset of Fig. 1d) confirmed the presence of O (53.21 wt.%), Si (35.62 wt.%), C (7.35 wt.%), N (1.98 wt.%) and Al (0.63 wt.%) elements on the surface of OMK. The HAADF-STEM image

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