



High-pressure homogenization associated hydrothermal process of palygorskite for enhanced adsorption of Methylene blue



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ABSTRACT

Palygorskite (PAL) was modified by a high-pressure homogenization assisted hydrothermal process. The effects of modification on the morphology, structure and physicochemical properties of PAL were systematically investigated by Field-emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FTIR), Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD) and Zeta potential analysis techniques, and the adsorption properties were systematically evaluated using Methylene blue (MB) as the model dye. The results revealed that the crystal bundles were disaggregated and the PAL nanorods became more even after treated via associated high-pressure homogenization and hydrothermal process, and the crystal bundles were dispersed as nanorods. The intrinsic crystal structure of PAL was remained after hydrothermal treatment, and the pore size calculated by the BET method was increased. The adsorption properties of PAL for MB were evidently improved (from 119 mg/g to 171 mg/g) after modification, and the dispersion of PAL before hydrothermal reaction is favorable to the adsorption. The desorption evaluation confirms that the modified PAL has stronger affinity with MB, which is benefit to fabricate a stable organic–inorganic hybrid pigment.

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1. Introduction

Palygorskite (PAL) is a naturally available nanoscale silicate clay mineral with rod-like crystal morphology and superior features including larger specific surface area, higher thermal stability, ideal aspect ratio, and plentiful surface functional groups. Also, it has abundant resource and eco-friendly advantages. Thus, PAL has been honored as the base materials of “greening the material worlds in 21st century” [1] and frequently used as green materials to fabricate various nanocomposites [2–4], catalysts [5–7], colloidal agents [8], adsorbents [9–11], and lubrication additive [12], etc. Recently, with the growing global attention on environmental pollution, the design and development of eco-friendly adsorption materials for the removal of dye, heavy metal ions, and other organic pollutants have attracted more attention. The natural PAL clay mineral shows great prospect to develop eco-friendly adsorbents.

However, the low adsorption capacity of natural PAL limited its practical application. Thus far, various methods, such as acid treatment [13], thermal treatment [14,15], organic modification [16,17], and mechanical treatment [18], have been employed to improve the adsorption capacity of PAL by altering its microscopic structure or introducing new functional groups. It is commonly recognized that the adsorption capacity of PAL is influenced by many factors including specific surface area, pore size, cation exchange capacity and surface groups, which are highly dependent on the intrinsic crystal structure and the dispersion degree of PAL rods.

As is known, the rods in natural PAL are existed as bundles or aggregates owing to the Van der Waals forces and hydrogen bonding interaction [19]. This means that natural PAL is only a precursor, instead of a real nanomaterial. So the disaggregation of PAL aggregates is the prerequisite for all the application. It has been demonstrated that the dispersion of clay mineral in water after being mechanically pretreated is an efficient method to disassociate the aggregates [20]. High-pressure homogenization process is an effective technique to disaggregate the crystal bundles of PAL. The high-pressure homogenization equipment could deliver pressure about 100 MPa, and the homogenizer studied in Stansted, U.K., in 1997 even achieved the pressure of 350 MPa [21]. During

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the homogenization process, the strong forces (shear, impact and cavitation) could overwhelm the interactions among the rod crystals (electrostatic and Van der Waals' forces) and instantly disperse the crystal bundles into individual rod crystals [22]. Different from the conventional mechanical treatment, the "cavitation effect" generated from high-pressure homogenization may transfer forces from the interior of crystal bundles to the exterior, and so it may effectively disperse the rod crystals without damaging the crystal structure and aspect ratio. In addition, this process is suitable for large-scale industrial processing.

Besides the dispersion of PAL rod crystals, the optimization of crystal structure is also important to improve its adsorption properties. Hydrothermal method is extensively used for the synthesis of novel materials, owing to the simple operation and mild reaction conditions [23]. It may evidently enhance the performance by inducing the tiny change of crystal structure. The hydrothermal treatment of PAL may be effective to regulate the crystal structure and form new functional groups. However, there are no reports about the associated mechanical high-pressure homogenization and hydrothermal process to improve the adsorption properties of PAL.

As a part of efforts to further explore the feasible approach to improve the adsorption capacity of PAL, in this work, the PAL crystal bundles were dispersed with the aid of high-pressure homogenization at 30 MPa and then treated by a simple hydrothermal process. The change of microstructure of PAL was investigated with Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and nitrogen adsorption–desorption isotherm techniques, and the synergistic effect of high-pressure homogenization and hydrothermal treatment on the adsorption properties of PAL for MB were evaluated systematically.

