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PREPARATION OF PHOSPHORIC ACID ACTIVATED CARBON FROM SUGARCANE BAGASSE BY MECHANOCHEMICAL PROCESSING

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Activated carbon was prepared from sugarcane bagasse with phosphoric acid activation by a mechanochemical process. The effects of milling time on adsorption properties and pore structure of activated carbon were evaluated. The results showed that phosphoric acid activation was assisted by the mechanochemical process, which can reduce the processing time and improve the adsorption performance of the prepared activated carbon. The iodine number, the methylene blue adsorption value, and the specific surface area of the prepared activated carbons were improved from 647.94 mg/g, 150 mg/g and 1075.21 m^2/g to 889.37 mg/g, 177 mg/g and 1254.52 m^2/g, respectively. Compared with conventional phosphoric acid activation, the activated carbon produced by the mechanochemical process achieved the advantages of shorter processing time, greater adsorption capacity, and higher adsorbed amounts of iodine, methylene blue, and nitrogen.

Keywords: Mechanochemical process; Phosphoric acid activation; Activated carbon

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INTRODUCTION

Activated carbon has received much attention in recent years due to its versatile applications in material science (Khezami *et al*. 2007; Danish *et al*. 2011). Generally speaking, activated carbon is prepared by physical or chemical activation methods (Jia *et al*. 2001; Olivares-Marín *et al*. 2011). In chemical activation, phosphoric acid has been known for several years and applied to different cellulosic and lignocellulosic material to prepare activated carbons (Molina-Sabio *et al*. 1995; Zuo *et al*. 2009, 2010). However, the conventional process for sample activation and carbonization by phosphoric acid takes 2 to 8 hours (Molina-Sabio *et al*. 2003; Marsh and Rodriguez-Reinoso 2006; Zeng *et al*. 2010) and is highly energy-consuming.

In this study, a novel method employing a mechanochemical process was used to produce activated carbon from sugarcane bagasse. Mechanochemistry uses mechanical energy to physically and chemically change the properties of matter by means of compression, shear, friction, impact, bending, and extending (Koch and Whittenberger 1996; Baláž 2008). Different from traditional methods, it is a technique of preparing nanometer particle products by taking advantage of the rotation and vibration of ball milling in the mechanochemical process to crush, grind, and mix the materials (Baláž *et al*. 2005).

Based on this principle, the activation process was dramatically improved by the mechanochemical effect, which led to increased adsorption performance of the products.

A series of experiments on milling time for developing adsorption properties and pore structures of activated carbon was conducted to further explore the effect of mechano-chemical processing on phosphoric acid activation in this work.

EXPERIMENTAL

Materials

Sugarcane bagasse was used as the raw material in this study. Its composition was 42.16% cellulose (nitric acid-ethanol method), 19.30% lignin (Klason), 36% hemicellulose (alkali extractions method), and 2.26% ash (combustion method). All chemicals used in this work were of analytical grade.

Preparation of Activated Carbon

Bagasse was crushed and sieved to 20-60 mesh. Then, it was air-dried and mixed with a 20% phosphoric acid solution for 2 h with an impregnation ratio of 2.0 based on the previous single-factor experiment. The impregnation ratio was defined as:

$$\text{impregnation ratio} = \frac{\text{weight of } H_3PO_4 \text{ in solution}}{\text{weight of bagasse}} \quad (1)$$

The impregnated mixture was milled continuously by a high-energy ball mill (BXQM0.4L, Instrument Co., Ltd. Nanjing) at room temperature with a ball:powder mass ratio of 5:1 and a rotational speed of 400 rpm. The heat treatment of the milled H_3PO_4-impregnated bagasse was conducted in a furnace (KDF-S80, JEOL, Japan), from 350 to 500 ºC for an appropriate time. In this work, 400 ºC of carbonization temperature was selected based on the previous single factor experiment. After heat treatment, the sample was washed with 10% hydrochloric acid to remove the ash. Then it was washed several times with hot water and dried at 105ºC.

