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JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Ammonium sulfide-assisted hydrothermal activation of palygorskite for enhanced adsorption of methyl violet

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ARTICLE INFO

Article history:
Received 5 February 2015
Revised 3 March 2015
Accepted 19 March 2015
Available online 26 July 2015

Keywords:
Palygorskite
Hydrothermal
Adsorption
Methyl violet

ABSTRACT

Herein, palygorskite (PAL) was activated *via* a simple hydrothermal process in the presence of ammonium sulfide, and the effects of activation on the microstructure, physico-chemical feature and adsorption behaviors of PAL were intensively investigated. The hydrothermal process evidently improved the dispersion of PAL crystal bundles, increased surface negative charges and built more active –Si–O$^-$ groups served as the new "adsorption sites". The adsorption property of the activated PAL for Methyl Violet (MV) was systematically investigated by optimizing the adsorption variables, including pH, ionic strength, contact time and initial MV concentration. The activated PAL exhibited a superior adsorption capability to the raw PAL for the removal of MV (from 156.05 to 218.11 mg/g). The kinetics for MV adsorption followed pseudo second-order kinetic models, while the isotherm and thermodynamics results showed that the adsorption pattern well followed the Langmuir model. The structure analysis of PAL before and after adsorption demonstrated that electrostatic interaction and chemical association of –X–O$^-$ are the prominent driving forces for the adsorption process.

Introduction

Dyes, as the main pollutants in textile wastewater, are usually toxic, non-biodegradable and harmful to both aquatic biosphere and human (Lotito et al., 2012; Cheng et al., 2014). Thus, it is extremely urgent to find an economic but effective method to remove dyes from wastewater. Recently, adsorption has been found to be one of the commonly used techniques for removing dyes. As a natural adsorbent, silicate clay minerals have attracted great attention, because they are environmentally friendly, stable, non-toxic and at lower risk of secondary pollution (Wang et al., 2014).

Palygorskite (PAL) is a special one-dimensional nanorod-like silicate clay mineral with a 2:1 ribbon-layer structure composed of two continuous tetrahedron sheets and one discontinuous octahedron sheet (Drits and Sokolova, 1971). This unique crystal structure of PAL endows it with higher specific surface area, better ion-exchange capacity, and superior thermal and mechanical stability (Murray, 2000; Chen et al., 2006; Sheikhhosseini et al., 2014). Owing to these

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http://dx.doi.org/10.1016/j.jes.2015.03.036

inherent advantages, PAL has been developed as a potential adsorbent to remove dyes (Hussin et al., 2011; Liu et al., 2012; Gómez et al., 2014; Wang et al., 2015a), color matters (Tian et al., 2014), heavy metals (Deng et al., 2013), *etc.* However, the adsorption capability of natural PAL is not satisfactory because the intrinsic "active adsorption sites" are very limited. Thus, it becomes extremely important to enhance the adsorption capability of natural PAL by creating new "adsorption sites" in PAL crystal *via* a simple but effective method. Our work (Zhang et al., 2015a) has confirmed that the PAL with some defects (instinctive or formed) and less associated minerals was more favorable to adsorption.

Hydrothermal or solvothermal treatment and functional modification of PAL have gradually raised concern, for this process may regulate the crystal structure and surface properties of PAL and then sharply enhance its adsorption properties (Wu et al., 2013). Although the relevant research is rare, hydrothermal activation has been confirmed to be an efficient technique to achieve great enhancement of adsorption properties compared to conventional methods (Zhang et al., 2015b). As part of a systematic research, it is significant to explore the effect of hydrothermal process on the crystal structure of PAL, and the relative structure–property relationship. This will lay a firm foundation for breaking the limitation of traditional modification methods and achieving a satisfactory adsorption property.

