

Preparation and Adsorption Properties of Biomass Activated Carbon from Ginger Stems

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Abstract: Biomass activated carbon (BAC) was produced from ginger stems by carbonization and activation presented high specific surface areas and mesoporous structures. The carbonization temperature of the ginger stems were controlled within 500~900°C. The optimal carbonization condition is as follows: carbonization temperature of 700°C, carbonization time of 6 h. The determined optimum activation condition is: temperature of 800°C, activator of KOH and carbonized product/alkali ratio of 1:4 (w/w). The carbonization yield, BAC yield and Brunauer-Emmett-Teller (BET) surface area were measured and the adsorption performance of BAC to nitrogen was investigated. The results showed that the nitrogen adsorption isotherm curve was as type I isotherm. It was finally determined that the BET surface area was 660 m²/g under the abovementioned optimal conditions of carbonization and activation. The FESEM analysis indicates that the obtained BAC is of micropore structure.

Keywords: ginger stems; biomass activated carbon; carbonization; activation

1 Introduction

The fast economic growth and intense population increase have resulted in global environmental deterioration and depletion of energy resources. Biomass activated carbon (BAC) has many advantages such as abundant sources, low price, large specific surface area, advanced pore structure, good thermal and chemical stability, and is widely used in many fields such as agriculture, chemical engineering, and



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energy storage^[1]. The source of raw materials for BAC is very extensive^[2]. According to previous reports, many agricultural and forestry byproducts such as dated kernels, walnut shells, waste tea leaves, corn cobs, coconut shells, beetroots, peanut shells, rice hulls, cotton hulls, banana skins, bamboo waste, olive pits, cherry pits, orange peels, coffee beans, corn stover, and tapioca have all been used in an attempt to produce low-cost BAC^[3]. In this scenario, ginger stems are solid waste normally accumulated and left in the field for a long time, reaching decomposition and producing unpleasant odors or are directly burned in the field, causing environmental pollution. And the main component of ginger stems is cellulose, a naturally renewable resource^[4].

The preparation method of BAC is divided into the carbonization and activation steps^[5]. The most common method to prepare BAC is thermal pyrolysis^[5], which is the thermal decomposition of organic materials in the absence of oxygen or with limited oxygen supply. Many pyrolysis activation factors affect product performance^[6]. For instance, pyrolysis temperature is the most important factor affecting the physical and chemical properties of BAC. In addition to more micropores and stronger hydrophobicity, higher pyrolysis temperatures usually imply higher ash content, cation exchange capacity, and specific surface area, thus providing a more effective removal of organic contaminants. The BAC porosity obtained through a simple pyrolysis carbonization is limited. Therefore, after carbonization, physical or chemical activation is performed to provide higher porosity to the BAC^[7]. The obtained product is of a more developed pore structure, larger specific surface area, and stronger adsorption capacity.

2 Experimental

2.1 Materials

Ginger Stems, obtained from Changyi, Shandong Province; KOH, NaOH (AR, $\geq 99.5\%$, Shanghai

Zhangyun Chemical Co., Ltd.); HCL (AR, $\geq 98.0\%$, Yantai Sanhe Chemical Reagent Co., Ltd.); HNO₃ (AR, $\geq 99.0\%$, Yantai Sanhe Chemical Reagent Co., Ltd.); H₂SO₄ (AR, $\geq 99.5\%$, Shanghai Jinlian Fine Chemical Factory); K₂Cr₂O₇ (AR, $\geq 99.5\%$, Yuxi Reagent Factory); KMnO₄ (AR, $\geq 99.8\%$, Tianjin Bodie Chemical Co., Ltd.); Na₂C₂O₄ (AR, $\geq 99.8\%$, Tianjin Chemical Reagent Sixth Factory); CH₃CH₂OH (AR, $\geq 96\%$, Qingdao Jiurun Fine Chemical Co., Ltd.).