Characterization of Prepared Activated Carbon

The adsorption performance of activated carbon was characterized by iodine number and methylene blue adsorption value according to *GB/T 12496-1999* (National Standards of P.R.C). The porosity was characterized by adsorption of N_2 in a semi-automatic adsorption apparatus (SSA-4200, BIO-EQUIP. Beijing). Prior to measuring the adsorption isotherm, the activated carbon was heated at 573 K for 4 h in a vacuum to clean its surface. The specific surface area of the activated carbon was calculated based on the adsorption isotherm data of N_2 by the Brunauer-Emmertt-Teller (BET) method. The micropore volume was calculated based on the amount of N_2 adsorbed under a relative pressure of 0.1 by the Barrett-Joyner-Halenda (BJH) method. Surface group information of carbons was obtained by Fourier transform-infrared spectroscopy (FT-IR，Nicolex 380, ThermoFisher Scientific) with wavenumbers 4000 to 400 cm^{-1} using 32 scans of 4 cm^{-1} resolution. Pellets were prepared by thoroughly mixing the carbon and KBr at the weight ratio of 1:200 in a small size agate mortar.

RESULTS AND DISCUSSION

The Adsorption Properties of Prepared Activated Carbon

Phosphoric acid activated carbon was prepared from sugarcane bagasse by a mechanochemical process. The adsorption performance of activated carbon was analyzed according to iodine number and methylene blue adsorption value, and the results are shown in Tables 1 and 2.

Table 1. Analysis of the Effect of Mechanochemical Processing and Carbonization Time on Adsorption Performance of the Activated Carbon

Sample	Iodine Number (mg/g)	Methylene Blue Adsorption Value (mg/g)
$AC_{0\text{-}400\text{-}1}$*	647.94	150
$AC_{0\text{-}400\text{-}2}$	737.22	180
$AC_{0\text{-}400\text{-}3}$	814.67	198
$AC_{45\text{-}400\text{-}0.5}$	808.15	180
$AC_{45\text{-}400\text{-}1}$	889.37	177
* $AC_{0\text{-}400\text{-}1}$ represents activated carbon prepared by milling for 0 minutes then carbonized at 400 ºC for 1 hour		

As shown in Table 1, the effect of mechanochemical processing on phosphoric acid activation was explored. During conventional phosphoric acid activation without the mechanochemical process, the iodine number and methylene blue adsorption value of activated carbon increased with the extension of carbonization time from 1 h to 3 h. After being carbonized for 3 h, the iodine number and methylene blue adsorption value of activated carbon reached 814.67 mg/g and 198 mg/g, respectively. The phosphoric acid activation assisted with mechanochemical process obtained good results in a shorter time, which demonstrates that this process can reduce processing time.

To further explore the effect of mechanochemical process on carbonization and the optimum conditions, the effects of milling time on the adsorption properties, physical properties, and pore structures of activated carbon were examined.

Table 2. Analysis of Effects of the Milling Time on Adsorption Performance and Physical properties of Activated Carbon

Sample	Iodine Number (mg/g)	Value of Methylene Blue Adsorption (mg/g)	Average Particle Size* (μ m)	Surface Area* (m^2/g)
$AC_{0\text{-}400\text{-}1}$*	647.94	150	213.29	1075.22
$AC_{15\text{-}400\text{-}1}$	827.80	165	126.84	1218.62
$AC_{30\text{-}400\text{-}1}$	870.95	172.5	94.80	1230.23
$AC_{45\text{-}400\text{-}1}$	889.37	177	47.78	1254.52
$AC_{60\text{-}400\text{-}1}$	864.54	171	39.91	1229.25
$AC_{75\text{-}400\text{-}1}$	768.48	135	35.47	1065.38
*$AC_{0\text{-}400\text{-}1}$ represents activated carbon prepared by milling for 0 minutes then carbonized at 400 ºC for 1 hour; Average size of particles were measured by BT-3900H Laser Particle size analyzer, BETTERSIZE Instrument Ltd.; The surface area of activated carbon was calculated by BET method.				

