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Effects of cellulose carbonization on biomass carbon and diatomite composite

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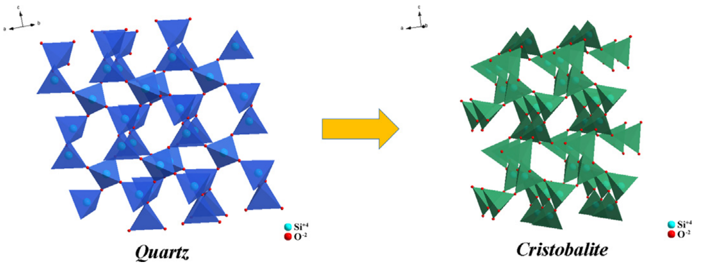
HIGHLIGHTS

- The crystallization process of opal was promoted by cellulose carbonization.
- The morphology was changed by cellulose carbonization at lower temperature.
- The MB absorption capacity was increased by cellulose carbonization.

GRAPHICAL ABSTRACT



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ABSTRACT

The biomass carbon and diatomite composite was prepared by hypoxia pyrolysis method, which adopted diatomite accompanied by cellulose as raw materials. The properties of carbonaceous samples were characterized by Thermal gravity-differential thermal analysis (TG-DTA), X-ray diffraction analysis (XRD), Scanning electron microscope analysis (SEM), Fourier transform infrared spectroscopy analysis (FT-IR), particle size analysis, Zeta potential analysis and MB adsorption capacity analysis. The XRD results showed that the crystallization temperature of opal phase was reduced nearly 350 °C by cellulose carbonization in biomass carbon and diatomite composite. The SEM analysis showed that the porous morphology of diatomite was changed by cellulose carbonization at lower temperature. The FT-IR results showed that the absorption peaks of Si—O—Si around 462 cm^{-1} and 1098 cm^{-1} were significantly weakened as biomass carbon increased. The MB absorption capacity of biomass carbon and diatomite composite was significantly increased by cellulose carbonization, q_e was in the range of 39.97–49.82 mg g^{-1}, thus the biomass carbon and diatomite composite which was environment friendly and inexpensive had the potential to be an excellent absorbent.

1. Introduction

Carbon materials had advanced rapidly over the past few years and were among the most promising materials that had already changed and would keep on changing human life in the future [1]. Biomass was a qualified carbon raw material for the synthesis of valuable carbon materials because it was available in high quality and huge amount, and was an environmental friendly renewable resource [2]. As carbon dioxide had been re-utilized in the formation process of biomass, the emission load of carbon dioxide could be reduced by converting the waste biomass into solid carbon material (biomass carbon), thus the biomass would become a new

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source of carbon materials which had been exploited and utilized all over the human civilization history [1]. Therefore, in order to solve the problems of environment and resources, more and more international scholars focused on the exploitation and utilization of biomass carbon [3]. The existing research on biomass carbon confirmed that there was a wide variety of biomass carbon raw materials which could effectively relieve the stress of environment and resources problems, and there were different strategies used to fabricate various carbon nanostructured materials with enhanced properties, thus the biomass carbon was with a wide variety of potential applications [4]. However, few researches had been carried on biomass carbon and mineral composite, and the effects of biomass carbonization on composite was rarely studied [5].

As the strong adsorption and filtration properties, diatomite was widely applied to treatment of wastewater, filter aid and light weight building materials [6]. The main mineral composition of diatomite was amorphous opal which was in different forms of porous diatom shell structure, and there was a large number of carboxyl covered on the surface of diatomite [7]. There were also some mineral impurities and diatomic biomass residual in the diatomite of natural output. The presence of mineral impurities directly restricted the utilization efficiency of diatomite [8]. It was well known that most of organic compounds could decompose at high temperatures, eventually yielding carbon [9]. Although removing organic matters through burning method was much effective, a large number of carbon dioxide which would deepen the greenhouse effect was produced in the combustion process, and the carbon dioxide would significantly reduce the actual utilization efficiency [10]. In order to avoiding the generation of carbon dioxide produced during the combustion process, the hypoxia pyrolysis method was finally adopted to prepare biomass carbon and diatomite composite material [11]. Our research group had adopt the carbonization method to dispose the diatomite, the intrinsic biomass in diatomite was transformed into biomass carbon, thus the biomass carbon and amorphous opal composite material was finally prepared [12]. As the little concentration of intrinsic biomass component in diatomite, cellulose which was adopted as the source of biomass was mixed into diatomite to investigate the effects of biomass carbonization. It was of great value to investigate the influence rules of biomass carbonization on micro-structure and properties of biomass carbon and diatomite composite [12]. The researches might arouse new ideas and laid theoretical basis for exploiting new carbonaceous composite, which would be conducive to high efficient utilization of natural biomass and mineral resources.