2.2 Experimental methods

Ginger stems were cut into pieces and placed in a tube furnace, which was flushed with N₂ for 5 min to remove the air. The carbonization was performed at 500–900°C and lasted for 1 h. KOH and NaOH were used as activators, respectively. After carbonization, the samples were activated at 800°C for 1 h. The pH value of the activated sample was adjusted with hydrochloric acid until the pH value of the solution was neutral. The dried sample was ground in a mortar and labeled according to different carbonization temperatures, carbonization time, activator type and activator amount.

2.3 Characterization methods

2.3.1 Carbonization yield and BAC yield

The carbonization yield and BAC yield are calculated as follows:

$$Y_1 = m_1/m_0 \times 100\% \quad (1)$$

$$Y_2 = m_2/m_0 \times 100\% \quad (2)$$

Where:

Y_1 —Carbonization yield, %;

Y_2 —BAC yield, %;

m_1 —The quality of the ginger stems after carbonization (before activation), g;

m_2 —The quality of the ginger stems after carbonization, activation and drying, g;

m_0 —Ginger stems (raw material) quality, g.

2.3.2 FT-IR analysis

The structure and chemical bonds of the samples were analyzed using FT-IR. The instrument used was the TENSOR27 fourier infrared spectrometer.

2.3.3 Brunauer-Emmett-Teller (BET) surface area analysis

The BET surface area of the sample was measured by using the Micromeritics ASAP 2020 automatic surface area and porosity analyzer. The pore size distribution and nitrogen adsorption and desorption curves of the sample were also analyzed.

2.3.4 Field emission scanning electron microscope (FESEM) analysis

The microstructure of the sample was observed using FESEM (JSM-6700F, Japanese Electronics Co., Ltd., Japan). The sample was coated with gold in vacuum before examination.

3 Results and discussion

3.1 Effects of carbonization temperature on carbonization yield

At first, we studied the effects of carbonization temperature because it is a major factor affecting the carbonization and BAC yield. It can be seen from Fig.1 that higher temperatures lead to lower carbonization yield. The carbonization yield decreased rapidly when the temperature was $>500^{\circ}\text{C}$, remaining steady after the temperature was $>800^{\circ}\text{C}$. The experimental results show that samples which were prepared at low temperatures ($<500^{\circ}\text{C}$) presented a fluffy structure, slightly shallow color, and clear uncarbonized traces. As the temperature exceeded 700°C , the sample color was black and the basic carbonization was complete. Considering the slight difference in carbonization yield between 700°C and 800°C and the fact that lower carbonization temperature implying lower energy consumption, a carbonization temperature of 700°C was determined. Complete carbonization results in a reaction between the disordered carbon atoms and the heteroatoms, which clears the pores of the clogged fiber cells at the beginning of the carbonization process. So at the beginning of the carbonization (500°C), molecular crosslinking or polycondensation mainly occurred. In addition to the volatilization of some non-carbonized elements at this stage, tar evaporation was the main

reason of weight loss. As the carbonization temperature increased, the reaction continued to occur, pores continued to expand, and new pores were generated, resulting in a lower carbonization yield. This process also accelerated the removal of non-carbonized atoms such as N, H, etc.

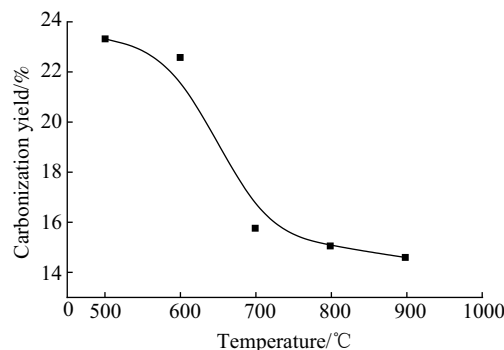


Fig.1 Carbonization yield versus carbonization temperature

3.2 Effects of carbonization time on the carbonization yield

Fig.2 shows the influence of carbonization time on carbonization yield. With increase in carbonization time, the carbonization yield gradually increased. This trend is a result of volatilization of the tar-class material loss, which caused the carbonization yield gradually decreased. After the pyrolysis was completed, a further increase in time did not affect the carbonization yield anymore. Therefore, a carbonization time of 6 h is preferable.