As shown in Table 2, the iodine numbers and methylene blue adsorption values of the activated carbon produced by mechanochemical process were significantly higher than those without mechanical processing, which indicates that the mechanochemical process helped to improve the adsorption performance of the activated carbon. With increasing milling time, the iodine number, as well as the methylene blue adsorption values, increased rapidly in the first 15 min then decreased until 45 min. After the sample was milled for 45 min., the adsorption performance of activated carbon decreased with the prolonging of milling time. So, the optimum milling time was determined to be 45 min.

The average size of the particle and surface area were measured after milling. The particles showed a clear trend in average size with an apparent decrease from 213.19 μm for unmilled powder to 35.47 μm after 75 min milling. In the surface areas, it showed an obvious increase from 1075.22 m^2/g for unmilled powder to a maximum of 1254.52 m^2/kg after 45 min, followed by a decrease to 1065.38 m^2/g after 75 min milling. Also, the results showed that the adsorption capacity and the surface area passed through a maximum, which was associated with the completion of size reduction.

The following mechanism for the mechanochemical process for activation is proposed. A strong impact force is produced at the collision point where the milling ball collides with the tank and the impregnated bagasse, which leads to lattice defects within the particles. Consequently, it reduces the activation energy of diffusion significantly and accelerates the diffusion of the activation reagent (H_3PO_4) into the inner portions of the raw material. The particles of the sample are refined by the action of the high-energy ball milling, which increases the specific surface areas of the sample. So in the first 45 min., increasing of the milling time, the iodine number and methylene blue adsorption increase. Afterwards, the specific surface areas decrease due to the continuous refining of particles and agglomeration of powder with the prolonging of milling time. Thereby, the adsorption properties of products decrease after 45 min. Moreover, under the action of mechnochemical effect, the surface chemical bonding of the reaction system is broken. Thus, unsaturated bonding, free electron ions, and lattice defects are generated, leaving the system in an unstable chemical activity state, which leads to the increase of the internal energy of reactants and the improvement of the surface adsorption capacity of the products (Venkataraman and Narayanan 1998; Urakaev and Boldyrev 2000).

The Pore Structure of Prepared Activated Carbon

To study the effect of the mechanochemical processing on the porous structure of activated carbon, the sample was characterized texturally by gas adsorption (N_2, 77 K). The differences between AC with mechanochemical processing and AC without mechanochemical processing are shown in Figs. 1 and 2, and Table 3.

Figure 1 shows N_2 adsorption-desorption isotherms of activated carbon at 77 K. Both of the isotherms are type II, which means that the activated carbons contained micro- and meso-sized pores. It is also clear from Fig. 1 that the adsorbed volume of N_2 on the Activated Carbon (AC) prepared by the mechanochemical process was higher, indicating that mechanochemical processing helps to improve the adsorption capacity of activated carbon. Table 3 displays porosity parameters deduced from the N_2 adsorption isotherms. As shown in Fig. 1 and Table 3, the BET surface area (S_{BET}) of AC by mechanochemical process was significantly larger than that of AC without such a process, which corresponds to the adsorption property of activated carbon.

