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Monolithic porous rectorite/starch composites: fabrication, modification and adsorption

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ABSTRACT

The monolithic rectorite/starch composites (PRSs) were fabricated by freezing the composite gels and exchanging ice with ethanol to obtain the porous structures. The rectorite layers were randomly oriented and covered with starch in the monolithic PRSs. Two modifications were treated without destroying the porous structures. Starch components were removed to obtain the calcinated PRSs (CPRSs); and starch components reacted with carbon disulfide to obtain the porous rectorite/starch xanthate composites (PRSXs). PRSs, CPRSs and PRSXs exhibited low density and high liquid adsorption due to the porous structures. CPRSs possessed the higher MB adsorption capacity than PRSs, because the resistance of starch on MB adsorption was eliminated. The chelation could form between xanthate groups and Pb (II), and improve the adsorption of Pb (II) of PRSXs. The maximum adsorption capacities could reach 277.0 and 180.8 mg g^{-1} for MB by CPRS and Pb (II) by PRSX, respectively. Moreover, CPRS could be effectively recycled by burning away the adsorbed MB dye; while PRSX could be easily regenerated with ethylenediaminetetraacetic acid disodium salt (EDTA) solution. The modification of PRSs had the potential applications on the treatment of cationic contaminations in water.

1. Introduction

Heavy metals and synthetic dyes are common pollutants from industrial effluent, which cause environmental problems because of their toxicity, carcinogenicity and undesirable aesthetic aspect [1–3]. It is imperative to appropriately treat industrial effluent—containing heavy metals and synthetic dyes before it is disposed into the environment.

Rectorite is a regularly interstratified clay mineral composed of the nonexpansible dioctahedral mica-like layer and the expansible dioctahedral smectite-like layer [4]. The rectorite structure is easily intercalated between the smectite-like interlayers to obtain the thin rectorite layers [4]. The interlayer cations Na^+ in rectorite were easily exchanged with either organic or inorganic cations, so rectorite can adsorb cationic metals and dyes such as Cu(II) [5], Pb(II) [6], Sr(II) [7], acid red [8], neutral red and methylene blue (MB) [9].

Because rectorite can be dispersed well in the water, the separation of rectorite from the water must be considered. Magnetic adsorption was proven to be an effective method due to its simple process and low energy consumption [10]. However, magnetic particles e.g., Fe_3O_4 particles) had to occupy the adsorption sites and decreased the adsorption capacity of rectorite, when they were introduced on rectorite surface [9]. Recently, many studies focused on three-dimensional architectures, composed of the randomly oriented graphene or graphene oxide layers. The gelations were prepared to assemble graphene layers and its derivatives into monolithic structures [11,12]. After the adsorption, the separation of these porous monolithic adsorbents from the water was much easier. Rectorite was also employed to prepare the porous monolithic networks, and consolidated with cationic guar gum [13]. In this work, starch and rectorite were composited to obtain the porous monolithic rectorite/starch composites (PRSs) using the process of aqueous gel precursor freezing, solvent exchange, and ethanol drying. Starch components could retard the adsorption process of rectorite, so two modifications (the removal of starch by calcinating and the introduction of xanthate groups) were operated without destroying the porous structures. MB dye and Pb^{2+} were chosen as the model compounds of synthetic dyes and heavy metals. The modifications were expected to improve the adsorption capacities for MB dye and Pb^{2+}.

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2. Experimental

2.1. Materials

Sodium rectorite was provided by Hubei Zhongxiang Rectorite Mine (Wuhan, China). Potato starch was purchased by Manitoba Starch Products (Manitoba, Canada). Soybean oil was produced by COFCO Northsea Oils & Grains (Tianjin) Co., Ltd., China. The MB dye was obtained from Tianjin Benchmark Chemical Reagent Co., Ltd. All other reagents were of analytical grade and commercially available.

2.2. Preparation of porous rectorite/starch composites (PRSs)

Rectorite (3.2 g, 4 g or 5 g) was dispersed in distilled water (100 mL) using ultrasonication for 10 min. 5 g potato starch was added, and heated at 95 °C for 30 min for starch gelatinization. The mixture was cooled at 5 °C to obtain the starch/rectorite gel. The gel was cut into the cubes (about 1 cm × 1 cm × 1 cm), and then frozen. The frozen cubes were immersed in ethanol to remove the ice (or water) three times with about 2 h each time. The cubes were then dried at 50 °C for 4 h to remove the ethanol. The porous starch/rectorite composites were obtained, and labelled as PRS3.2, PRS4 and PRS5, respectively. When rectorite was not added, the porous starch (PS) was obtained.

2.3. The modification of PRSs

PRSs were calcined from room temperature to 500 °C in air with 10 °C/min heating rate in a muffle furnace. The structures of rectorite could be destroyed at the higher temperature, while polymer components were left much at the lower temperature. The calcined PRS3.2, PRS4 and PRS5 were labelled as CPRS3.2, CPRS4 and CPRS5.

