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Full Length Research Paper

Preparation of activated carbon from a renewable agricultural residue of pruning mulberry shoot

Jun Wang[1]*, Fu-An Wu[1,2]*, Meng Wang[1], Ning Qiu[1], Yao Liang[1], Shui-Qin Fang[1] and Xing Jiang[1]

[1]College of Biological and Environmental Engineering, Jiangsu University of Science and Technology, Zhenjiang 212018, P. R. China.
[2]Sericultural Research Institute, Chinese Academy of Agricultural Sciences, Zhenjiang 212018, P. R. China.

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In this study, element composition of pruning mulberry shoot was evaluated by element analysis. On the basis of this, pruning mulberry shoot–based activated carbon was prepared from by chemical activation with phosphoric acid (H_3PO_4), which particles were displayed by the scanning electron microscope (SEM) micrographs. The influence of impregnation temperature, impregnation ratio, H_3PO_4 concentration, pyrolysis temperature, and pyrolysis time on the iodine adsorption capacity and yield of the prepared activated carbon were investigated and discussed. Results showed that, pruning mulberry shoot is a good and cheap agricultural residue for the production of activated carbon, with carbon, hydrogen and nitrogen contents of 44.58, 6.37 and 1.45% (w/w, dry basis), respectively. With an impregnation temperature of 80℃, an impregnation ratio of 2:1 (v/w), a H_3PO_4 concentration of 50%, an pyrolysis temperature of 500℃, and an pyrolysis time of 2 h, the activated carbon with better iodine adsorption capacity and yield were 887.35 mg/g and 38.12%, respectively. SEM experimental results indicated the potential use of pruning mulberry shoots as a precursor in the activated carbon preparation process, thus, representing an economically promising material.

Key words: Pruning mulberry shoot, activated carbon, preparation, chemical activation.

INTRODUCTION

The commercial production of mulberry leaves in Asian countries is an important agricultural activity, especially, in some regions that are considered marginal areas for conventional crops. Mulberry, *Morus alba* L., belongs to the family of Moraceae, and has been cultivated in China, India, Korea, Japan and Thailand where the leaves are used as food for silkworms (Wang et al., 2008). Unfortunately, the agricultural and industrial activities derived from such crops generate waste that constitutes a serious environmental problem. For example, pruning mulbery shoot is a typical agricultural residue generated in the mulberry industrial process (Fukui, 2008) (Figure 1). Nowadays, the average annual dry matter biomass of pruned mulberry shoot is 1.7 kg/plant, or approximately 17.0 - 22.5 t/ha, and the mulberry field area was about 11.14 million mus in China (Lu et al., 2009). Hence, 5.57 million tons dry pruning mulberry shoots are available China per year and China has become the largest in producing country in the world.

Pruning mulberry shoots exceed household needs for fuel-wood because household energy requirements are met with multiple sources (Akbulut and Durmus, 2009), which is high compared to the annual biomass growth of many fast growing trees and perennial herbaceous energy crops (Akbulut and Ozcan, 2009). However, most of the pruning mulberry shoots are used only as fertilizer and a small proportion is used as a constituent of fish feed or even regarded as industrial waste (Kandylis et al., 2009). Therefore, lots of pruning mulberry shoots had not been fully utilized. Indeed, disposal of pruning mulberry shoot is a serious problem, because parasitic insect and pathogenic microorganism in the waste are fatal damage to mulberry field due to their simple accumulation. Thus, governments must enforce the legislation of controlled this waste disposal to avoid harmful effects to mulberry field and corresponding environment.

Considerable quantities of agricultural residues result from the annual harvesting and processing of various

*Corresponding author. E-mail: fuword@163.com.

Figure 1. Pruning mulberry shoot is a typical agricultural residue generated in the mulberry industrial process. **A:** Mulberry shoot is a key part of mulberry tree; **B:** Cutting mulberry shoot is a normal work in mulberry field industry annually; **C:** Parasitic insect and pathogenic microorganism in pruning mulberry shoot are fatal damage to mulberry field due to their simple accumulation.

agricultural crops grown in the world. More recently, these agricultural residues have been shown to have potential as precursor materials in the preparation of activated carbons, usually with comparable adsorptive capacity with that of commercial activated carbons (Suzuki et al., 2007). Activated carbon is a well known as porous material with large specific surface area, is useful in adsorption of both gases and solutes from aqueous solution (Ioannidou and Zabaniotou, 2007), which has been widely used in chemical engineering, food and pharmaceutical industries. China produces more than 5.57 million tons of pruning mulberry shoots annually. However, the amount of pruning mulberry shoots available is far in excess of local uses. There is no report on the preparation of mulberry shoot-based activated carbon. Therefore, the aim of this study was to evaluate the feasibility of pruning mulberry shoot as a precursor for activated carbon production.