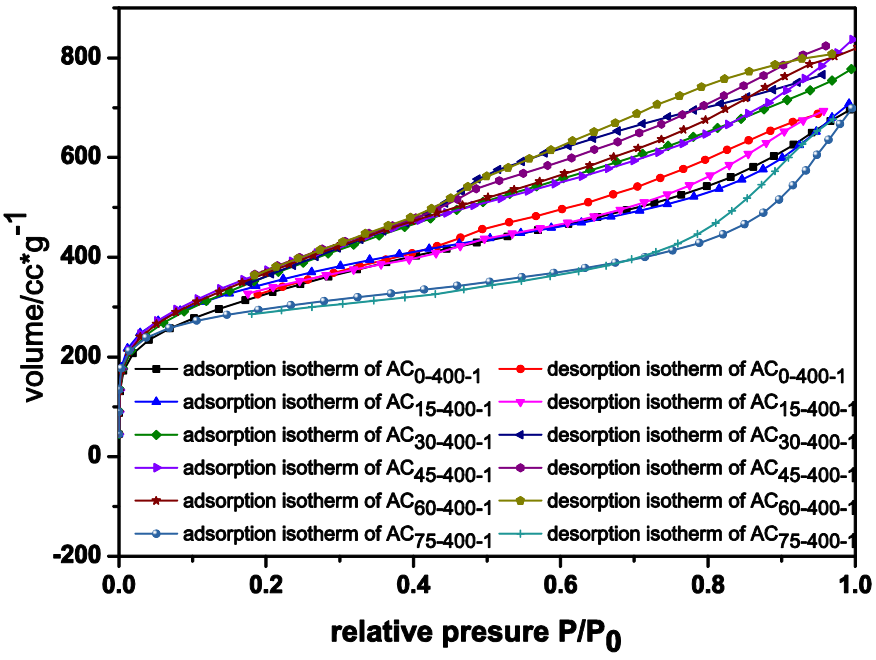

Fig. 1. Adsorption-desorption isotherm of N_2 at 77K

Table 3. S_{BET} and Pore Structure of Prepared Activated Carbon

Sample	N_2 Adsorption		
	S_{BET}[a] (m^2/g)	V_t[b] (mL/g)	V_{micro}[c] (mL/g)
$AC_{0\text{-}400\text{-}1}$	1075.22	1.083	0.513
$AC_{15\text{-}400\text{-}1}$	1218.62	1.101	0.554
$AC_{30\text{-}400\text{-}1}$	1230.23	1.208	0.576
$AC_{45\text{-}400\text{-}1}$	1254.52	1.301	0.580
$AC_{60\text{-}400\text{-}1}$	1229.25	1.277	0.572
$AC_{75\text{-}400\text{-}1}$	1065.38	1.086	0.458

a- the specific surface area of activated carbon calculated by BET method;
b- the total adsorption volume of activated carbon calculated by BJH method;
c- the micropore volume of activated carbon calculated by BJH method

The results showed that both the total volume and the micropore volume of the activated carbon increased, indicating that the activated carbon produced by mechano-chemical processing had the advantage of greater adsorption capacity.

Figure 2 shows the pore size distributions (PSDs) of the two activated carbons obtained by the BJH method. The PSDs show a sharp peak in the micropore range, with the maximum around 0.4 and 1.4 nm for all samples. This indicates that phosphoric acid activation by mechanochemical process resulted in development of micropores of a few sizes.

