# Analysis of the Physical and Chemical Properties of Activated Carbons Based on Hulless Barley Straw and Plain Wheat Straw Obtained by $H_3PO_4$ Activation

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High specific surface area activated carbon was prepared by improving the process conditions of phosphoric acid activation and hulless barley straw and plain wheat straw as raw materials. The effects of the activation time on the pore structure and specific surface area of two types of activated carbon were investigated. The results revealed that soaking straws in the high concentrations of $H_3PO_4$ for 0.5 h to ensure complete soaking and then removing the straws from $H_3PO_4$ solution to activate was beneficial to the infiltration of $H_3PO_4$ in the raw material, and there was an increase in the surface area of activated carbon. The largest specific surface area of activated carbon prepared from plain wheat straw and hulless barley straw was 1524 $m^2/g$ and 1885 $m^2/g$, respectively. Thermogravimetric analysis and scanning electron microscopy showed that the higher cellulose content, higher hemicellulose content, and smaller fiber morphology in hulless barley straw compared with wheat straw were the main reasons for the more abundant pore structure and higher specific surface area of the activated carbon.

*Keywords: Hulless barley straw; $H_3PO_4$ activation; Activated carbon; Activation time*

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## INTRODUCTION

Activated carbon is widely used in adsorption storage, adsorption, separation, catalytic processes, supercapacitors, and other aspects of gas fuel due to its developed pore structure and large adsorption capacity (Bhaumik and Mondal 2015; Mashhadi *et al.* 2016a). The main raw materials used in preparing activated carbon are sawdust (Snyder *et al.* 2007), all types of coal (Hameed *et al.* 2007), coconut shell (Mao *et al.* 2014), agricultural waste (Mashhadi *et al.* 2016b), and some polymers (Guo *et al.* 2011). Studies on the preparation of activated carbon from hulless barley straw have been less reported. Hulless barley is a unique plant in the western plateau of China. Hulless barley straw is not suitable for power generation material and animal feed because of its lower heat and nutrition. A large amount of straw is usually used as fuel or returned directly to the field (Srivastava *et al.* 2006). The incomplete combustion and slow degradation of low temperature and hypoxia in the plateau results in the pollution of the local atmosphere and the acidification of soil (Fan *et al.* 2011). The preparation of activated carbon using hulless barley straw has alleviated the environmental pollution problem and provided a reasonable outlet for the utilization of the straw.

The raw material of activated carbon directly affects its physical and chemical properties. The main components of general biomass include hemicellulose, cellulose, lignin, water, extractives, and inorganic components (Huijgen *et al.* 2010). The content and structure are important factors affecting the physical and chemical properties of activated carbon. Hulless barley and wheat are gramineous plants (Tan *et al.* 2008). As a result of the different growth environments in plateaus and plains, hulless barley straw and wheat straw have different contents and morphologies of cellulose and hemicellulose (Ioannidou and Zabaniotou 2007). Therefore, the two types of straw-based activated carbon have different physical and chemical properties (Wu *et al.* 2014).

$H_3PO_4$ activation is a common method for the preparation of activated carbon due to its low energy consumption, low pollution, and high yield (Arvelakis *et al.* 2010). The raw material is usually mixed with different $H_3PO_4$ concentrations ranging from 30% to 60% in a certain impregnation ratio of 0.5 to 2.5, and then activated at higher temperatures (Cui *et al.* 2015; Ghosh *et al.* 2016; Zhu *et al.* 2016). As the temperature rises, phosphoric acid depolymerizes the organic polymers (cellulose, hemicellulose, and lignin) of the raw material into small fragments, which form pores after washing. When the temperature is higher than 450 °C, small molecule fragments lose protection due to loss of sublimation at a high temperature, resulting in shrinkage, which ultimately leads to a decrease in pore structure (Baquero *et al*. 2003). Compared with the method of activated carbon preparation activated by low concentration of phosphoric acid, increasing the concentration of phosphoric acid can shorten the activation time and reduce energy consumption (Suárez-Garcia *et al*. 2001). However, immersing the raw material in a high concentration of phosphoric acid during the entire activation process will cause the reduction of specific surface area and yield of activated carbon (Jagtoyen and Derbyshire 1998). One view is that a high concentration of phosphoric acid solution will form a polyphosphate film to cover the developed pores (Hared *et al*. 2007); another view is that the high concentration of phosphoric acid, which tends to swell the raw material, makes the developing pores continue to expand and collapse (Montané *et al*. 2005).