The general process to prepare activated carbon is based on carbonizing and activating the natural carbonaceous biomass (Tay et al., 2009). Activation step of activated carbon process may be achieved either physically or chemically. Recently, chemical activation has been shown as an efficient method to obtain activated carbons with high surface area and narrow micropore distribution (Adinata et al., 2007). In the chemical activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents and oxidants, such as H_3PO_4 (Corcho-Corral et al., 2006; Sun et al., 2007; Alhamed, 2008), K_2HPO_4 (Aber et al., 2009), Na_2HPO_4, H_2SO_4 (Gercel et al., 2007), K_2CO_3 (Adinata et al., 2007), $ZnCl_2$ (Wang et al., 2009; Alhamed and Bamufleh, 2009), $AlCl_3$ (Ioannidou and Zabaniotou, 2007), KOH (Ramos-Fernandez et al., 2008; El-Hendawy, 2009; Cardoso et al., 2008) and NaOH (Kobayashi et al., 2006), and heating it at various temperatures. As an activation agent, H_3PO_4 is widely used in the preparation of activated carbons from lignocellulosic products and offers some advantages such as non-polluting character and ease of elimination by extraction with water (Sun et al., 2007).

Moreover, H_3PO_4 inflicted physical and chemical modifications on the botanical structure by penetration, particle swelling, and partial dissolution of biomass, bond cleavage and reformation of new polymeric structures resistant to thermal decomposition (Alhamed, 2008; Nakagawa et al., 2007). Therefore, this study has focused on the preparation of activated carbon from pruning mulberry shoot collected from a mulberry field in China. Although many studies in the literature have been reported concerning the production of activated carbon from biomass by H_3PO_4 activation (Corcho-Corral et al., 2006; Sun et al., 2007; Alhamed, 2008; Nakagawa et al., 2007), there is no study regarding preparation process of mulberry shoot-based activated carbon in the presence of H_3PO_4.

In this study, pruning mulberry shoot, generated from the mulberry industry in China, was utilized as a raw material for the production of activated carbon powder. The influence of impregnation temperature, impregnation ratio, H_3PO_4 concentration, pyrolysis temperature, and pyrolysis time of the prepared activated carbon on the pore development and yield of resultant activated carbon were investigated and discussed.

MATERIALS AND METHODS

Materials

Pruning mulberry shoots were collected during the summer season in West campus, Jiangsu University of Science and Technology, Jiangsu Province, China. The material was repeated cleaned with tap water until the color of the leachate was clear, then oven dried for 6 h at 105°C. The starting materials were crushed and powered by a herb disintegrator (Qinzhou Sanyang Package Equipment Co., Ltd) and then sieved through the mesh number 60.

All chemicals used in the investigation were of analytical grade. Double distilled water was used for preparation of all required solutions.

Preparation methods of activated carbon

A typical chemical method is carried out in the preparation process of pruning mulberry shoot-based activated carbon, which is mainly consisted of activation and pyrolysis steps (Ioannidou and Zabaniotou, 2007). In activation step, dried pruning mulberry shoots with the mass of 6 g was soaked in a 50 mL 50% H_3PO_4 solution for 14 h at impregnation temperature (20, 60, 80, 90 or 100°C), the investigated impregnation ratio (1:1, 1.5:1, 2:1, 2.5:1 or 3:1) and concentration of H_3PO_4 solutions (40, 50, 60, 70 or 80%) were proposed by single-factor method, respectively. The impregnation ratio is given by:

$$\text{impregnation ratio} = \frac{\text{weight of } H_3PO_4 \text{ solution}}{\text{weight of pruning mulberry shoot}}$$

The soaked pruning mulberry shoot was first filtered, washed using double distilled water to remove residues acid, dried in an oven at 105℃, and then it was placed in a stainless steel horizontal tubular furnace and the inert stream of nitrogen gas made to flow through the furnace for 30 min with the flow rate of 100 cm^3 min^{-1}. After that, the furnace was heated at pyrolysis temperature (300, 400, 500 or 600℃) and kept at this temperature for 0.5, 1, 2 or 3 h, both were proposed using single-factor method. Finally, the produced activated carbon was cooled in the inert atmosphere and washed with 1.5 M HCl solution and then with double distilled water until the pH of washing effluent reached 7.

