Activated carbons prepared from phosphoric acid activation of grain sorghum

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Abstract

The production of activated carbons from grain sorghum with phosphoric acid activation has been studied by means of two processes, i.e., one-stage and two-stage. The former comprises simultaneous carbonization and activation after impregnation; the latter, the carbonization of the precursor at 300 °C for 15 min, followed by the activation of the resultant char after impregnation with phosphoric acid. The preparation conditions, e.g., activation duration, phosphoric acid concentration, and activation temperature, have been varied to determine the optimal processing conditions. The optimal activation conditions for the highest surface areas have been determined to be 600 and 500 °C with a phosphoric acid concentration of 35% for the one-stage and two-stage processes, respectively. The two-stage process has been found to greatly enhance the porosity development, especially the microporosity. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Activated carbons have well-developed pore structures and are widely used as adsorbents, catalysts, and catalyst supports. They can be manufactured from a variety of precursors by physical or chemical activation. Physical activation is usually carried out in two steps: the first is carbonization of the raw material in an inert atmosphere at a temperature below 700 °C, and the second is activation in the presence of steam, carbon dioxide, and/or air at temperatures between 800 and 1000 °C. Chemical activation is generally carried out in one step, which consists of impregnation of the raw material with a strong dehydrating agent, typically phosphoric acid, and then heating the mixture to temperatures of 400–800 °C to simultaneously form and activate the carbon.

The general mechanism for the physical activation is better understood today because a large number of publications in the scientific literature have focused on it. Several studies of chemical activation have been conducted with zinc chloride, which has been found to maximize the adsorptive capacity and bulk density of activated carbons produced from lignocellulosic materials such as peach stones (Molina-Sabio et al., 1995). However, phosphoric acid is preferred because of the problems of corrosion, inefficient chemical recovery, and environmental disadvantages associated with zinc chloride. Phosphoric acid activation has been applied to coconut shell (Laine et al., 1989), peach stones (Molina-Sabio et al., 1995, 1996), coals and hardwoods (Jagtoyen et al., 1992; Solum et al., 1995; Jagtoyen and Derbyshire, 1993, 1998), and shells of nuts like almond, pecan, English walnut, black walnut and macadamia nut (Toles et al., 1998, 2000). These precursors are of cellulosic or lignocellulosic origin. It has been shown that the impregnation ratio, which is the weight ratio of impregnant to precursor, and the activation temperature govern the properties of the resultant activated carbons. Recently, Jagtoyen and Derbyshire (1998) presented a comprehensive account of the mechanisms of phosphoric acid activation. Nevertheless, it appears that no study has been conducted to date on the chemical activation of cereal grains such as sorghum, which are composed primarily of starch. The production of activated carbons from whole grain sorghum with phosphoric acid activation by means of two processes, i.e., one-stage and two-stage, were examined in the current study. The former followed the traditional chemical activation technique which is well documented in the

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literature; the latter was a process developed in our work (Diao et al., 1999).

2. Methods

2.1. Materials

Whole-grain sorghum with a moisture content of 15% and a grain diameter between 3 and 4 mm served as the precursor to produce activated carbons. The elemental analysis of the grain is shown in Table 1. The grain was obtained from the Department of Biological and Agricultural Engineering at Kansas State University. The activation agent of choice was *ortho*-phosphoric acid manufactured by Fisher Scientific (ACS certified). The concentration of the acid, as received, was 85% (wt). Aqueous solutions with concentrations of 10%, 20%, 35% and 50% (wt) were prepared for the impregnation of the precursors.

Nitrogen with a purity of 99.995%, supplied from a compressed gas cylinder, provided the inert gas environment under atmospheric pressure for carbonization and activation. Liquid nitrogen and ultra-pure carrier grade compressed nitrogen (nitrogen content of 99.9995%) served as coolant and adsorbate for the gas adsorption experiments, respectively.

2.2. Facilities

Carbonization and activation were conducted in a custom-fabricated tubular furnace under a steady flow of gaseous nitrogen. The electrical-resistance furnace had an inner diameter of 10.2 cm and a length of 55 cm. Cylindrical baskets made from 60 mesh stainless steel gauze served as the sample containers. The mesh size was such that it prevented sample loss.

Weighing was performed with a precision of 0.1 mg. Drying of samples was carried out in a thermal drying oven. Gas adsorption/desorption data were obtained with fully automated gas sorption analyzers (Quantachrome NOVA-1200 and AUTOSORB-1-MP).