As the aim to enhance the adsorption properties of PAL and explore the correlation between structural changes and adsorption properties, herein, the PAL was modified by one-step hydrothermal process in the presence of small amount of ammonium sulfide. The structure changes of PAL were investigated and the adsorption properties were systematically evaluated using methyl violet (MV) as the model adsorbate. The adsorption capability, adsorption kinetics and effect of adsorption parameters were evaluated to explore the adsorption mechanism.

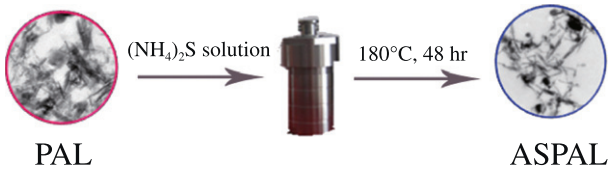
1. Experimental

1.1. Materials

Natural PAL was produced from Huangnishan Mine (Jiangsu, China). Ammonium sulfide ($(NH_4)_2S$, AR grade), ammonium hydroxide and MV (AR grade) were purchased from Aladdin Industrial Inc. (Shanghai, China). Sodium chloride (NaCl) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other reagents used are all of analytical grade and all solutions were prepared with distilled water.

1.2. Pretreatment of PAL

The natural PAL was pretreated with 5% of aqueous solution of hydrochloric acid at the solid/liquid ratio of 1:10 to remove the carbonate and other water-soluble impurities. After being mechanically stirred at 800 r/min for 2 hr, the resultant suspension was passed through a 200-mesh sieve to remove undesirable quartz. Then the resultant suspension was centrifuged at 4500 r/min to separate the solid. The solid product was dried to a constant weight at 105°C, smashed and passed through a 200-mesh sieve to obtain powders with the particle size less than 75 μm.



Scheme 1 – Schematic diagram of the hydrothermal activation process. PAL: palygorskite. ASPAL: PAL modified with ammonium sulfide.

1.3. Hydrothermal activation of PAL

As illustrated in Scheme 1, 1.0 g of PAL powder was dispersed into 50 mL of aqueous solution of ammonium sulfide (0.048 mol/L) under continuous stirring. One hour later, the suspension was transformed into a Teflon-lined stainless steel autoclave with a volume capacity of 100 mL, and maintained at 180°C for 48 hr. After that, the autoclave was naturally cooled to room temperature. The resultant suspension was centrifuged at 4500 r/min to separate the solid product, and the solid was fully washed with deionized water to remove free ions. Finally, the solid was dried at 65°C under vacuum, gently ground and passed through a 200-mesh sieve. The modified PAL with ammonium sulfide was marked as ASPAL, and the pretreated PAL was used as the control sample.

1.4. Batch adsorption experiments

Batch adsorption experiments were performed to evaluate the adsorption performance of the pretreated PAL and ASPAL. Typically, 15 mg of adsorbent was mixed with 15 mL of MV olution (initial concentration, 300 mg/g; initial pH, 7), followed by shaking at 180 r/min in a thermostatic shaker (THZ-98A, INESA, Shanghai, China) at 30°C for 60 min to reach the adsorption equilibrium. Afterward, the MV solution was separated from the mixture by centrifugation. The concentrations of MV before and after adsorption were determined using UV–Vis spectrophotometer (UV 765, Precision & Scientific Instrument Co., Ltd., Shanghai, China) at the maximum absorbance wavelength 583 nm and calculated from the absorbance using a standard calibration curve. The adsorption capacity of MV on the adsorbents is calculated by Eq. (1):

$$q = (C_0 - C_t) \times V/m \quad (1)$$

where, V (mL) is the volume of MV solution, C_0 (mg/L) is the initial concentration of MV solution, C_t (mg/L) is the concentration of MV in the solution at a given time (t), and m (mg) is the mass of adsorbent.

The main influence factors for the adsorption of MV onto PAL, including pH values, contact time, initial concentration of MV solution, temperature, and ionic strength were studied. The pH value of MV solution was adjusted with dilute NaOH or HCl solutions (0.1 mol/L) to a pH range of 2–10 to study the effect of pH on dye removal. Different amounts of NaCl were