



The role and mechanism of K_2CO_3 and Fe_3O_4 in the preparation of magnetic peanut shell based activated carbon



Shengli Zhang^{a,*}, Lichun Tao^a, Yulei Zhang^a, Zhikai Wang^a, Guangjun Gou^b, Man Jiang^b, Chinpao Huang^c, Zuowan Zhou^{b,*}

^a Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, 610031 Chengdu, Sichuan, China

^b Key Laboratory of Advanced Materials Technology of the Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, 610031 Chengdu, Sichuan, China

^c Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA

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ABSTRACT

The impact of K_2CO_3 and Fe_3O_4 on the porosity development and the magnet evolution within magnetic peanut shell based activated carbon (MPSAC) was systematically studied. At the impregnation stage, K_2CO_3 was found to undergo one anionic hydrolysis. The formed KOH disrupted the key ester linkages between lignin and carbohydrates and removed a part of guaiacyl lignin. At the pre-carbonization stage, the introduction of K_2CO_3 greatly modified the carbonization behavior of peanut shell, shifting the weight loss peak from 350 °C to 255 °C. Meanwhile, a primary pore structure was developed, and some nanoscopic K_2CO_3 was detected. At the activation stage, a series of K-related species such as $K_2CO_3 \cdot 1.5H_2O$, K_2CO_3 , K_2O and K was formed, which was connected with the development of abundant micropores within MPSAC. Magnetic additive Fe_3O_4 functioned as an activation promoting agent while providing the Fe source. Above 500 °C, the porosity structure increased the contact area between Fe_3O_4 and the reduction gases including CO and H_2 . Fe_3O_4 was reduced and successively converted into FeO and Fe with the increase of activation temperature. After that the Fe source was further converted into Fe_3C .

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1. Introduction

Magnetically modified activated carbon offers the advantage of easy separation and recovery after catalytic runs or environmental remediation by a simple magnetic process. At present, magnetic activated carbon (MAC) is mainly prepared by a two-step method which combines activated carbon with magnetic material by mixing, adsorption, chemical co-precipitation and reactivation [1–3]. A two-step method has several disadvantages of a complicated and costly process and the loss of adsorption capacity. In contrast, MAC made by a one-step method can maintain high specific surface area and stable magnetic properties because the magnetic additive is added to the raw material and involved in the whole process of preparing activated carbon. But few reports on the one-step method focused on the preparation of magnetic coal based activated carbon by a physical activation method [4].

According to the general principle of activated carbon, the intrinsic properties of activated carbon mostly depend on the raw material and the production method [5]. The carbon precursors produced by biomass are completely different from those made of coal. The former is mainly non-graphitizable carbon, which is difficult to yield graphitic carbon at high temperature, and the latter is graphitizable carbon. Moreover, an

interest has been growing in the use of low-cost and abundantly available lignocellulosic materials as raw materials for the preparation of activated carbon in recent years [6–8]. As far as preparation methods are concerned, a chemical activation method has extensively been used because it could keep the carbonization and the activation step proceeding simultaneously compared with a physical activation method. When activated carbon is prepared by a chemical activation method, it is crucial to choose the appropriate activating agents. As one of the prevalent chemical activating agents including $ZnCl_2$, H_3PO_4 , NaOH, KOH and K_2CO_3 , K_2CO_3 is not only weakly corrosive and environment-friendly, but also is well compatible with the biomass [9–11]. Moreover, a large amount of K_2CO_3 was formed when KOH was used as an activating agent in previous investigations [12,13]. Hence, K_2CO_3 is expected to play an important role in the porosity development. Nevertheless, the mechanism of the activation process is not yet completely elucidated.

