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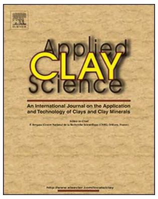

Research paper

Highly dispersed sepiolite-based organic modified nanofibers for enhanced adsorption of Congo red

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ABSTRACT

Acid-activated sepiolite fibers (ASEP) were grafted with amino groups using (3-aminopropyl) triethoxysilane to prepare an emerging organic-inorganic hybrid nanofibers (NH_2-ASEP). Owing to the high surface area and pore volume, and the highly dispersed nanofibers with functional amino-groups, the prepared NH_2-ASEP exhibited good adsorption performance towards Congo red (CR) anionic dye. It displayed a large sorption capacity (522 mg/g at pH = 8.0, 25 °C), low sorption equilibrium time (within 10 min), and renewability. Equilibrium adsorption data of NH_2-ASEP towards CR dye were evaluated using Freundlich, Langmuir and Sips isotherm models, and the Langmuir isotherm exhibited a better fit with a maximum adsorption capacity of 539.71 mg/g, which is very close to the experimental data and higher than those of the reported fiber adsorbents. The adsorption process of CR dye onto NH_2-ASEP surface followed a pseudo-second order rate expression. Highly dispersed sepiolite-based organic modified nanofibers have great potential applications in the fields of water treatment, membrane separation, catalysis, pH responsive delivery and other environmental remediation.

1. Introduction

Sepiolite (SEP), a microcrystalline hydrated magnesium silicate of theoretical unit cell formula $Si_{12}O_{30}Mg_8(OH,F)_4(H_2O)_4{\cdot}8H_2O$, is a natural fibrous clay mineral and commonly used as a stable inorganic matrix due to its the high mechanical performance and thermal stability or chemical durability (Alcantara et al., 2015; Ma and Zhang, 2016; Shen et al., 2016). However, pristine sepiolite nanofibers contain the serious fiber aggregation, which has greatly limited the development and application of sepiolite fibers-based nanomaterials. Thus, it is very necessary and important to disaggregate sepiolite fibers. Organic modification may be a good solution because it could increase the steric hindrance of fibers by introducing larger organic molecular chains and strongly reducing the contact surface between fibers, then enhancing repulsion among fibers to make reaggregation difficult upon drying (Garcia et al., 2011; Zhou et al., 2016). Pristine sepiolite contains small surface areas and a little hydroxyl groups, which is unfavorable for the efficient interaction with organic solvents to prepare organic–inorganic hybrid materials. So it is necessary to pre-activate pristine sepiolite prior to organic modification. Actually, natural minerals usually should be pretreated for efficient applications (Hou et al., 2017; Long et al., 2017a,b; Peng and Yang, 2017; Shen et al., 2017; Yan et al., 2017a, 2018b; Zuo et al., 2017). Acid activation is a common method employed to improve the surface properties of clay minerals (Barrios et al., 1995; Rodríguez et al., 1996). For sepiolite nanofibers, acid activation can effectively increase the surface areas and surface silanol groups (Si—OH) (Galan, 1996; Myriam et al., 1998). (3-aminopropyl)triethoxysilane (APTES), as one relatively stable organosilane precursor for organic modification, is widely used (Xue et al., 2010; Yang et al., 2012). And the grafting method is commonly used for organic modification by covalently linking organosilane species with surface hydroxyl groups. Although the organosilane modified sepiolite had been used as adsorbent for dye pollutants removal, the chemical modification process was often tedious, time-consuming, and with low efficiency, and it was difficult to introduce high density of functional groups to the adsorbents (Qin et al., 2016). In addition, the surface area and pore volume of organosilane modified sepiolite decreased significantly and the fiber of organosilane modified sepiolite became reaggregation, which are not conducive to the adsorption of the dyes (Marjanović et al., 2013; Moreira et al., 2017).

From the above discussion, the highly dispersed sepiolite-based organic modified nanofibers with large surface area and pore volume

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are still lacked for the efficient adsorption of dye pollutants. To attain the above requirements, in this work, pristine sepiolite was pre-activated by acid treatment, and then we specially designed the method of APTES grafting to obtain the highly dispersed sepiolite-based nanofibers with large surface area and pore volume, and highly dispersed functional amino-groups at low temperature for a short time. Congo red (CR) was selected as the model aionic dye to evaluate the adsorption performance. We examined the effect of various experimental parameters, including solution pH, contact time, and initial dye concentration to provide more information about the adsorption characteristics of NH_2-ASEP hybrid nanofibers. The adsorption isotherms and kinetics were also investigated in detail.

2. Experimental

2.1. Materials

Pristine sepiolite (SEP) used in this work was obtained from Hebei, China. 3-aminopropyltriethoxysilane (APTES) and Congo red (CR) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China), and analytical reagents and deionized water were used in all experiments.

2.2. Preparation of acid-activated sepiolite (ASEP)

The acid-activation of sepiolite (SEP) was performed as follows: 6.0 g sepiolite micro-powder was immersed in 300 mL HCl solution (2 mol/L) at 80 °C for 8 h under magnetic stirring, and then repeatedly washed with deionized water until Cl^- could not be detected with the $AgNO_3$ test. Then, the sample was dispersed in a mixed solution of deionized water (75 mL) and ethanol (75 mL) by ultrasonic treatment (200 W, 24 kHz) for 2 h to break up the aggregates in the suspension. The suspension was centrifuged at 3000 rpm to collect the supernatant, washed with deionized water several times, then dried at 105 °C, the final product was designated as ASEP.

