Preparation and characterization of high-surface-area activated carbon fibers from silkworm cocoon waste for congo red adsorption

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ABSTRACT

Herein, we report the preparation of activated carbon fibers from silkworm cocoon waste via the combination of $(NH_4)_2HPO_4$-pretreatment and KOH activation. The morphology, phase structure and surface chemistry constitute of the obtained ACFs were characterized by X-ray diffraction, IR spectroscopy, Micro Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, thermal analysis and N_2 adsorption—desorption isotherm. The effects of various factors such as the concentration of $(NH_4)_2HPO_4$ and the activation time of KOH were also evaluated. These results demonstrated that the synthesized ACFs retained the fibrous morphology of silkworm cocoon waste, and exhibited highly defective graphite layer structure. A large amount of surface oxygen-containing functional groups were found on the ACFs surface. The obtained samples exhibited high BET surface areas ranging from 1153 to 2797 $m^2\ g^{-1}$, total pore volumes of 0.64—1.74 $cm^3\ g^{-1}$ with micropore volume fractions between 75.2 and 93.6%. In addition, we also evaluated the congo red (CR) adsorption performance of the obtained ACFs. The CR adsorption fitted well to the pseudo-second-order kinetic model. Adsorption isotherm data indicated that the adsorption of CR onto ACFs was monolayer adsorption which followed well the Langmuir isotherm model. The maximum adsorption capacity of CR was 512 $g\ kg^{-1}$. The mechanism of the adsorption process was also described from the intraparticle diffusion model.

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1. Introduction

The energy exploitation of biomass is getting increased attention all over the world since it is environment-friendly, it is clean (zero net CO_2 emission), and it minimizes the disposal problems of by-products in agricultural industry [1]. Furthermore, biomass exploitation, as an attractive economic and technological solution, can generate added value products. Activated carbon fibers (ACFs) are amorphous carbonaceous fibers with high internal surface areas and functionalized surfaces, which are used extensively as sorbent-materials in industrial purification and chemical recovery operations [2]. ACFs are mainly synthesized from viscose cellulose fiber [3], pitch fiber [3] and polyacrylonitrile resin fiber [3]. Various biomass resources also have been used to prepare ACFs, such

as flax fiber [4], oil palm fiber [5] and cotton fiber [6]. Biomass can be precursors of ACFs either through carbonization followed by activation or through a direct activation, during which porosity develop and some surface chemical functions generate on the carbon matrix [7].

Activated carbon can be produced through physical or chemical activation. The physical activation is a two-step process, where pyrolysis in an inert atmosphere normally at 400–600 °C is performed before partial gasification to develop the porosity at higher temperature [3,7]. In contrast, the chemical activation is a one-step process involving impregnation with a chemical such as $ZnCl_2$, KOH or H_3PO_4, where the porosity of activated carbons is created by dehydration reactions of activating reagent [3,7]. As a chemical reagent for activation, potassium hydroxide is very powerful in developing microporous activated carbons with extremely high surface area [8]. KOH activation involves the reduction of hydroxide and intercalation of K atoms into the carbon structures. Further heating drives out the metal from the structure of carbon to develop structure with high porosity and surface area [9]. The surface area, pore size and distribution as well as elemental composition of the activated carbon depend on the KOH concentration, activation temperature and carbon sources used [10]. Recently, it was reported that activated carbons with high surface area had been prepared by KOH activation of pre-carbonized biomass [11]. It was found that the pretreatments, whether they were mechanical or chemical, all led to a significant removal of ashes from the initial biomass and increased the BET surface area [12].

$(NH_4)_2HPO_4$ is widely used as a fire retardant due to its ability to lower the pyrolysis and combustion temperature of biomass [13]. In addition, $(NH_4)_2HPO_4$ can expand the biomass structure and forming the pores at higher temperature (800–900 °C) [14]. Therefore, $(NH_4)_2HPO_4$ is regarded as an effective agent to produce ACFs with high yield and porosity.