Peanut shell, an agricultural solid waste abundantly available in China, can reach 4.4 million tons, most of which is discarded or burned off in stacks, causing the resource dissipation and environmental pollution [14]. In a recent study, we have reported the single-method synthesis of magnetic activated carbon from peanut shell in the existence of K_2CO_3 and Fe_3O_4 [15]. The present work was to assess the roles of K_2CO_3 and Fe_3O_4 in the preparation of magnetic peanut shell based activated carbon (MPSAC). Especially, the K- and Fe-related species formed at three different stages including the impregnation, pre-carbonization and activation ones were to be investigated deeply. The

* Corresponding authors.

E-mail addresses: zhang222@home.swjtu.edu.cn (S. Zhang), zwzhou@home.swjtu.edu.cn (Z. Zhou).

mechanisms of the porosity development and the magnet Fe_3C evolution were to be elucidated by a series of reactions.

2. Experimental

2.1. Materials

Peanut shell precursor collected from a local agricultural market in Chengdu, Sichuan province of China, were first washed with deionized water for several times, and then dried in an oven at $110\text{ }^\circ\text{C}$ for 24 h. The dried samples were ground with a grinder and sieved into an average particle size of less than 1.0 mm and then stored in airtight containers for further experimentation.

All reagents used were of analytical grade. Methylene blue and iodine supplied by Tianjin Binhai Kedi Chemical Reagent Co., Ltd., China, were used as adsorbates. Anhydrous potassium carbonate (K_2CO_3) used as the chemical activating agent was received from Chengdu Kelong Chemical Reagent Company. Ferrosulfuric oxide (Fe_3O_4 , supplied by Shanghai Shanhai Gongxue No. 3 Experiment Factory) was used as the magnetic additive.

2.2. Precursor characterization

The moisture and ash content of the peanut shell material were measured in accordance with the Standard Test Methods GB/T 2677.2-93 and GB/T 2677.3-93 in China, respectively. The cellulose, hemicellulose and lignin in peanut shell were determined according to TAPPI methods T 203 om-93, T 223 cm-01 and T 222 om-02, respectively. The analysis results are as follows: moisture 9.76%, cellulose 43.91%, hemicellulose 9.18%, lignin 27.86% and ash 2.56%.

2.3. Optimization of preparation conditions

The effects of the activated temperature and time have been provided in our previous article [15]. The effects of the pre-carbonized temperature and time, the impregnation ratio of K_2CO_3 and Fe_3O_4 to peanut shell are described in Supplementary material.

2.4. Samples preparation

Ten grams of peanut shell was mixed by stirring with a suspension solution of K_2CO_3 (5 g) and Fe_3O_4 (0.5 g) at room temperature, and dried at $110\text{ }^\circ\text{C}$ for 24 h. The resultant impregnated sample was pre-carbonized at $300\text{ }^\circ\text{C}$ for 1 h, and then activated at $750\text{ }^\circ\text{C}$ for 1.5 h. After cooling, the activated sample was washed with deionized water until the pH of the filtrate was about 7–8, then dried at $110\text{ }^\circ\text{C}$ for 12 h to obtain magnetic peanut shell based activated carbon (MPSAC).

At the same time, blank and reference samples were prepared according to the above procedure. Blank sample (BS) was only peanut shell. Reference sample 1 (RS1) was peanut shell treated with K_2CO_3 and reference sample 2 (RS2) was peanut shell treated with Fe_3O_4 .

In order to explore the formation mechanism of porosity structure and magnet Fe_3C in MPSAC, a series of unwashed samples were preserved for further analysis.

2.5. Samples characterization

The weight loss of peanut shell and the impregnated sample with K_2CO_3 and Fe_3O_4 added during thermal treatment were analyzed using a thermogravimetric analyzer (TQAQ50, TA Instruments, USA). The samples were heated from room temperature to $800\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere. The X-ray diffraction (XRD) patterns of the impregnated sample, the pre-carbonized samples, the activated samples and the related unwashed samples were collected by Diffractometer X'Pert Pro (Panalytical, Holland) using Cu K α radiation ($\lambda = 0.15418\text{ nm}$) operated at 40 kV and 25 mA. Scans were performed in the 2θ range from 5 to 85° .