Analysis

An elemental analysis was carried out using a CHN elemental analyzer (Elementar Vario EL III, Germany). The yield of the prepared activated carbon was estimated from the following equation:

$$\text{yield of activated carbon (wt \%)} = \frac{\text{weight of activated carbon}}{\text{weight of pruning mulberry shoot}} \times 100$$

The surface areas of the activated carbons were characterized by the adsorption capacity towards iodine determined using a standard method (GB/T12496.1-12496.22, China), whereby values must have a degree of adjustment (R^2) of over 0.995.

Scanning electron micrographs (SEM) of the prepared activated carbon was recorded by the scanning electron microscope (HITACHI S-3400, Japan).

RESULTS AND DISCUSSION

Elemental composition of pruning mulberry shoot

The composition of biomass affects the development of pore structure of solids during activation and pyrolysis processes, so the elemental composition of pruning mulberry shoot analyzed by a CHN elemental analyzer is shown in Table 1. It is observed from the table, carbon, hydrogen and nitrogen contents of pruning mulberry shoot are 44.58, 6.37 and 1.45% (w/w, dry basis), respectively. Agricultural residues are produced in huge amounts in the world, the contents of these elements in the literature are in the range of 41.23 - 53.00% for carbon, 4.63 - 6.90% for hydrogen, and 0.32 - 2.63% for nitrogen, respectively (Ioannidou and Zabaniotou, 2007). Table 1 clearly demonstrates that the contents of carbon, hydrogen and nitrogen contents of pruning mulberry shoot are very close to the results reported in the literature. Therefore, pruning mulberry shoot is a good and cheap raw material for the production of activated carbon.

Table 1. Element composition of pruning mulberry shoot.

Property	1st value (wt %)	2nd value (wt %)	Average value (wt %)
N	1.48	1.41	1.45
C	44.52	44.65	44.58
H	6.34	6.40	6.37

Preparation process of pruning mulberry shoot–based activated carbon preparation

Traditional method of chemical activation with H_3PO_4 consists in impregnation of the raw material with water solution of the acid followed by pyrolysis in inert atmosphere at temperatures between 350 - 600℃. Hence, a two-step method has been adopted for the preparation of activated carbon, where the first step involves the impregnation treatment of pruning mulberry shoot with H_3PO_4 solution for 14 h, followed by drying at 105℃ for 24 h; the second step involves the pyrolysis at high temperature. In this study, the influence of impregnation temperature, impregnation ratio, H_3PO_4 concentration, activation temperature, and activation time on the iodine adsorption capacity and yield of the prepared activated carbon were investigated and discussed by using single-factor method.

Effect of impregnation temperature

The percentage yield and mg/g iodine adsorption capacity of activated carbon were used as two parameters to choose the optimum preparation conditions of pruning mulberry shoot-based activated carbon. The effect of impregnation temperature on iodine adsorption capacity and yield of the activated carbon prepared was studied when starting material was soaked in a 50% H_3PO_4 solution for 14 h with an impregnation ratio of 1:1 (Figure 2).

It is observed from Figure 2, impregnation temperature appears to be a key factor affecting the yield and iodine adsorption capacity of the prepared activated carbon. It is evident that increasing the impregnation temperature serves to increasing the yield and iodine adsorption capacity of the prepared activated carbon with a signification enhancement in the preparation process occurring as the impregnation temperature increased from 20 to 80℃, however, decreasing the yield and iodine adsorption capacity of the prepared activated carbon as the impregnation temperature increased from 80 to 100℃.

This result indicated that the maximum yield (39.77%) and iodine adsorption capacity (884.37 mg/g) of the prepared activated carbon was obtained when impregnation temperature was 80℃.

