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A comparative study about adsorption of natural palygorskite for methylene blue

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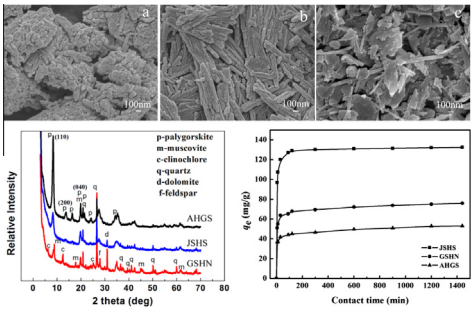
HIGHLIGHTS

- The structure features of three palygorskites from different sources were studied.
- Mg-rich palygorskite has higher aspect ratio of rod-like crystals.
- Mg-poor palygorskite shows higher adsorption capacity for MB.
- The trioctahedral structure feature is favorable to the adsorption of MB.
- MB molecules may attach on the surface and enter into the channels of palygorskite.

GRAPHICAL ABSTRACT



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ABSTRACT

Various methods including acid treatment, heat treatment and surface modification have been used to improve the adsorption properties of natural palygorskite. However, the comparative study about the effect of source of palygorskite on the adsorption properties remains a gap to be filled. Here we first studied the structure and chemical composition of three palygorskite samples from Jiangsu, Anhui and Gansu Provinces of China using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and X-ray Fluorescence Spectrometry (XRF). Subsequently, the adsorption properties of the palygorskites for methylene blue (MB) were evaluated and compared. The palygorskite from Jiangsu (JSHS) is Mg-poor and has an analogous dioctahedral structure. The palygorskite from Anhui (AHGS) is Mg-rich, and has an intermediate structure of dioctahedron and trioctahedron. The palygorskite from Gansu (GSHN) also has an intermediate structure of dioctahedron and trioctahedron, but is associated with muscovite, clinochlore, dolomite and feldspar. The maximum adsorption capacity of the palygorskites from JSHS, GSHN, AHGS for MB at 303 K is 158.03, 98.34, 77.92 mg/g, respectively. It was found that a lower Mg content and the dioctahedral structure of palygorskite are favorable to its adsorption for MB. More negative value of Gibbs free energy ($\triangle G^0$) for JSHS further illustrates that JSHS has higher efficiency in removing the MB molecules than the others. The adsorption mechanism studies suggest that the zeolitic H_2O plays a fundamental role in the interaction between MB and palygorskite.

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1. Introduction

Clay minerals are frequently used as adsorbents to remove dyes [1], heavy metals [2] and surfactant [3] from aqueous solutions owing to their abundance and low cost. Palygorskite is a kind of 2:1 phyllosilicate with nano-sized rod-like morphology. Palygorskite has high surface area, moderate cation exchange capacity and excellent salt resistance in comparison with other clay minerals, which are advantageous for its application as adsorbents to remove various dyes in wastewater [4–6]. However, adsorption efficiency of natural palygorskite is low and should be improved for practical application. Various methods have been tried to improve the adsorption capacity of palygorskite for dyes, such as optimizing the experimental conditions [4,5,7], acid activation [8], thermal treatment [9,10] and surface modification [11], etc. However, comparative study about the effect of source of palygorskite on the adsorption properties remains a gap to be filled.

Many studies have managed to find the relationship between structure and chemical composition of palygorskite. Bradley [12] inferred the composition of palygorskite with an ideal formula of $(OH_2)_4(OH)_2Mg_5Si_8O_{20}{\cdot}4H_2O$ in Attapulgus, Georgia. Chryssikos et al. [13] studied 18 palygorskite samples from different localities in Portugal, Mexico and Spain, and found that palygorskite has an intermediate structure of dioctahedron and trioctahedron, and its structural scheme was consistent with other literatures [14–16]. Suárez et al. [17] proposed that palygorskite can be classified in three types regarding its chemical composition and the X-ray diffraction (XRD) patterns: aluminic-palygorskite with dioctahedral extreme, magnesic-palygorskite with trioctahedral extreme and intermediate-palygorskite with dioctahedral character.

The adsorption capacity of palygorskite is determined by many factors including specific surface area, pore size and cation exchange capacity, which basically depend on the chemical composition and structure of palygorskite. It is the source of palygorskite mainly determines its chemical composition and structure. Study about the influences of source of palygorskite on its adsorption capacity is rare up to now. Here three representative palygorskite samples from Jiangsu, Anhui and Gansu Provinces of China were used to adsorb methylene blue (MB). The aim of this study is to reveal the influences of chemical composition and structure of natural palygorskite on the adsorption capacity for MB, which may provide a basis for the application of natural palygorskite as adsorbents for dye molecules.

