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Research paper

Preparation and cyclic utilization assessment of palygorskite/carbon composites for sustainable efficient removal of methyl violet

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ABSTRACT

Palygorskite/carbon composites were constructed by using the spent bleaching earth after bleaching of animal fat as feedstock via one-step calcination and deemed to be adsorbents for the efficient removal of methyl violet. And continuous cyclic adsorption of methyl violet using the obtained palygorskite/carbon composites was emphatically evaluated by continuous adsorption-calcination process in this study. The results unveiled that the formed carbon species were closely anchored on the palygorskite surface, and the as-prepared palygorskite/carbon composites always exhibited a high adsorption capacity for methyl violet though the calcination temperature, initial pH, initial concentration of dye and contact time varied. By a simple thermal regeneration process, the exhausted adsorbents were recycled repeatedly for methyl violet removal. Interestingly, no obvious decrease in the adsorption capacity of the palygorskite/carbon composites prepared at 300 °C was detected after ten times cycles calcination. It developed a novel avenue to fully utilize spent bleaching earth and exhausted palygorskite/carbon composites.

1. Introduction

Adsorption method represents one of the best available environmental control technologies to remove contaminants due to its extraordinary superiorities including low cost, flexible operation, insensitivity to toxic chemical compounds in water, and the diversification of the involved adsorbents (Yang et al., 2018; Portinho et al., 2017). Recently, the clay minerals/carbon composite is served as a promising adsorbent for the treatment of wastewater because of the exceptional chemical properties, excellent environmental compatibility, well-developed porous structure and rich functional groups (Kazak et al., 2017; Liang et al., 2017; Yadav et al., 2018). However, the regeneration of the exhausted adsorbents is proved to be a complicated and time-consuming process with low desorption rate, which results in the secondary pollution and the limited applications (Rathore and Mondal, 2017). A common practice has been performed to dispose the spent clay minerals/carbon composites in landfill or its incineration. However, it is wasteful and ungreen since the spent clay minerals/carbon composites are not fully utilized *via* a reasonable means. Hence, the regeneration of the spent clay minerals/carbon composites is important to minimize the effects caused by its disposal taken into account of the economical, environmental and energy benefits.

The approaches for regeneration can be categorized to be chemical regeneration (Bouazza et al., 2018), thermal treatment (Marques et al., 2017), supercritical fluid extraction (Da Costa Lopes et al., 2016), wet oxidation (Cabrera-Codony et al., 2017) and electrochemical regenerations (Sharif et al., 2017), etc. The microwave assisted regeneration is known as an encouraging method recently owing to the substantial reduction in regeneration period and the creation of productive regenerated product (Çalışkan et al., 2012). Whereas, chemical regeneration method, wet oxidation, and supercritical fluid regeneration inevitably involve high pressure and temperature, which seem to be providing a particularly hostile economy (Ma et al., 2016). In turn, the preference of a proper regeneration technique extremely relies on the features of adsorbate (i.e., toxicity, radioactive and erosive), types of adsorption (i.e., physisorption or chemisorption) and the costs of regeneration (Nahm et al., 2012). Despite the emergence of new technologies, thermal regeneration is still found to be better solution in adsorbent recycling processes due to low-cost, environmental-friendly, high-efficiency and non-secondary pollution (Gao et al., 2014; Nigri et al., 2017), which is beneficial to the reduction of deleterious aftereffects on the environment, considered as the “footprint” of remediation

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(Stawiński et al., 2017).

Our research group presented a simple method for the preparation of low-toxicity, cost-effective, green-process, large-scale and high-performance palygorskite/carbon (Pal/C) composites from the spent bleaching earth as adsorbents for water purification (Tang et al., 2015). In this study, the continuous cyclic adsorption property of the obtained Pal/C composites, which were fabricated by one-step calcination based on the spent bleaching earth after bleaching of animal fat, was emphatically evaluated by continuous adsorption-calcination process using methyl violet (MV) as a common and representative pollutant. The physical and chemical properties of Pal/C composites were analyzed in detail. The evaluation of calcination temperature, initial pH, initial dye concentration, contact time and regeneration temperature were systematically carried out.

2. Experimental section

2.1. Materials and characterization

Natural Pal was obtained from Huangnishan Mine (Xuyi County, Jiangsu Province, China), and the chemical composition of Pal was given in Table S1. Crude animal fats (lard oils) were provided by a local processor. And then lard oils were prepared by rendering adipose tissues of the corresponding animals. The rendering was operated at 90–100 °C for 2 h in the oven. MV was purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., China. The characteristics and chemical structure of this dye were listed in Table S2. All other chemicals with analytical grade were used as received without further purification. Ultrapure water (18.25 MΩ cm) was used for all the experiments.