Effect of impregnation ratio

The impregnation ratio is another critical parameter that affects the quality of the carbon. An optimum impregnation ratio of 1:1 - 4:1 depending on the precursor has been reported to yield highest surface area carbon (Srinivasakannan and Abu Bakar, 2004). Hence, the effect of impregnation ratio (1:1, 1.5:1, 2:1, 2.5:1 or 3:1)

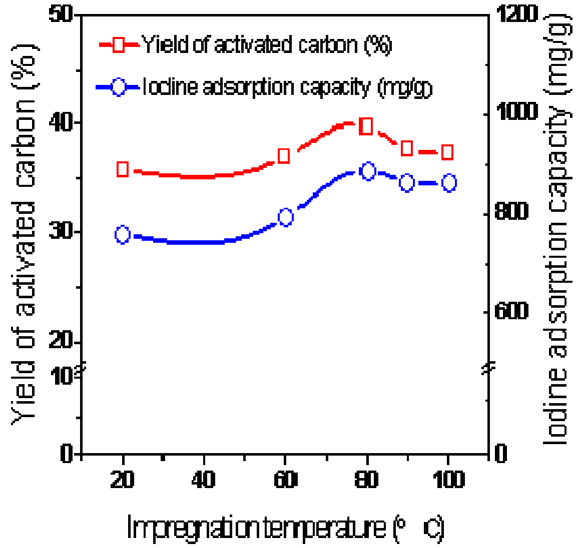

Figure 2. Effect of impregnation temperature on iodine adsorption capacity and yield of activated carbon

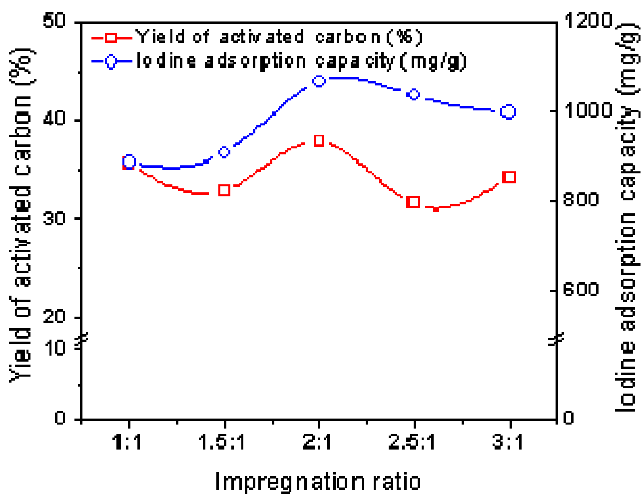

Figure 3. Effect of impregnation ratio on iodine adsorption capacity and yield of activated carbon.

on iodine adsorption capacity and yield of the activated carbon prepared was studied by using single-factor method (Figure 3).

As can be seen from Figure 3, when the impregnation ratio increased from 1:1 to 2:1, the yield and iodine adsorption capacity of the prepared activated carbon increased from 35.59 to 37.80% and 886.14 mg/g to 1067.77 mg/g, respectively. However, when the impregnation ratio increased from 2:1 to 3:1, the yield and iodine adsorption capacity of the prepared activated carbon increased from 37.80 to 34.11% and 1067.77 mg/g to 997.45 mg/g, respectively. The maximum yield and iodine adsorption capacity of the prepared activated carbon was obtained when impregnation ratio was 2:1.

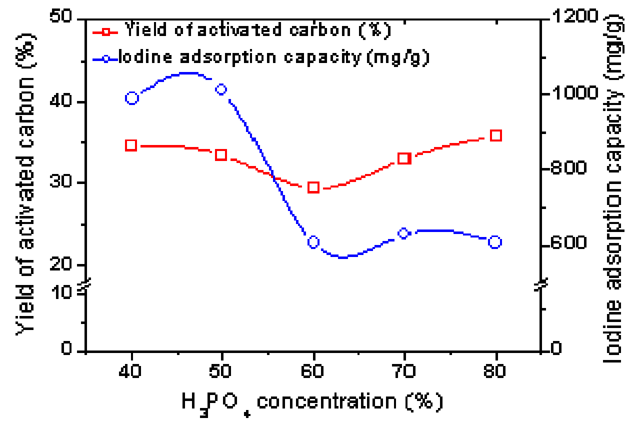

Figure 4. Effect of H_3PO_4 concentration on iodine adsorption capacity and yield of activated carbon.

Effect of H_3PO_4 concentration

The adsorption capacities towards iodine and yield of activated carbons prepared from pruning mulberry shoot impregnated H_3PO_4 with five different concentrations (40, 50, 60, 70 and 80%), impregnation ratio 2:1 are shown in Figure 4.