However, for some raw material with a smaller density, its direct mixing makes the $H_3PO_4$ become mainly distributed on the bottom of the container, and a certain concentration gradient is formed longitudinally, causing the material to be impregnated unevenly (Yadav *et al.* 2013). Activated carbon prepared by this method has a lower specific surface area and yield.

In this study, hulless barley straw and plain wheat straw were soaked in high-concentration phosphoric acid for 0.5 h to ensure complete soaking and then removed from phosphoric acid to a convection oven for air drying and solidification. This method is conducive to the rapid and uniform penetration of phosphoric acid into the interior of the raw material while preventing the reduction of specific surface area caused by over-activation of phosphoric acid. The effects of the activation time on the pore structure and specific surface area of two types of activated carbon were studied.

## EXPERIMENTAL

### Materials

The hulless barley straw and wheat straw used were harvested from an average elevation of 2300 m (Qinghai, China) and 200 m (Shandong, China), respectively. The two types of straws were cut into 0.5 cm long segments, dried to a constant weight, and stored in a desiccator.

## Methods

### Preparation of activated carbon

Hulless barley straw and wheat straw were soaked in an 80% $H_3PO_4$ solution for 0.5 h and then removed to a convection oven at 140 °C for 1 h. The activation of both mixtures was carried out in a laboratory muffle furnace under $N_2$ flow. In the tubular furnace, the temperature was increased at approximately 5 °C/min from room temperature to 450 °C and maintained at 450 °C for 0.5 h to 2.5 h. Afterward, the two activated carbons were washed several times with deionized water, and 0.1 M HCl was added to remove ash byproducts. The products were washed with deionized water until pH 7 was reached. The activated carbons were dried at 110 °C for 24 h and stored in a dryer. The activated carbons prepared using hulless barley straw and wheat straw were recorded as HAC-t and LAC-t, where "t" indicates the activation time in h.

### Characterization of activated carbon

The pore structure characteristics of the resulting carbons were determined by nitrogen adsorption at -196 °C using an automatic ratio surface and aperture analyzer (3h-2000ps4, Bei Shi De, Beijing, China). Before the test, the activated carbon samples were degassed at 200 °C for 6 h to remove moisture and gas impurities. The surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore diameter distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method.

## RESULTS AND DISCUSSION

As shown in Fig. 1, the pyrolysis of hulless barley straw and wheat straw is divided into four stages: drying and water loss, transition, rapid pyrolysis, and carbonization (Mall *et al.* 2005a, b). At a heating rate of 10 K/min, when the DTG curve showed the first weight loss peak, the hulless barley straw and wheat straw weight losses were 3.9% and 4.6%, respectively, which was caused by the evaporation of the combined water in the straw. At the second weight loss peak of the DTG curve, the two curves fell sharply, and the hulless barley straw and wheat straw weight losses were 68.8% and 56.1%, respectively. The cellulose and hemicellulose of the two types of straws rapidly decomposed in this stage.