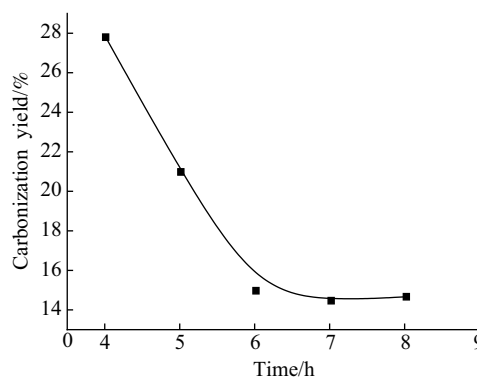


Fig.2 Carbonization yield versus carbonization time

3.3 Effects of carbonized product/alkali ratio (w/w) on BAC yield

As seen in Fig.3, the dosage of alkali significantly

impacts the BAC yield. When the carbonized product/alkali ratio was higher than 1:2, there was nearly no change in the BAC yield. This behavior occurred because as the carbonized product/alkali ratio increased, the alkali and the fiber were in full contact with each other and reacted sufficiently with carbon at high temperature to form small pores. However, as part of the carbon was etched, gases such as carbon dioxide and carbon monoxide were produced, resulting in a lower BAC yield. Therefore, a further increase in the dosage of alkali did not significantly affect the BAC yield.

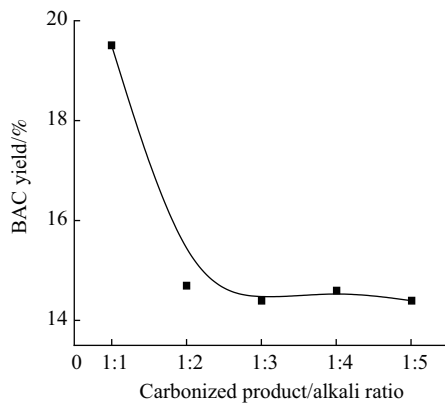


Fig.3 BAC yield verses carbonized product/alkali ratio

3.4 Effects of carbonization temperature on the BET surface area of BAC

We also explored the BET surface area of the BAC under different conditions (carbonization temperature, carbonization time and carbonized product/alkali ratio) in wet condition which means that the ginger stems were pre-impregnated in an alkali solution (KOH or NaOH) for 30 min at room temperature. This method can produce the porous structure of the BAC to increase the BET surface area.

The effects of carbonization temperature, carbonization time and carbonized product/alkali ratio on the BET surface area are listed in Table 1~Table 3.

From Fig.3 and Table 3, it can be seen that when the carbonized product/alkali ratio (w/w) is 1:2 and 1:4, the BAC yield was not of much difference, but under the condition of carbonized product/alkali ratio of 1:4, the BET surface area of the prepared BAC was greatly

Table 1 Effect of carbonization temperature on BET surface area of BAC

Carbonization temperature/°C	BET surface area/(m ² ·g ⁻¹)	Pore volume/(m ³ ·g ⁻¹)	Pore size/nm
500	53.9	0.069	5.13
600	183	0.142	3.09
700	660	0.403	2.44
800	407	0.108	3.04
900	299	0.095	4.35

Table 2 Effects of carbonization time on BET surface area of BAC

Carbonization time/h	BET surface area/(m ² ·g ⁻¹)	Pore volume/(m ³ ·g ⁻¹)	Pore size/nm
4	367	0.249	5.88
5	565	0.398	3.87
6	652	0.402	2.44
7	632	0.402	2.35
8	533	0.356	4.78

Table 3 Effect of carbonized product/alkali on BET surface area of BAC

Carbonized product/alkali ratio (w/w)	BET surface area/(m ² ·g ⁻¹)	Pore volume/(m ³ ·g ⁻¹)	Pore size/nm
1:1	13.1	0.035	10.7
1:2	146	0.184	4.09
1:3	270	0.238	3.98
1:4	660	0.403	2.45
1:5	480	0.368	3.09

improved. Under the condition of carbonized product/alkali ratio of 1:4 (w/w), carbonization temperature of 700°C, carbonization time of 6 h, the maximum BET surface area of BAC was obtained, at 660 m²/g. This result demonstrates that in wet condition, the ginger stems were pre-soaked in alkali, which penetrated the fiber structure. Then, at a certain carbonization temperature, alkali and carbon can fully react to generate a microporous structure.