2. Materials and methods

2.1. Preparation of the samples

The biomass carbon and diatomite composite was prepared by hypoxia pyrolysis method which adopted diatomite accompanied by cellulose as raw materials [13]. The diatomite (HongYi, China) was adopted as the source of diatomite, the concentration of SiO_2 in diatomite exceeded 85 wt%, the concentration of biomass in diatomite was 5.3 wt%. The carboxy methyl cellulose (YANXING CHEMICAL, China) was adopted as the source of biomass, whose chemical formula was $[C_6H_7O_2(OH)_2CH_2COONa]_n$, the viscosity (2% water solution, 25 °C) was 900 ~ 1200mPa.s, the degree of substitution (D.S) was $\geq$0.65. The cellulose and diatomite were mixed together following certain concentration ratio (cellulose: diatomite = 0, 0.4, 0.6, 0.8, 1, respectively), the corresponding cellulose concentrations were 0 wt%, 28.6 wt%, 37.5 wt%, 44.4 wt%, 50 wt%, respectively. After ball-milling for 12 h, each uniform compound of equal quality was poured into a 30 mL high alumina crucible which was covered by a small crucible cover. Then all the crucibles were put at the bottom of a 500 mL high alumina crucible which was filled with active carbon to form hypoxia condition. Finally, the big crucible was covered by a great crucible cover. The samples were hypoxia calcined in high temperature furnace at 400 °C, 600 °C, 800 °C, 1000 °C, 1200 °C, respectively, the heating rate was 10 °C/min and the constant temperature time was 4 h [14].

2.2. Characterization of the samples

The TG-DTA Analysis of sample was measured by Microcomputer Differential Thermal Balance (HCT-3, China), the heating rate was 10 °C/min. The crystalline phase of sample was investigated by X-ray diffractometer (DX-2700, China), the X-ray tube which used a Cu target was working at the power of 35 kV and 25 mA. The morphology of sample was measured by Scanning electron microscope (EM-30, Korea). The Fourier transform infrared spectroscopy of sample was obtained by Fourier transform infrared spectrometer (NICOLET380, USA). The particle size of sample was measured by laser particle size analyzer (JL9200, China). The Zeta potential of sample was measured by Micro electrophoresis apparatus (JS94K2, China).

2.3. Adsorption experiments

In a typical run of MB (Methylene Blue, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$; Relative Molecule Weight: 373.90 g/mol) adsorption test, 0.01 g sample was added to a 30 mL MB solution (concentration: 30 mg/L); then, the mixture was strongly shaken for 1 h in an oscillator (HY-4, China) to ensure complete mixing at room temperature [15]. The mixture was centrifuged at 10000 rpm for 10 min by high speed centrifuge (HC-3018, China), and the supernatant was collected and characterized by UV–vis spectrophotometer (T6-NC, China), which was performed on a spectroscopy at wavelength of 664 nm [16]. All experiments were conducted at 25 °C, 0.01 g of 50 wt% cellulose mixed diatomite sample, which was hypoxia calcined at 1200 °C, was added to 30 mL of MB aqueous solution with a fixed concentration (30 mg/L) under stirring in dark condition. The concentrations of dyes left in supernatant solutions after different time intervals (1–10 h) were determined. The adsorption isotherm was simulated using the Langmuir and Freundlich model. The adsorption capacity (q_e) of the samples for MB was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity; C_o and C_e (mg L^{-1}) were respectively the initial and equilibrium MB concentrations; V (L) was the volume of the solution (0.03L); and m (g) was the mass of the adsorbent (0.01 g).

3. Results and discussion

3.1. TG-DTA analysis

The TG-DTA curves of pure cellulose and diatomite were shown in Fig. 1(a) and Fig. 1(b), the TG-DTA-DTG curves of 50 wt% cellulose mixed diatomite composite were shown in Fig. 1(c). In Fig. 1(a), there was a continuous band of 12.6 wt% mass loss appeared in TG curve of cellulose up to 200 °C, it mainly involved the removal of physically adsorbed water molecules. Notably, there were two mass losses located at 293 °C and 613 °C, whose mass losses were 32.98 wt% and 12.31 wt%. The two exothermic peaks in DTA curve indicated that the two mass losses were both belong to exothermic reaction, the carbonization of cellulose was clearly a process of releasing energy. In Fig. 1(b), the TG curve of diatomite showed