Silkworm cocoons are natural polymeric composite shells made of continuous silk strands with the length in the range of 1000–1500 m and conglutinated by sericin [15]. Compared with other ACFs precursor such as synthetic polymer fibers, silkworm cocoons are renewable and eco-friendly. Normally, the silkworm cocoons are expensive. However, the silkworm cocoons which are fragmentary or dirty often are discarded as industrial wastes. Therefore, silkworm cocoon waste can be another potential alternative to produce ACFs. Moreover, raw silkworm cocoons consist of two proteins, sericin and fibroin [16], which would be a suitable replacement of viscose cellulose fibers for the ACFs precursor. To the best of our knowledge, no study has been conducted on the preparation of activated carbon fibers from silkworm cocoon waste. In this work, we focused on the utilization of silkworm cocoon waste as raw material for the preparation of ACFs applying a simple two-step process involving $(NH_4)_2HPO_4$-pretreatment and KOH activation. We illustrated the relationship between the different preparation conditions and the properties of the silkworm cocoon-derived ACFs. In addition, we investigated the detailed characterization of synthesized ACFs and evaluated the CR adsorption performance of such carbonaceous materials. It has been demonstrated that the combination of $(NH_4)_2HPO_4$-pretreatment and KOH activation could effectively increase the carbon yield of ACFs without sacrificing the

surface area and porosity. Compared with the conventional preparation method of ACFs from synthetic polymer fibers, the preparation of ACFs from silkworm cocoon waste was found to be a more facile and effective way to obtain ACFs with high surface area and adsorption capacity.

2. Material and methods

2.1. Sample preparation

Silkworm cocoon waste (Jinan silk product factory) was used as raw material for the preparation of ACFs. Before use, silkworm cocoon wastes were washed by hot water (100 °C) and then dried at 100 °C for 24 h. A typical synthetic procedure of ACFs was as follows: 8 g of silkworm cocoon waste was soaked in 50 mL $(NH_4)_2HPO_4$ solution (10%, mass fraction). The liquid/solid mixture was stirred continuously at ambient temperature for 1 h to allow penetration of the $(NH_4)_2HPO_4$ into the silkworm cocoon waste. The immersed sample was dried at 100 °C for 24 h and then carbonized at 600 °C for 2 h under a constant N_2 flow of 60 cm^3 min^{-1}. The obtained materials were washed with de-ionized water until the water was neutral. 5 g of the resulting chars were immersed in 50 cm^3 KOH solution with different concentrations (33.7–78.5 mg/cm^3) and stirred continuously for 8 h. The dry mixture was heated at 800 °C under N_2 flow of 60 cm^3 min^{-1}, and maintained for 1, 2, 3 and 4 h, respectively. For comparison, 5 g of silkworm cocoon waste without $(NH_4)_2HPO_4$ pretreatment was carbonized at 600 °C under N_2 for 2 h, and then soaked in 50 cm^3 KOH solution (56.1 mg/cm^3). After drying, the materials were heated at 800 °C under N_2 for 3 h.

2.2. Sample characterization

The morphologies of the samples were characterized by using field emission scanning electron microscopy (FEI QUANTA FEG250, USA). The phase structure was investigated by X-ray diffraction with Cu Kα radiation source (Model D8-Advance, Germany) operated at 40 kV and 100 mA. The pore structure of the obtained sample was analyzed by nitrogen adsorption–desorption at 77 K on a surface area analyzer (ASAP2020M + C, Micrometrics, GA, USA). The surface area of sample was evaluated by the Langmuir model and Brunauer Emmett Teller (BET) model, while the pore size distribution was estimated by Barrett Joyner Halenda (BJH) theory. The FT-IR spectra were obtained by Nicolet 380 FT-IR (Nicolet, USA). The chemical states of samples were studied by X-ray photoelectron spectroscopy (PHI1800, Physical Electronics, MN, USA). The Micro Raman spectrometer (RM-1000, Renishaw, GL, UK) was used to investigate the conformation state of graphite in the ACFs. Thermogravimetric experiments were carried out with a thermal analyzer (TGA6, Perkin Elmer, USA) to investigate the pyrolysis process and activation mechanism.

2.3. Adsorption experiments

The adsorption performance of the as-prepared ACFs was tested for the adsorption of Cogon Red (CR, CAS 573-58-0,