3.5 FT-IR analysis

The FT-IR spectrum of ginger stems is shown in Fig.4. The absorption peak at 3419 cm⁻¹ was attributed to the hydroxy stretching vibration of alcohols and phenols, and at 2945 cm⁻¹ was the saturated hydrocarbon-based —CH₂ stretching vibration. The FT-IR analysis proved that the structure of the saturated hydrocarbon group

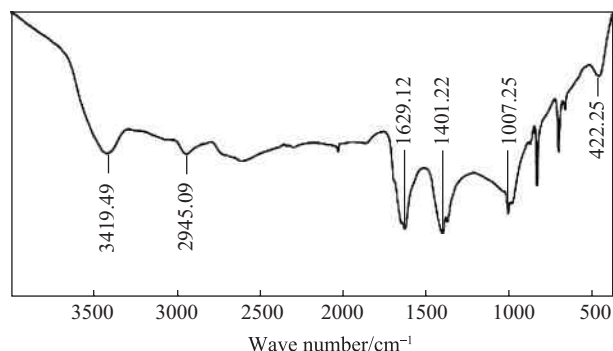


Fig.4 FT-IR spectrum of ginger stems

was contained in the ginger stems. Absorption peaks at 1629 cm^{-1} and 1401 cm^{-1} were considered to be derived from the special bond stretching vibrations of C and C in olefins and benzene rings. The absorption peaks at 1007 cm^{-1} could be attributed to esters, phenols, and ethers. It can be inferred that ginger stems contain alcohol (phenol) hydroxyl, amine, or ether groups.

The characteristic peaks of the BAC in the infrared spectrum are shown in Fig.5. The peak at 422 cm^{-1} was attributed to the hydroxyl and the corresponding C=C characteristic peak. Wave number of the $2900\sim1600\text{ cm}^{-1}$ absorption peaks did not appear in the FT-IR spectrum of the BAC. This happened because KOH applied in the activation process had a strong corrosive effect which destroyed the organic structure of the ginger stems and decomposed it into carbon.

3.6 FESEM analysis

Fig.6 shows the surface morphology of the BAC observed by FESEM. It can be seen from Fig.6, on the surfaces, there are traces of high-temperature burning and alkali corrosion, and a large number of pore structures. This result demonstrates that alkali activators are essential for the formation of the BAC porosity.

3.7 BET surface area

In this experiment, the specific surface area was determined by the Micromeritics ASAP 2020 automatic surface area analyzer. Upon a comparative analysis, it was concluded that the parameters

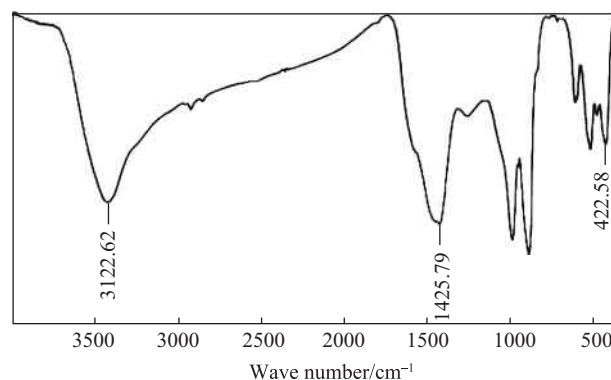


Fig.5 FT-IR spectrum of BAC

of the BAC prepared using KOH as an activator were slightly more superior than that when NaOH was used. The pore structure parameters of the two BAC samples using different activators were listed in Table 4. As can be seen from Table 4, KOH presented a slightly better activation potential than NaOH. The average pore size of both samples was less than 2 nm, and the BAC presented a large-proportion porous structure.