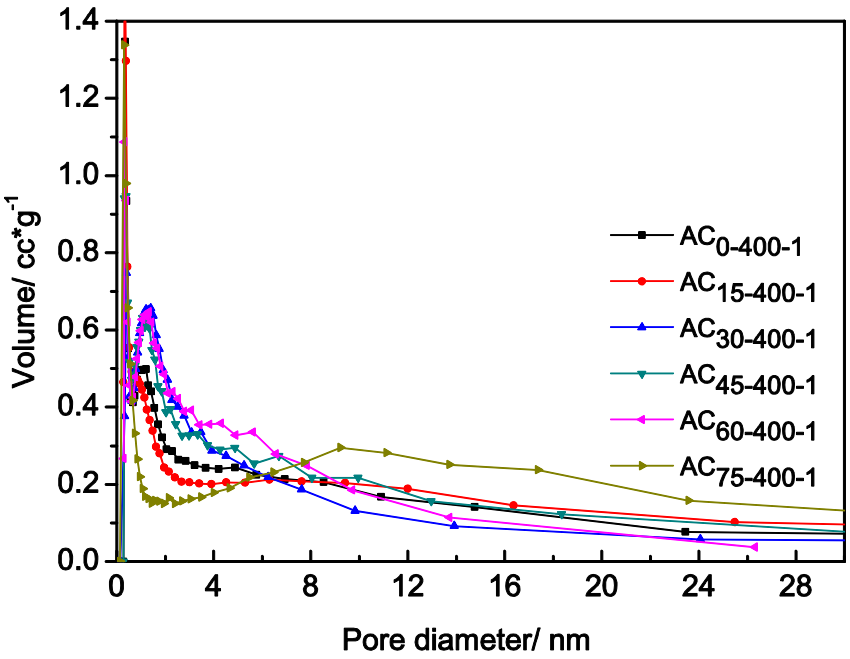

Fig. 2. Influence of mechanochemical process on pore size distribution of activated carbon

The FT-IR Analysis of the Activated Carbon

Information about the surface functional groups and structures of the prepared activated carbon was obtained by FT-IR spectroscopy (Olivares-Marín *et al*. 2006). The activated carbon was prepared from bagasse and milled for 45 min. (namely, AC_{45}); this activated carbon was compared with the sample obtained by conventional phosphoric acid activation without mechanochemical process (namely, AC_0).

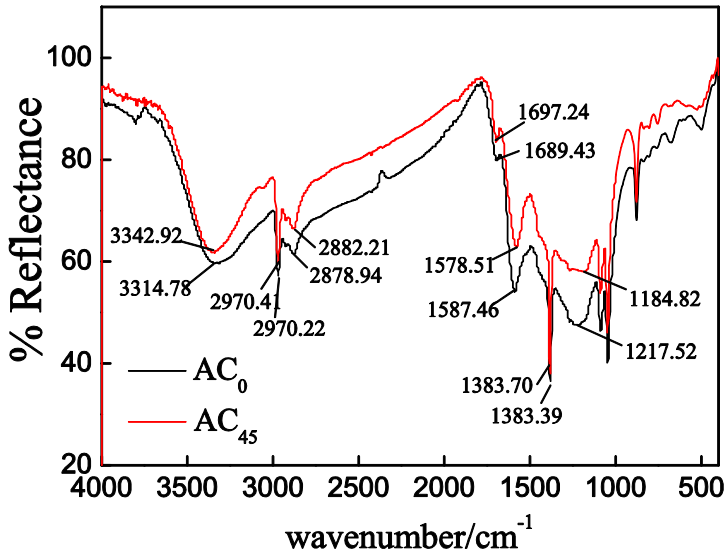

Fig. 3. FT-IR analysis of the activated carbon

As shown in Fig. 3, the FT-IR spectra for samples are almost the same, which indicates that the mechano-chemical process had no significant effect on the surface functional groups and structures of the prepared activated carbon. The stretching vibration mode of O-H bond is present at 3320 cm^{-1}, the bonds of C-H in methyl group and methylene group appear at 2880 and 2970 cm^{-1}, respectively, and the stretching of C=O appears at 1690 cm^{-1}. Aromatic skeletal vibration is clearly indicated by absorption at 1580 cm^{-1}. Absorptions at 1383 and 1180 cm^{-1} were assigned to the deformation mode of C-H and the stretching vibration of C—O and C—C, respectively.

CONCLUSIONS

1. Phosphoric acid activated carbon with high adsorption capacity was prepared from sugarcane bagasse by mechanochemical processing. The iodine number, the methylene blue adsorption value, and specific surface area of the prepared activated carbon are 889.37 mg/g, 177 mg/g, and 1254.52 m^2/g, respectively.
2. Compared with the conventional phosphoric acid activation, the phosphoric acid activated carbon produced by mechanochemical process exhibited the advantages of less processing time, greater adsorption capacity, and higher adsorbed volume of iodine, methylene blue, and nitrogen.
3. Ball milling time affects the pore structure and adsorption performance of the prepared activated carbon. The optimum ball milling time in the present study was 45 min.

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