The physical morphologies of peanut shell, the pre-carbonized samples and the activated samples were observed using scanning electron microscopy (SEM). A Quanta 200 SEM (FEI Com, Holland) with a 20 kV excitation voltage was used. The samples were coated with a gold film to improve their conductivity and the quality of the SEM images. The FT-IR spectra of peanut shell, the impregnated sample and the pre-carbonized sample was obtained on an FT-IR spectrophotometer Nicolet 5700 (Thermo, USA) using a KBr disk containing 1% finely ground samples. Sixty-four scans were taken for each sample from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . The high-resolution transmission electron microscope (HRTEM) observation of the unwashed pre-carbonized sample and the TEM of the activated sample MPSAC-750 were carried out on a JEM-2100F transmission electron microscope (JEOL Com., Japan). The specific surface areas and pore structural parameters of the activated samples were carried out using a TristarII3020 surface area and pore size analyzer (Micromeritics Instruments, USA). N_2 was used as adsorptive gas at 77 K. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation. The total pore volume was estimated based on the N_2 volume at a relative pressure of 0.99. Micropore volume and micropore specific surface area were obtained using the t -plot method. In addition, the pore size distribution was determined by using the BJH model. The adsorptive properties of the pre-carbonized samples and the activated samples were measured by using iodine and methylene blue as adsorbates. Iodine number and methylene blue number were determined based on the Standard Test Method (GB/T12496.8-1999 and GB/T12496.10-1999, testing standard of activated carbon in China). The residual iodine concentration was determined by titration with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution, and the remaining methylene blue concentration was evaluated with a 722S spectrophotometer. The magnetic properties of the activated samples were measured using vibrating sample magnetometer (JDAW-2000, Changchun Yingpu Magneto-electric Corp., China).

3. Results and discussion

3.1. Decomposition characteristics of peanut shell and the impregnated sample

The TG/DTG curves of peanut shell and the impregnated sample with K_2CO_3 and Fe_3O_4 added were shown in Fig. 1. From Fig. 1, it can be seen that the weight loss of peanut shell in N_2 atmosphere occurred in three stages in the temperature range of $30\text{--}800\text{ }^\circ\text{C}$. The first weight loss peak at $30\text{--}125\text{ }^\circ\text{C}$ was corresponding to the removal of water, giving the weight loss at about 9.0%. As the temperature increased, the decomposition of lignocelluloses occurred in the second stage, while the weight loss of 51.12% was observed at $125\text{--}400\text{ }^\circ\text{C}$. Yang et al. [16] and Gašparovič et al. [17] reported that the decomposition of hemicelluloses and cellulose started over the range from $200\text{--}380\text{ }^\circ\text{C}$ and $250\text{--}400\text{ }^\circ\text{C}$,

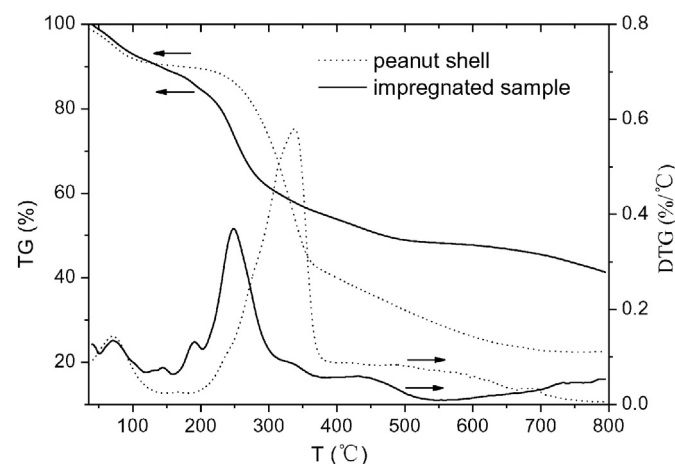


Fig. 1. TG-DTA curves of peanut shell and the impregnated sample with K_2CO_3 and Fe_3O_4 .

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