The concentration of H_3PO_4 has influenced significantly the adsorption ability of the samples, as can be seen from Figure 4, H_3PO_4 concentration seemly appears only to be a key factor effecting iodine adsorption capacity of the prepared activated carbon in its range of 40 - 80%. The maximum iodine adsorption capacity of the activated carbon prepared was 1012.20 mg/g with a H_3PO_4 concentration of 50%. However, the change of yield of the activated carbon prepared in H_3PO_4 concentration range of 40 - 80% was very small. This result indicated that H_3PO_4 causes chemical changes in the precursor facilitating formation of activated carbon at lower temperatures. H_3PO_4 promotes the pyrolytic decomposition of the starting material and the formation of cross-linked structure: (1) The decomposition is promoted by the catalytic effect of H_3PO_4 on the bond cleavage reactions; (2) The cross-linked phenomenon is due to interactions between H_3PO_4 and biomass in the precursor leading to formation of phosphate linkages between the fragments in the biomass (Budinova et al., 2006; Jagtoyen and Derbyshire, 1998).

Therefore, on the basis of above theory, the optimum H_3PO_4 concentration in activation step was 50%.

Effect of pyrolysis temperature

The temperature of pyrolysis is yet another vital parameter which affects the physical characteristics of the activated carbon. The effect of pyrolysis temperature on iodine adsorption capacity and yield of the activated carbon prepared was studied by using single-factor method (Figure 5).

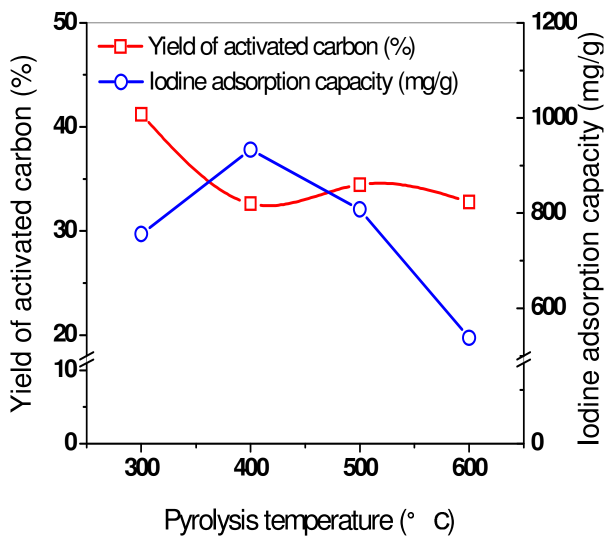

Figure 5. Effect of pyrolysis temperature on iodine adsorption capacity and yield of activated carbon.

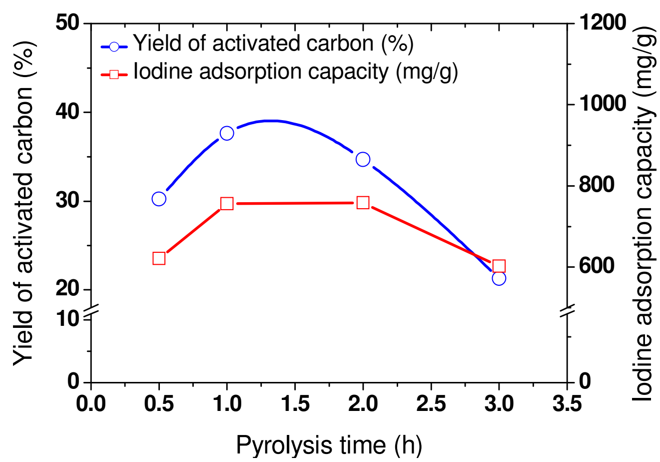

Figure 6. Effect of activation time on iodine adsorption capacity and yield of activated carbon.

It is observed from Figure 5, the yield of the activated carbon prepared decreased from 41.23 to 32.79% with the increase in pyrolysis temperature in the range of 300 - 600℃. However, the iodine adsorption capacity of the prepared activated carbon increased from 756.42 to 933.84 mg/g with an increase in the range of 300 - 400℃, after then, decreased from 933.84 to 538.36 mg/g with an increase in the range of 400 - 600℃. Based on comprehensive consideration of yield and iodine adsorption capacity of the activated carbon prepared, 500℃ was chosen for optimum pyrolysis temperature.