Carbon disulfide 0.8 mL was added in 20 mL 0.5% NaOH solution with vigorous stirring. 1 g PRS3.2 (or PRS4 or PRS5) was immersed into the mixture. The reaction was processed at 30 °C for 2 h, and then washed with ethanol three times. The porous rectorite/starch xanthate composites were dried, and respectively labelled as PRSX3.2, PRSX4 and PRSX5. The more the added carbon disulfide was, the more the xanthate groups in PRSXs were. However, the superfluous carbon disulfide resulted in the decomposition of starch, which became soluble.

2.4. Scanning electron microscope (SEM)

The fracture surfaces of PS, PRS3.2, CPRS3.2 and PRSX3.2 were coated with gold, and viewed with a Hitachi S-4800 scanning electron microscope.

2.5. Fourier transform infrared spectroscopy (FTIR) spectra

FTIR spectra of PRSs, CPRSs and PRSXs were tested on a BIO-RAD FTS3000 IR Spectrum Scanner. The grinded sample powders were dispersed in KBr and pressed into transparent slices for testing.

2.6. X-ray diffraction (XRD)

CPRSs powders were placed in a sample holder for XRD. XRD patterns were recorded in reflection mode by a Bruker D8-S4 Pioneer operated at a CuKα wavelength of 1.542 Å.

2.7. Thermogravimetric analysis (TGA)

Thermal properties of CPRS powders were tested using a ZTY-ZP type thermal analyzer. Sample weights varied from 10 to 15 mg. Samples were heated from room temperature to 800 °C at a heating rate of 15 °C/min in a nitrogen atmosphere.

2.8. Specific surface area

Nitrogen adsorption–desorption measurements were performed with an Autosorb-1 specific surface area analyzer (Quantachrome Instruments, USA).

2.9. Apparent density

The apparent density was defined as the mass of the porous material divided by the total volume occupied.

2.10. Adsorption of water, ethanol and soybean oil

The dried porous rectorite-based materials (weight = w_0) were immersed individually in water, ethanol or soybean oil for 0.5 h at room temperature. The mixtures were filtered in a funnel. When no more water, ethanol or soybean oil was dropped from the filter paper, the porous rectorite-based materials were weighed (w). The adsorption capacity was calculated as follows:

$$\text{Absorption capacity} = \frac{w - w_0}{w_0} \qquad (1)$$

2.11. Adsorption of MB dye

Adsorption experiments were conducted using glass bottles containing 20 mL MB dye (37.39 mg/L, i.e. 0.1 mmol/L) and 5 mg PRSs and CPRSs at pH = 5. The glass bottles were placed on a slow-moving platform shaker in water bath and MB solutions were taken at different time intervals during the adsorption. The dye (MB) concentrations were analyzed by UV-Vis spectrometry at 662 nm and relative dye adsorption versus reaction time determined at temperatures of 30 °C.

In adsorption isotherm testing, the concentration of the adsorbent was 0.25 g/L and the dye concentrations changed from 0.01 to 0.8 mmol/L. These experiments were carried out at 30 °C and all suspensions were shaken on a rotary shaker at 100 rpm to reach the adsorption equilibrium.

2.12. Adsorption of Pb^{2+}

Adsorption experiments were conducted using glass bottles containing 1 g/L of the adsorbents (REC, CPRS3.2, PRSXs) and $PbNO_3$ solution (0.2 g/L Pb^{2+}) at pH = 5. The glass bottles were placed on a slow-moving platform shaker for a certain period of time during the adsorption process. To investigate the effect of mole ratio on equilibrium adsorption capacity, the Pb^{2+} concentrations were tested after the adsorbents were placed in $PbNO_3$ solution for 2 h. The Pb^{2+} concentrations in the solution were analyzed using an atomic adsorption spectrometer (Thermo Scientific iCE 3000) to determine the adsorbed amounts of Pb^{2+} at 30 °C.

In adsorption isotherm study, the concentration of the adsorbent was 1 g/L and the Pb^{2+} concentrations changed from 0.08 to 0.5 g/L. These experiments were carried out at 30 °C and the bottles were shaken on a rotary shaker at 100 rpm for 2 h to reach the adsorption equilibrium.

2.13. The regeneration of CPRSs and PRSXs

For the readsorption study of MB dye, 5 mg CPRS3.2 was added to 15 mL of MB dye solution (37.39 mg/L), and shaken on the shaker at 100 rpm for 24 h. CPRS3.2 was taken out from the solution, and MB concentrations in the solutions were analyzed by UV-Vis spectrometry. The dye-adsorbed CPRS3.2 was calcined for 10 min at 500 °C in