2. Materials and methods

2.1. Materials

Palygorskite (PAL) clay, with the chemical composition of SiO₂ 52.37%, MgO 6.92%, Al₂O₃ 11.67%, CaO 1.91%, Na₂O 0.27%, Fe₂O₃ 7.91%, and K₂O 1.49%, as determined by a MiniPal 4 X-ray fluorescence spectrometer (PANalytical Co., Netherlands), was produced from Huangnishan Mine in Xuyi County of Jiangsu province of China. Before use, PAL clay was extruded for three times and treated with 2% of H₂SO₄ solution at the solid/liquid ratio of 1/10 to remove the carbonates. Methylene blue (MB, indicator grade) with the formula of C₁₆H₁₈N₃SCl was purchased from Alfa Aesar A Johnson Matthey Company and used without further purification. All other reagents used are of analytical grade, and all the aqueous solution was prepared with deionized water.

2.2. High-pressure homogenization treatment of PAL clay

50.0 g of pre-treated PAL was dispersed in 500 mL of deionized water under mechanical stirring at 800 rpm for 120 min to form a homogeneous suspension. Subsequently, the suspension was homogenized at 30 MPa using a high-pressure homogenizer (GYB-3004, Shanghai Donghua High Pressure Homogenizer Factory, Shanghai, China). The solid was separated by a centrifugation at 5000 rpm for 20 min, dried at 105 °C for 4 h, ground and passed through a 74 μm screen to obtain the product. The water-dispersed PAL (without homogenization) was prepared by a similar procedure. The un-homogenized and homogenized samples were marked as RPAL and HPAL, respectively.

2.3. Hydrothermal treatment of PAL clay

50.0 g of RPAL or HPAL powder was uniformly dispersed in 60 mL of deionized water under stirring (800 rpm) at a solid/liquid ratio of 1/200. The resultant suspension was transformed into a 100 mL Teflon Tank, sealed and reacted at 180 °C for 12 h, 24 h and 48 h, respectively. After cooled to room temperature, the solid product was separated by centrifugation at 5000 rpm, dried at 60 °C under vacuum to constant mass. The dried product was ground and passed through a 200-mesh screen for further use. The hydrothermally treated PAL samples were marked as RPAL-HT_x and HPAL-HT_x for (*x* is the reaction time).

2.4. Adsorption experiment

The adsorption experiments were conducted by contacting 0.0250 g of adsorbent with 25 mL of MB solution (200 mg/L) on an orbital shaking THZ-98A at the speed of 150 r/min and temperature of 30 °C until adsorption equilibrium was reached. The adsorbent was separated from the solution by centrifugation, and the concentration of MB solution before and after adsorption was examined with a Specord 200UV/vis spectrophotometer at the maximum absorbance wavelength of 665 nm. Then the amounts of MB adsorbed per unit mass of adsorbent can be calculated from the concentration difference of MB in the initial and final solution according to the following equation (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q_t (mg/g) is the adsorption amount of MB at 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 adsorbent used.

2.5. Acid- and base-resistance experiment

The experimental procedure of acid- and base-resistance of the dye-loaded PAL is as follows: the MB-loaded PAL was added into different concentrations of HCl and NaOH solution, respectively. Then, the solid was separated from the solution by centrifugation, and the amount of MB in the solution was determined by the procedure in Section 2.4.

2.6. 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 JSM-6701F Field-emission scanning electron microscopy (JEOL, Japan) and TEM (TECNAI-G2-F30, FEI) after dispersing the samples in the ethanol. Powder X-ray diffraction (XRD) patterns were collected 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 measured on an ASAP 2020 M nitrogen adsorption analyzer (Micromeritics Instrument Corporation) at 77 K by the Brunauer–Emmett–Teller (BET) method. The pore volume (PV) and pore-size distribution were estimated by the Barrett–Joyner–Halenda (BJH) method. Zeta potential was measured on a Malvern ZEN3600 Zeta voltmeter (Britain). The solid/liquid ratio of the suspension for test is 0.5/100 (w/w), dispersed with deionized water by high-speed stirring.

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