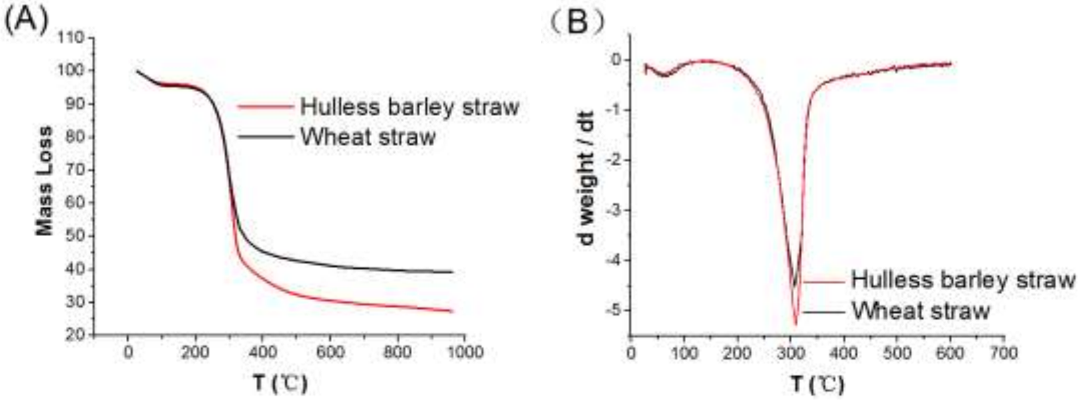

**Fig. 1.** The TG (A) - DTG (B) of hulless barley straw and wheat straw

From the proportion of weight losses of the two types of straws, it was concluded that the content of cellulose and hemicellulose in hulless barley straw was higher than that in wheat straw. After the curve entered the carbonization stage, lignin slowly decomposed, the sample quality slowly decreased, and the curve was relatively gentle.

Table 1 shows the specific surface area of HAC and LAC at different activation times. Activated carbons were prepared with a specific surface area of 805 $m^2/g$ from wheat straw at 900 °C using $CO_2$ activation (Zhang *et al.* 2014). Activated carbons were prepared with a specific surface area of 915 $m^2/g$ from hulless barley straw at 600 °C using zinc chloride activation (Ma *et al.* 2016). Activated carbons were prepared with a specific surface area of 1279 $m^2/g$ from wheat straw at 450 °C using $H_3PO_4$ activation (Lu *et al.* 2011). The comparison revealed that $H_3PO_4$ activation had the advantages of low energy consumption and good activation effect. Compared with the activation method of directly mixing straw with low concentration of $H_3PO_4$, straws were soaked in a high concentration of $H_3PO_4$ and removed for activation, which is beneficial for the infiltration of $H_3PO_4$, increase of surface area, and yield of the activated carbon.

**Table 1.** Specific Surface Area, Pore Diameter, and Yield of Activated Carbon Products with Different Activation Times

| Sample Name | BET ($m^2/g$) | Diameter (nm) | Yield (%) |
|---|---|---|---|
| HAC-0.5 | 1150 | 3.13 | 34.7 |
| LAC-0.5 | 1389 | 3.57 | 31.4 |
| HAC-1 | 1383 | 3.52 | 33.2 |
| LAC-1 | 1533 | 3.96 | 28.4 |
| HAC-1.5 | 1788 | 3.97 | 30.5 |
| LAC-1.5 | 1435 | 4.21 | 25.6 |
| HAC-2 | 1885 | 4.05 | 28.1 |
| LAC-2 | 1321 | 4.56 | 23.2 |
| HAC-2.5 | 1787 | 4.16 | 27.5 |
| LAC-2.5 | 1241 | 4.85 | 21.6 |

Table 1 shows that the extension of the activation time has different effects on the activated carbon produced using the hulless barley straw and plain wheat straw. In the activation time of 0.5 h to 1 h, the specific surface area of LAC was higher than HAC. Since hulless barley is grown in plateaus with sufficient sunlight and oxygen deficits, the content of cellulose and hemicellulose in hulless barley straw is higher than that in plain wheat straw, and its fiber morphology is smaller and finer than that in plain wheat straw (Li *et al.* 2013). At the shorter activation time, it is difficult for this small fiber morphology to form a large number of pores, and some cellulose and hemicellulose have not been hydrolyzed. Only mesopores and macropores are formed in the external matrix. In contrast, the fiber morphology of plain wheat straw is relatively large, and the density is small. Thus, it is easier to form a large number of pores and obtain a higher specific surface area of activated carbon at the shorter activation time. However, as the activation time increased, the specific surface area of HAC gradually increased and the specific surface area of LAC gradually decreased. At the activation time of 2 h, the specific surface area of HAC was 564 $m^2/$ g higher than LAC. A high concentration of $H_3PO_4$ through the external channel into the hulless barley straw fiber not only formed a large number of mesopores and macropores in the external matrix, but also formed a large number of micropores through the hydrolysis of cellulose and hemicellulose, thereby increasing the specific surface area rapidly. However, a high concentration of $H_3PO_4$ can enter the plain wheat straw fibers relatively quickly, and the activation process had been completed in about 1 h. With the extension of activation time, the pores structure that formed was gradually corroded, resulting in the fusion of adjacent pore structures to form the larger pores structure, and reduced the development of the surface area and pores. When the activation time exceeded 2 h, the activated carbon prepared by hulless barley straw also exhibited a decrease in specific surface area and an increase in pore size. As the activation time increased, the yield of the two types of activated carbons decreased. The yield of hulless barley straw-based activated carbons was higher than the plain wheat straw-based activated carbons, demonstrating that the hulless barley straw was an excellent biomass precursor for the preparation of porous activated carbons.

