Research paper

Effects of solvothermal process on the physicochemical and adsorption characteristics of palygorskite

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ABSTRACT

Palygorskite (PAL) was treated with various organic solvents including methanol (MT), ethanol (ET), isopropanol (IPA), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) via a facile solvothermal process. The effects of various solvents and reaction parameters on the microstructure, morphology and adsorption properties of PAL were intensively investigated. Fourier transformation infrared spectrometry (FTIR) and thermogravimetric (TG) analyses confirmed that some solvent molecules could be encapsulated in the tunnels of PAL and the polarity of solvent molecules plays an important role for their interaction with PAL. Field-emission scanning electron microscopy (FESEM) shows that the solvothermal treatment results in a better dispersion of PAL crystal bundles. The treated PAL by various solvents has relatively higher adsorption capacity (from 119 mg/g to 154 mg/g) and removal efficiency for methylene blue (MB) than the raw PAL, and the improved electrostatic and hydrogen-bonding interactions between MB and PAL are mainly responsible for the enhancement of adsorption properties. The adsorption properties of PAL for MB were greatly affected by the characters of solvents, and DMF-treated PAL gives the best adsorption and removal capabilities for MB.

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1. Introduction

Palygorskite clay is a natural nonmetallic commodity with the main component of palygorskite (PAL, also called as attapulgite), which widely distributed throughout the world (Singer and Galan, 1984). PAL belongs to non-planar hydrous phyllosilicate groups (Guggenheim et al., 2006). The ideal crystal structure of PAL and its theoretical formula $Si_8O_{20}(Al_2Mg_2)(OH)_2(OH_2)_4 \cdot (H_2O)_4$ was firstly proposed by Bradley (1940). It is composed of a 2:1 phyllosilicate ribbons, which are linked to the arranged alternately SiO_4 tetrahedra along a set of $Si-O-Si$ bonds and the discontinuous octahedral sheets, extending along the c-axis of the fiber to form tunnels with the size of 0.37 nm × 0.64 nm. The ideal PAL crystal has a dioctahedral character in which the octahedral sites were occupied by Mg ions. However, much research (Drits and Sokolova, 1971; Paquet et al., 1987; Galán, 1996; Galán and Carretero, 1999; Suárez et al., 2007; Chryssikos et al., 2009) have found that the octahedral cations in PAL can be partially replaced by di- or tri-valent cations (Mg^{2+}, Al^{3+}, Fe^{3+} or Fe^{2+}) in the formation process of minerals due to the isomorphic phenomenon, and usually four of the five octahedral sites were occupied by these cations with

an R^{2+}/R^{3+} ratio close to 1. The M3 position is always occupied by Mg (Güven, 1992; Suárez and García-Romero, 2006), and M2 can be occupied by Al^{3+} or Fe^{3+}. Thus, natural PAL was commonly recognized as intermediate between di- and trioctahedral phyllosilicates (Galán and Carretero, 1999; Gionis et al., 2007; Chryssikos et al., 2009) or polysomatic formulation (Suárez and Garcia-Romero, 2013). The isomorphic substitution of cations with different valents produces the permanent negative charges in the crystal cell of PAL. Meanwhile, four H_2O molecules in per half unit-cell, including zeolitic water and other structural water, are existed in the channels of PAL or coordinated to octahedral cations. Thus, the special nanorod-like crystal structure and plentiful pores of PAL make it have found potential applications in many industrial areas such as absorbents (Xue et al., 2010; Giustetto and Wahyudi, 2011; Liu et al., 2012), colloidal agents (Bezerril et al., 2006; Bodzay et al., 2011), reinforcing fillers (Li et al., 2008; Su et al., 2012; Alcantara et al., 2014) and versatile carriers (Kevadiya et al., 2011; Papoulis et al., 2013). Generally, these promising applications are highly dependent on the dispersion degree, surface properties and microscopic crystal structure of PAL nanorods. Thus, many physical and chemical methods have been developed to modify PAL for improving its various usage properties.

Up to now, many physical approaches, such as high-speeding shearing, extrusion, grinding and ultrasonication, have been adopted to process PAL, and the specific surface area, porosity and dispersibility of PAL rods can be improved to a certain degree because the crystal bundles or

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aggregates of natural PAL were effectively dispersed under the action of mechanical forces (Neaman and Singer, 2000; Mendelovici, 2001; Chen et al., 2010; Liu et al., 2012). However, the physical approaches can only excavate the intrinsic properties of PAL, but fail to create new active sites inside the crystal. So, they can only enhance the properties of PAL to a limited degree. Thus, the chemical methods have attracted much attention and have been widely concerned in both academic and industrial areas.

Acid treatment was frequently employed to modify PAL for improving its properties (Corma et al., 1987; Chen et al., 2007; Frini-Srasra and Srasra, 2010). It was confirmed that the moderate acid treatment may dissolve out the metal ions in the crystal backbone of PAL and break the inert bonds, and so numerous new active sites could be created and the adsorption properties were greatly improved. Thermal treatment may remove the zeolitic water molecules in the tunnels of PAL and break some inert bonds, and thus improve the adsorption capability (Gonzalez et al., 1990; Chen et al., 2006). Frost and Mendelovici (2006) and Zhang et al. (2010) modified PAL by an organification process to improve the usage properties. The introduction of new organic functional groups on the surface of PAL is helpful to improve its adsorption properties. These researches give the common views that the performance of PAL is derived from, but is also controlled by the microstructure and surface properties, and to explore the influence of structure change on the properties of PAL is significant for both the academic research and deep industrial application.