2. Experimental

2.1. Materials

The raw palygorskite clay minerals from Huangnishan (Jiangsu Province, China), Guanshan (Anhui Province, China) and Huining (Gansu Province, China) were treated using a three-rolling grinder for one time and passed through a 200-mesh sieve. The samples were denoted as JSHS, AHGS and GSHN according to their locations. All the samples were heated at 105 °C for 4 h to remove moisture or any contaminants before adsorption experiments. MB (indicator grade) was purchased from Alfa Aesar and used without further purification.

2.2. Characterization

The morphology of the palygorskite samples was observed using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL) after coated with a gold film, and a transmission electron microscope (TEM, JEM-1200 EX/S, JEOL). The palygorskite samples for TEM observation were prepared according to the following procedure. The samples were dispersed in distilled water using ultrasound for 30 min, and then were deposited on a copper mesh with a carbon micropore film. The Fourier transform infrared (FTIR) spectra were recorded in the 4000–400 cm^{-1} range on a Nicolet NEXUS FTIR spectrometer using the KBr pellets. The XRD patterns were collected on an X'pert PRO diffractometer with Cu-Ka radiation (40 kV, 30 mA). Scans were made at room temperature from 3° to 80° with a step of 0.02°/s. The thermal analysis data were collected using a Diamond TG-DTA 6300 thermoanalyzer, heating from 40 to 800 °C under a nitrogen atmosphere. The heating rate is 10 °C/min. The specific surface areas were determined using Micromeritics, ASAP2020 with N_2 as an adsorbate at 77 K. The specific surface areas (S_{BET}) were evaluated by the BET method, the micropore volume (V_{micro}), micropore area (S_{micro}) and external surface area (S_{ext}) were calculated by the t-plot method. The total pore volume (V_{total}) was estimated from the volume of N_2 adsorbed at a relative pressure $P/P_0 = 0.97$. All the samples were heated at 105 °C for 4 h to remove moisture or any contaminants before measurements. X-ray Fluorescence (XRF) analyses were performed on SHIMADZU, EDX-GP to obtain the chemical composition of the samples by pelleting palygorskite powder with boric acid powder at a mass ratio of 1:7.

2.3. Batch adsorption experiment

The aqueous solution of MB with the concentration of 1000 mg/L was prepared by dissolving MB powder in deionized water and then diluted into different concentrations for further use. The pH value of MB solution was adjusted using 1 mol/L of HCl or NaOH solution. For adsorption studies, 50 mg of palygorskite sample was contacted with 25 mL of MB solution in a 50 mL Erlenmeyer flask and shaken on a thermostatic shaker bath (THZ-98A) at 150 rpm for a certain time. Thereafter, the suspension was centrifuged at 5000 rpm for 10 min. The initial and residual concentrations of MB were measured using a Specord 200 UV/visible spectrophotometer (Germany) at the maximum absorbance wavelength of 670 nm. The amount of adsorbed MB at time t, q_e (mg/g) was calculated using the following equation:

$$q_e = \left(\frac{c_0 - c_t}{m}\right) \times V \quad (1)$$

where c_0 (mg/L) is initial concentration of MB, c_t (mg/L) is the concentration of MB at time t, V (L) is volume of solution used, and m (g) is the mass of palygorskite sample. Calibration curve was plotted with absorbance as a function of MB concentration in solution. The palygorskite-MB composite was dried at 150 °C for 4 h and ground to 200-mesh to be prepared as palygorskite-MB pigment, named as JSHS-MB, GSHN-MB and AHGS-MB, respectively.

3. Results and discussion

3.1. Characterizations

3.1.1. SEM and TEM analyses

The morphology of palygorskite samples from JSHS, AHGS and GSHN of China are obviously different from each other. The SEM and TEM images of palygorskite samples are shown in Figs. 1 and 2, respectively. As can be seen from the SEM image, palygorskite in JSHS appeared as lump aggregates of short rods (Fig. 1a), and palygorskite in AHGS showed platy aggregates of long rods arranged in order (Fig. 1b). Palygorskite in GSHN is associated with other lamellar minerals (Fig. 1c), which are identified as mixture of associated minerals such as muscovite, clinochlore, quartz, dolomite and feldspar by XRD patterns (Fig. 3). Palygorskite rods may exist as individual rods or as elongated bundles of many rods (Fig. 2). The three palygorskite samples also exhibit differences in