Effect of pyrolysis time

The pyrolysis time is another important parameter that affects the quality of the activated carbon. The effect of pyrolysis time on iodine adsorption capacity and yield of the activated carbon prepared was studied by using single-factor method (Figure 6).

As can be seen from Figure 6, a similar trend has been observed for iodine adsorption capacity and yield of the prepared activated carbon, so activation time appears to be a key factor affecting both two parameters in its range of 0.5 - 3.0 h. The maximum iodine adsorption capacity and yield of the activated carbon prepared was 756.04 mg/g and 37.63% for 1 h at 500℃. Therefore, the optimum pyrolysis time in pyrolysis step was 1 h.

Based on comprehensive consideration of yield and iodine adsorption capacity of the activated carbon prepared, process parameters for preparation of activated carbon from pruning mulberry shoot were optimized as follow: impregnation temperature 80℃, impregnation ratio 2:1, H_3PO_4 concentration 50%, pyrolysis temperature 500℃, and pyrolysis time 1 h. On the basis of this optimum condition, the iodine adsorption capacity and yield of the activated carbon prepared was 887.35 mg/g and 38.12%, respectively.

SEM characteristics of pruning mulberry shoot–based activated carbon

Figure 7 display the scanning electron microscope (SEM) micrographs for particles of the pruning mulberry shoot–based activated carbon prepared at two magnifications (100× and 30.0 k×).

As can be seen from Figure 7, the low magnification micrographs (A) illustrate the irregular size and shape of individual grains; at the higher magnification, the micrographs (B) show irregular and heterogeneous surface morphology, and appear varieties of pores in different widths. Therefore, with increase in the magnification, the material presented a more irregular surface which could be due to a more complex network of pores. This supports the notion that increase H_3PO_4 soaking temperature at a higher impregnation ratio can intensify the attack of the acid on the botanical structure, altering the surface morphology of pruning mulberry shoot-based activated carbon.

Conclusion

The optimal preparation process of activated carbon from pruning mulberry shoot was successfully achieved by using single-factor method in this study. With an impregnation temperature of 80℃, an impregnation ratio of 2:1 (v/w), a H_3PO_4 concentration of 50%, an pyrolysis temperature of 500℃, and an pyrolysis time of 2 h, the activated carbon with better iodine adsorption capacity and yield were 887.35 mg/g and 38.12%, respectively. Elemental analysis results and scanning electron microscope micrographs indicated that pruning mulberry shoot is a good and cheap raw material for the production of activated carbon.

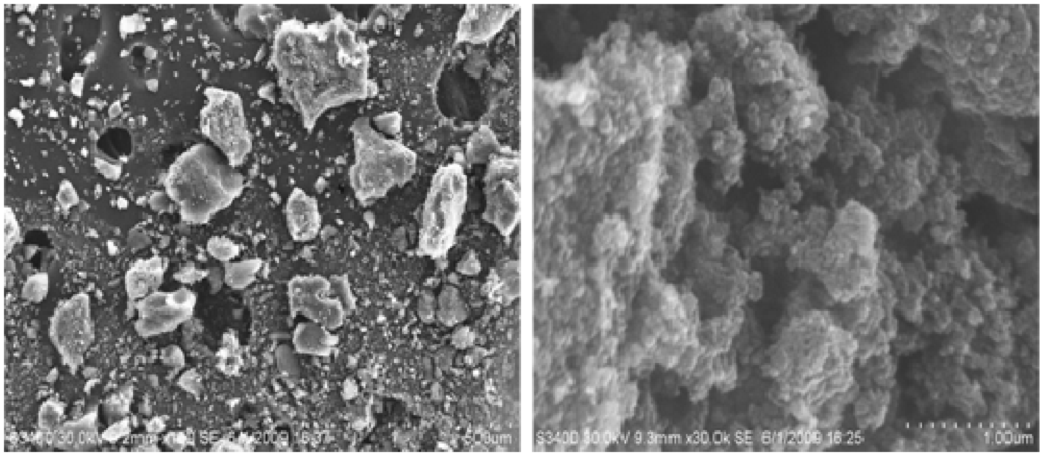

Figure 7. Scanning electronic micrograph for the pruning mulberry shoot-based activated carbon (A: magnification: 100×, B: magnification: 30.0k×).

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