Solvothermal is a wet chemical process that has been extensively employed to synthesize new inorganic nano-materials (Rajamathi and Seshadri, 2002; Yao and Yu, 2007; Lu et al., 2008). This treatment method can induce the dispersion of crystal bundles as well as the change of surface properties and microscopic crystalline structure. Also, the solvent molecules may interact with PAL and generate a great impact on its properties because they may replace the water molecules in the crystal of PAL. Our previous research (Xu et al., 2013a) found that organic solvent molecules may generate stronger interaction with PAL, which causes the change of physical and chemical properties of PAL. Similarly, Darvishi and Morsali (2010) reported the synthesis and characterization of nano-sepiolite by solvothermal method, and proposed that the solvothermal process may facilitate the dispersion of fibers into nanoscale size. The solvothermal methods have gradually highlighted their advantages over enhancing the usage properties of PAL by improving (or optimizing) the microstructure. However, rare research regards on the treatment of PAL with solvothermal process as well as its effect on the adsorption properties.

Based on above background and our previous works (Xu et al., 2013a, 2013b), we further treated PAL with various solvents including methanol (MT), ethanol (ET), isopropanol (IPA), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) by a simple solvothermal process. The effect of different organic solvents on the microstructure of PAL as well as the interaction between PAL and solvent molecules was also investigated. The combination mechanism of various types of solvents with PAL was explored by the FTIR, TG, XRD and SEM analyses, and the adsorption properties of treated PAL for MB dye were systematically evaluated.

2. Experimental

2.1. Materials

PAL comes from Huangnishan Mine located on Xuyi county of Jiangsu Province and provided by Huida mineral-Sci Co. Ltd. (Jiangsu, China). Its chemical composition is SiO_2 52.37%, MgO 6.92%, Al_2O_3 11.67%, CaO 1.91%, Na_2O 0.27%, Fe_2O_3 7.91%, and K_2O 1.49% as determined by a MiniPal 4 X-ray fluorescence spectrometer (PANalytical Co., Netherlands). Methylene blue (MB, indicator grade) with the formula of $C_{16}H_{18}N_3SCl$ was purchased from Alfa Aesar A Johnson Matthey Company and used without further purification. MT, ET, IPA, DMF and

DMSO are all of analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All other reagents are of analytical grade and all aqueous solution is prepared with double deionized water.

2.2. Solvothermal treatment of PAL

PAL was firstly treated with 2 wt.% of H_2SO_4 solution at the solid/liquid ratio of 1/10 to remove the carbonates. The resultant suspension was passed through a 300-mesh sieve to remove the undesirable quartz. The suspension was collected and centrifuged at 5000 r/min for 20 min to separate the solid from the solution, and the solid product was fully washed with distilled water until pH ~ 7. The solid was oven-dried at 105 °C for 4 h, and then smashed and passed through a 200-mesh screen for further use.

The pretreated PAL powder was dispersed in 60 mL of different organic solvents (MT, ET, IPA, DMSO and DMF) at a solid/liquid of 1/200 (m/v) by mechanical stirring. Then, the resultant dispersion mixture was transformed into a 100 mL sealed Teflon reactor, and reacted at 180 °C for 12 h, 24 h and 48 h, respectively. The reaction product was naturally cooled to room temperature, separated by centrifugation at 5000 r/min, and then dried to a constant mass at 60 °C under vacuum.

2.3. Adsorption experiment

The PAL samples (0.0250 g) were mixed with 25 mL of MB solution (initial concentration is 200 mg/g) on a THZ-98A orbital shaking at the constant speed of 150 r/min and the temperature of 30 °C for 6 h to reach adsorption equilibrium. The solid was separated from the solution by centrifugation at 5000 r/min, and the supernatant was collected to analyze the residual concentration of MB after adsorption. The concentration of MB in the solution was determined using a Specord 200 UV/vis spectrophotometer at the maximum absorbance wavelength of 665 nm. The amounts of MB adsorbed by per unit mass of adsorbent were calculated by the difference value of MB concentration in solution before and after adsorption according to the following Eq. (1):

$$q_t = (C_0 - Ct)V/W \qquad (1)$$

where, q_t (mg/g) is the adsorption capacity of PAL for MB at the time t (min); C_0 and C_t (mg/L) are the initial and final concentration of MB solution, respectively; V (L) is the volume of MB solution used; W (g) is the mass of the adsorbent used.

2.4. Characterization

FTIR spectra were recorded on a Fourier transform infrared spectrometry (Thermo Nicolet NEXUS TM, USA) in the range of 4000–400 cm^{-1} using KBr pellets. The morphology was observed with a Field-emission scanning electron microscopy (FESEM, JEOL JSM-6701F SEM, Japan) after dispersing and coated the samples with gold film. Powder X-ray diffraction (XRD) analyses were performed using a X-ray diffractometer with Cu anode (PAN analytical Co. X'pert PRO), running at 40 kV and 30 mA. The specific surface area (S_{BET}) was determined by the Brunauer–Emmett–Teller (BET) method (the instrument error is smaller than 5%). The pore volume (PV) and pore-size (PZ) distribution were estimated by the Barrett–Joyner–Halenda (BJH) method at 77 K (ASAP 2020 M, Micromeritics Instrument Corporation). Zeta potential was measured using a Zeta voltmeter (Malvern Zeta voltmeter (ZEN3600), Britain). TG and DSC analyses were carried out using a STA 6000 (PerkinElmer Instrument Co., Ltd. USA) under N_2 atmosphere at a heating rate of 10 °C/min to study the thermal behaviors of the samples over a temperature range from 25 to 800 °C.