SEM was used to observe the surface morphology of activated carbon. As shown in Figs. 2A and 2B, at the activation time of 1 h, the two activated carbons mostly exhibited micropore and mesopore structures. The surface of HAC-1 was relatively smooth, with only a slightly less visible pore structure, and the number of pores was significantly lower than LAC- 1. Figure 2C shows that the elongation of the activation time made the pore diameter larger, the pore wall thinner, and the pores appeared looser, indicating that the interior of HAC-2 had an abundant porous structure. Figure 2D shows that the extension of the activation time caused the corrosion of the pores structure and disappearance of the pore wall of LAC-2. The pore diameter of the micropores increased rapidly, and the pores collapsed and fused to form the larger pores structure. Large-diameter impurities are apparent in Fig. 2D, indicating that excessive activation of the raw material by a high-concentration phosphoric acid solution formed polyphosphate that adhered to the activated carbon surface, thereby preventing the raw material from contacting the external environment. These impurities are difficult to remove during washing.

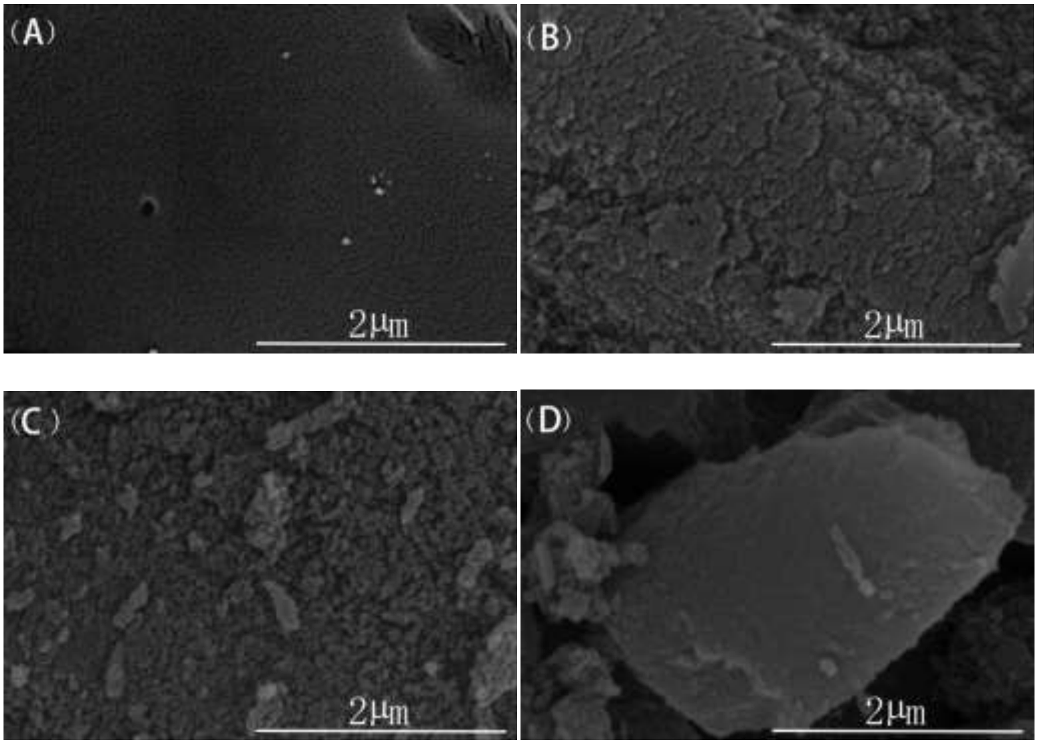

**Fig. 2.** SEM images of HAC-1 (A), LAC-1 (B), HAC-2 (C), and LAC-2 (D)

Figure 3 shows the $N_2$ adsorption isotherm curve for different activation times. The four isotherms belong to type IV as defined by the International Union of Pure and Applied Chemistry (IUPAC). When the relative pressure $P/P_0$ was low, the $N_2$ adsorption increased rapidly, indicating the presence of micropores and the filling of micropores via adsorption. The point at $P/P_0 = 0.02$ indicated the saturation adsorption of the monolayer and that multilayer adsorption began at this stage. From the position of the inflection point, the numbers of micropores in HAC-1 and LAC-1 were roughly the same. As the relative pressure $P/P_0$ increased, the adsorption capacity was not constant but increased slowly with a certain slope because of multilayer adsorption on non-micropores on the external surface (Rouquerol *et al.* 1999). Based on a comparison of the two adsorption curves in Fig. 3A, it was concluded that the mesopores and macropores of LAC-1 were more developed than HAC-1.