Table 4 Pore structure parameters of BAC

Activator	BET surface area/($\text{m}^2\cdot\text{g}^{-1}$)	Average pore size/nm
NaOH	645	1.96
KOH	790	1.84

3.8 Nitrogen adsorption and desorption curves

In this experiment, the BAC prepared by the KOH activation reagent was optimized for nitrogen adsorption and desorption experiments.

The results were used to establish the isothermal curves for nitrogen adsorption and desorption (as shown in Fig.7).

In Fig.7, the isotherm curves of nitrogen adsorption and desorption of BAC indicate that the curves belong

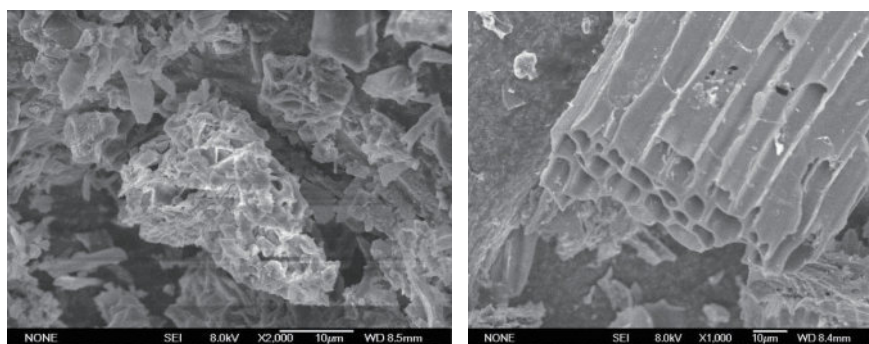


Fig.6 FESEM images of the BAC derived from ginger stems

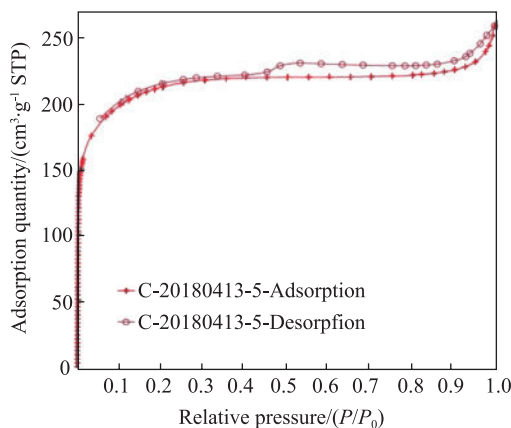


Fig.7 Isotherm adsorption and desorption curves of N₂

to the type I isotherm, reflecting the existence of many microporous structures. When the relative pressure was in the low-pressure region, e.g., P/P_0 was less than 0.1, the nitrogen adsorption curve rose rapidly indicating that there was a strong force between the activated carbon and nitrogen, which further confirmed that the BAC possessed a microporous structure, and the BAC adsorption properties improved. When the relative pressure was within the medium pressure zone, P/P_0 between 0.3 and 0.8, the absorption curve rose very slowly and plateaued. The nitrogen condensed and accumulated in the pores of the BAC under the medium pressure zone, hence, the adsorption of nitrogen onto the activated carbon tended to be gentle. There were a few mesoporous structures in the BAC. When the relative pressure is within the high pressure zone ($P/P_0 > 0.9 \sim 1.0$), the absorption curve rose rapidly, indicating the presence of BAC macropores or particle packing pores.

4 Conclusions

In this work, discarded ginger stems were used to prepare biomass activated carbon (BAC) with high adsorption capacity and low production cost. The BET surface area affects the adsorption performance of BAC. The optimal conditions for the preparation of BAC were determined by single factor variable experiments. The results showed that when the carbonization temperature was 700°C, the carbonized product/alkali ratio was 1:4 and the carbonization time was 6 h, and when the activator was KOH, the activation temperature was 800°C and the activation time was 1 h, a higher BAC

yield could be obtained and the BAC had microporous structure for adsorption performance. However, it is still necessary to ensure that the Brunauer-Emmett-Teller (BET) surface area is maximized so that the BAC can exert the maximum effect. In future studies, other biomass renewable sources will be used to prepare products that can contribute to a sustainable development.

Acknowledgments

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