2.3. Preparation of sepiolite-based organic modified nanofibers (NH_2-ASEP)

Preparation of the sepiolite-based organic modified nanofibers was performed by the grafting method using (3-aminopropyl) triethoxysilane (APTES). To improve the dispersibility of hydrophilic ASEP in hydrophobic toluene, anhydrous methanol was introduced to pre-disperse the ASEP powders. During the preparation process of ASEP, the suspension was centrifuged at 3000 rpm after ultrasonic treatment to collect the supernatant, then washed with methanol several times and pre-dispersed in methanol (50 mL) by ultrasonic treatment. 125 mL of toluene was then added to the suspension under vigorous stirring. The reaction mixture was charged into a three-necked flask and purged with N_2. The flask was put into an oil bath at 75 °C to evaporate the methanol (the boiling points of methanol and toluene are 64.7 and 110.6 °C, respectively), leading to high dispersion of ASEP in toluene, further grafting APTES at 75 °C for 2 h, the APTES was slowly added into the reaction system (the ratio of ASEP/APTES was 1:5 (g:mL) with magnetic stirring at a speed of 200 rpm under a nitrogen atmosphere. Then the suspension was centrifuged at 8000 rpm to collect the resultant sample, and then washed with anhydrous toluene and ethanol successively, dried at 105 °C to a constant weight, and ground. The final product was designated as NH_2-ASEP.

2.4. Characterization

The chemical composition of sepiolite sample was determined by means of PANalytical Axios mAX wavelength dispersive X-ray Fluorescence (XRF) spectrometer. X-ray diffraction (XRD) analysis was performed on a Bruker-AXS D8 Advance diffractometer using Cu Kα radiation (0.15406 nm), operated at 40 kV and 40 mA in a scanning range of 5–80° (2θ). Fourier transform infrared (FTIR) spectra were recorded in a Perkin-Elmer Spectrum One spectrometer, using the KBr pellet technique. Spectra were recorded between 400 and 4000 cm^{-1}, with a nominal resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Escalab 250Xi spectrometer equipped with an Al Kα monochromator X-ray source. The binding energy (BE) was referenced to the C 1s peak at 284.6 eV. N_2 adsorption measurements were performed at 77 K using a Micromeritics ASAP 2020 gas sorption instrument. Before measurement, the samples were degassed at 120 °C for > 6 h. The specific surface areas were calculated using the multi-point BET (Brunauer-Emmett-Teller) method and the total pore volumes (V_{tot}) were estimated from the adsorbed volume at a relative pressure (P/P_0) of 0.995. The pore size distributions were determined by the adsorption branch of isotherms using the BJH (Barett–Joyner–Halenda) method. The micropores area (S_{micro}) and the micropore volume (V_{micro}) were obtained via t-plot analysis. Scanning electron microscopy (SEM) combined with EDS analysis was conducted on a Tescan Mira3 LMU. Scanning transmission electron microscopy (STEM) observations combined with EDS analysis were performed using a Titan G2 60–300 microscope operated at an accelerating voltage of 300 kV. Zeta potential measurements were made on a Delsa440sx instrument. Samples were suspended in deionized water (0.3 g/L) and dispersed by sonication before each point was measured manually at designated pH values after adjustment with either 0.1 M HCl or 0.1 M NaOH at 25 °C.

2.5. Adsorption experiments

Batch adsorption experiments were performed in 100 mL beakers containing Congo red (CR) dye solutions under magnetic stirring at 120 rpm. The influence of pH on CR removal was studied by adjusting CR solutions (700 mg/L) to different pH values (4.0, 6.0, 8.0, 9.0, 10.0, and 12.0) using 0.1 mol/L HCl or NaOH solution and agitating 50 mL dye solution with 0.05 g adsorbent at 25 °C for 8 h. The effect of adsorption time on dye removal was determined using 50 mL dye solutions (500 mg/L, pH = 8.0) by adding 0.05 g adsorbent at 25 °C for set intervals of time. The effect of the initial dye concentration on dye removal was determined by agitating 50 mL of CR solution with various dye concentrations by adding 0.05 g adsorbent at 25 °C for 8 h.

After adsorption, the mixture was rapidly centrifuged in a laboratory centrifuge at 6000 rpm for 10 min. The dye concentration was determined using a Unic 7200 UV–Vis spectrophotometer. The absorbance at a specific wavelength was measured for CR (500 nm). A calibration curve for CR was constructed by diluting the solution to various known concentrations and recording their absorbance at 500 nm. The adsorption capacity of CR was calculated through the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the amount of adsorption dye (mg/g) at equilibrium, C_0 is the initial concentration of CR in solution (mg/L), C_e is the equilibrium concentration of CR in solution (mg/L), m is the mass of adsorbent (g), and V is the volume of the CR solution (L).

2.6. Desorption and reusability analysis

Desorption of CR from NH_2-ASEP was investigated using a NaOH solution (0.01 M). Fresh adsorbent was loaded with CR by agitating a mixture of 0.08 g sample and 80 mL CR solution (100 mg/L) at 25 °C for 1 h. The mixture was centrifuged and the centrifugate was analyzed for the amount of dye adsorbed using a UV–Vis spectrophotometer. The CR loaded adsorbents were washed with distilled water to remove unabsorbed dye. The desorption process was performed by adding 80 mL of NaOH (0.01 M) to the washed adsorbents and shaking them for 1 h. The centrifugate was analyzed for the amount of CR desorbed from

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