Fourier transform infrared (FTIR) spectra were recorded in transmittance mode in the wavenumber region of 4000–400 cm^{-1} using a FTIR spectrometry (Thermo Nicolet 6700, Thermo Fisher, USA). X-Ray diffraction (XRD) patterns were conducted with an X'Pert PRO diffractometer (X'Pert PRO, PAN analytical Co., Netherlands) furnished with a Cu-Kα radiation source (n = 1.540598 Å, 40 kV, 40 mA) from 3 to 80° (2θ). The surface morphology of samples was detected by scanning electron microscope (SEM, JSM-6701F, JEOL, Ltd. Japan). The samples were fixed on the copper stubs and treated by gold sputtering, and the elemental compositions were determined by a coupled Kevex energy dispersive spectrometer (EDS). The morphologies of the samples were observed using a JEM-2010 transmission electronic microscope (TEM) (JEOL, Tokyo, Japan). Prior to TEM observation, the samples were ultrasonically dispersed in ethanol for 10 min and then deposited on a copper grid covered with a perforated carbon film. Thermogravimetric analysis (TGA) was determined using a Perkin-Elmer STA 6000 thermogravimetric analyzer under O_2 atmosphere at a heating rate of 10 °C/min. The Raman spectrum (Raman) was recorded on a Horiva (Lab Ram HR-800) spectrometer. The Brunner-Emmet-Teller (BET) specific surface area was analyzed by an ASAP 2020 instrument (Micromeritics, USA) at 77 K through the judgment of N_2 adsorption-desorption isotherms. Zeta potentials of suspensions were measured on a Malvern Zetasizer Nano system with irradiation from a 633 nm He-Ne laser (Malvern Zeta voltmeter, ZEN3600, Britain) after the sample was fully dispersed in deionized water (0.5%, w/v). The absorbance was measured at room temperature by using a UV 765 spectrophotometer (Precision & Scientific Instrument Co., Ltd., Shanghai, China).

2.2. Preparation of Pal/C composites

In a typical procedure, 20.0 g of the obtained spent bleaching earth from lard oil (LSBE) (see Supporting information and Fig. S1) was calcinated at different temperatures of 200, 300, 400, 500 and 600 °C. The calcination was performed in air atmosphere up to the desired temperature with a heating rate of 10 °C/min, followed by held at the final temperature for 2 h. The preparation conditions of the resultant samples were summarized in Table S3.

2.3. Adsorption experiments

The adsorption experiment of all samples toward MV was implemented in a series of centrifuge tubes (50 mL) containing 20 mg of the adsorbents and 20 mL 200 mg/L of MV, and then the mixtures were shaken in a thermostatic shaker at 25 ± 2 °C for a certain adsorption time. Afterwards, Pal/C composites were separated by centrifugation and an appropriate amount of supernatant was sampled and diluted to the desired concentration for determination using a UV–vis spectrophotometer by supervising the adsorption behavior at the maximum absorption wavelength of 582 nm. Then, the adsorption capacity (Q_e, mg/g) and the removal ratio (R, %) for MV was computed from the differences in the concentration before and after the adsorption according to the following Eq. (1) and Eq. (2), respectively:

$$Q_e = (C_0 - C_e) \times V/m \quad (1)$$

$$R\ (\%) = (C_0 - C_e)/C_0 \times 100\% \quad (2)$$

where Q_e is the adsorption capacity for MV at equilibrium or at time t (mg/g), C_0 and C_e meant the MV concentration before and after the adsorption (mg/L), V and m represented the total volume of MV solution (mL) and the weight of adsorbents used (mg), respectively.

To better understand the adsorption characters involved in the overall pollutants adsorption process, the effect of pH, initial concentration and contact time was systematically performed by evaluating the adsorption of Pal/C-300 to MV. The initial concentration of pollutants was set as 50–600 mg/L, and contact time in the range of 10–360 min was studied with the initial concentrations of 50, 200 and 500 mg/L, respectively. The influence of initial pH on the MV adsorption was analyzed in the pH range from 2 to 12 with an interval of 2. All the adsorption experiments were undertaken in triplicates to obtain the mean values. The relative standard deviation was less than 2% in this study.

2.4. Regeneration of spent Pal/C composites

For the reusability of spent Pal/C composites, Pal/C-300 was employed as the probe for investigation. The regeneration of Pal/C-300 could be realized by repeated adsorption-calcination cycles after adsorption of MV. In the thermal regeneration process, the exhausted adsorbents were placed in a furnace, and then calcined with a heating rate of 10 °C/min up to varied temperatures (200, 300, 400, 500, 600, 700 and 800 °C) for 2 h in air atmosphere to burn off the organics. The adsorption experiments of regenerated Pal/C composites were conducted by addition of 20 mg adsorbent in 20 mL 300 mg/L MV solution at 298 K for 6 h. The adsorption capacity of the reactivated Pal/C composites after each adsorption-calcination cycles was evaluated under the identical conditions. For this study, ten consecutive thermal regeneration cycles were carried out.

3. Results and discussion

3.1. Structural characterization

3.1.1. FTIR spectra analysis

FTIR spectra were provided to demonstrate the chemical structure and components of LSBE and the as-prepared Pal/C composites derived from LSBE at different calcination temperatures (200, 300, 400, 500 and 600 °C) (Fig. 1a). The characteristic absorption bands of Pal at 3554 (3428), 1635, 1038 and 516 cm^{-1} are observed in the spectrum of LSBE, which are attributed to the stretching vibration of O—H, H—O—H bending vibration, Si—O—Si stretching vibration and the deformation of tetrahedral sheet, respectively, revealing the presence of Pal in LSBE