As shown in Fig. 3B, two samples exhibited typical characteristics of type IV adsorption isotherms. As shown in the adsorption isotherms of HAC-2, there was a significant increase at the point where the relative pressures $P/P_0 = 0.02$ and $P/P_0 = 0.8$, indicating that with the extension of time, the cellulose and hemicellulose of hulless barley straws were hydrolyzed into a large number of small molecules. These small molecules formed rich micropores and mesopores; moreover, a few macropores formed inside the activated carbon after washing. As shown in the adsorption isotherms of LAC-2, there was a significant reduction at the relative pressures $P/P_0 = 0.02$, demonstrating that some of the formed pores were blocked by the polyphosphate produced due to over-activation. At the same time, some developing pores formed mesopores and macropores under the action of high concentrations of phosphoric acid. Therefore, when the activation process had been completed, the extension of activation time resulted in the reduction of the specific surface area and the yield of activated carbon.

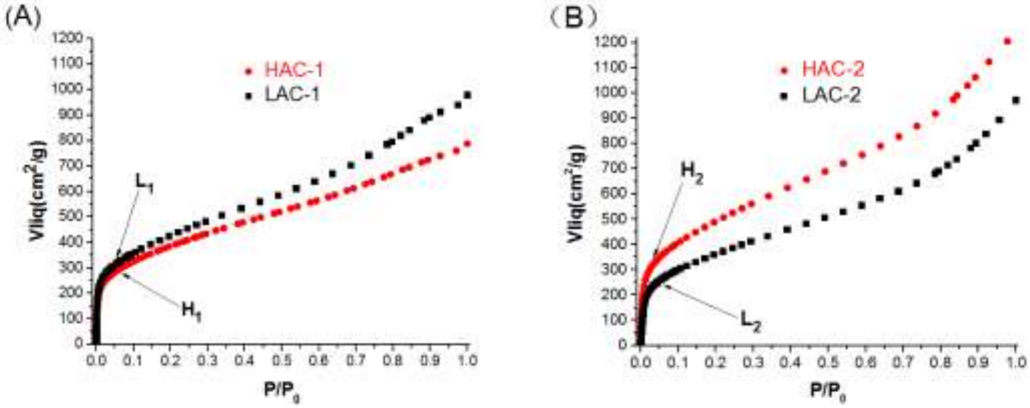

**Fig. 3.** $N_2$ adsorption isotherms at -196 °C on activated carbon in the activation time of 1h (A) and 2 h (B )

## CONCLUSIONS

1. Compared with the activation method of directly mixing straw biomass with a low concentration of $H_3PO_4$ solution, the activation method of soaking straw in a high concentration of $H_3PO_4$ solution and removing the straw from $H_3PO_4$ solution to activate was beneficial to the infiltration of the $H_3PO_4$ solution, and abundant pores formed during the preparation of activated carbon.

2. Activated carbons prepared using hulless barley straw had higher specific surface area attributed to the higher content of cellulose and hemicelluloses, and smaller fiber morphology than plain wheat straw, demonstrating that hulless barley straw was an excellent biomass precursor for the preparation of porous activated carbons.

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