2.3. Procedure

2.3.1. One-stage process

About 3.5 g of sorghum was impregnated with 10 ml of a phosphoric acid solution with a selected acid con-

centration for 24 h. The impregnation ratio, X_p, was calculated by assuming that all the acid in the 10 ml of solution was taken up by the precursor. This ratio is expressed as grams of phosphorus per gram of dry precursor (Molina-Sabio et al., 1995).

The wet impregnated sorghum was dried at 100 °C in an oven for 12 h and subsequently activated in a nitrogen atmosphere at a prescribed temperature. The resultant activated carbon was cooled in a stream of gaseous nitrogen and then washed batchwise at ambient temperature with demineralized water until the pH of the filtrate reached approximately 6–7. The leached carbon was then filtered, dried at 100 °C, and weighed.

The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original sorghum with both weights on a dry basis, i.e.,

$$\text{Yield} = \frac{W_2}{W_0} \times 100\%, \tag{1}$$

where W_0 is the original mass of the precursor on a dry basis; and W_2 the mass of the carbon after activation, washing, and drying.

2.3.2. Two-stage process

Approximately 4 g of sorghum was initially carbonized at 300 °C for 15 min. After cooling in a nitrogen flow, the char was ground to about 100 mesh and approximately 2 g were steeped in 10 ml of a phosphoric acid solution with a selected acid concentration for 24 h. Subsequently, the wet impregnated char was dried in an oven at 100 °C for 12 h. The impregnation ratio was based on the weight of the first-stage char. Again, all the acid in the 10 ml of solution was assumed to be taken up by the char.

The impregnated char was then activated in a nitrogen atmosphere at a selected temperature. After activation, the carbon was cooled in a stream of gaseous nitrogen and then washed batchwise at ambient temperature with demineralized water until the pH of the filtrate was approximately 6–7. The leached carbon was then filtered, dried at 100 °C, and subsquently weighed. The yield of the activated carbon is defined as in Eq. (1).

2.4. Characterization

All the carbons were dried at 130 °C until they were essentially moisture-free. Their nitrogen adsorption/desorption data were then obtained with the aforementioned gas sorption analyzers. Analysis of these data provided various properties pertaining to the porosity of the carbons.

The total surface area, S_{BET}, and the micropore volume, V_0, were determined by fitting the data to the BET (Brunauer, Emmett and Teller) equation (Yong and Crowell, 1962; Parfitt and Sing, 1976) and the D–R

Table 1
Elemental analysis of grain sorghum

Element	C	H	N	O
wt%	43.43	7.10	0.95	48.52

Note: (a) Oxygen was obtained by difference. (b) Ash content was 1.25 wt%.

(Dubinin–Radushkevich) equation (Dubinin, 1960, 1967; Dubinin, 1980), respectively. The total pore volume, V, was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined, which was 0.983 for all samples.

The average pore radius, r_p, was estimated by applying the following equation:

$$r_p = \frac{2V}{S_{BET}}. \qquad (2)$$

The pore-size distribution (PSD), i.e., the distribution of pore volume with respect to the pore size, of mesoporous activated carbons was approximated from the desorption isotherm and computed by the BJH (Barrett, Joyner and Halenda) method (Barrett et al., 1951); that of microporous carbons, by the DFT (density functional theory) method (Seaton et al., 1989; Lastoskie et al., 1993, 1994; Olivier et al., 1994).

2.5. Statistical analyses

All experiments were repeated 3–5 times to ensure reproducibility. Statistical analyses were performed using Sigmaplot for Windows version 3.01 from Jandel. Replications generally agreed within ±10%.

3. Results and discussion

3.1. One-stage process

3.1.1. Selection of experimental conditions
The results of preliminary experiments demonstrated that no substantial activation was achieved at activation temperatures of 300–400 °C for the one-stage process. The BET surface areas of these carbons were only 1–3 m^2/g. Usually, phosphoric acid activation is conducted at relatively low temperatures, around 400–500 °C. Therefore, activation temperatures of 450, 500, 600, and 700 °C were chosen for the subsequent experiments.

Based on preliminary observations, it appeared that different phosphoric acid concentrations had distinct effects on the physical characteristics of the impregnated grains. After impregnation and subsequent drying, sorghum grains impregnated with a solution of 10% H_3PO_4 remained intact, and only the outer portion of the grains turned black; almost all those impregnated with a 20% H_3PO_4 also remained intact, and only the exterior turned black. When the concentration of H_3PO_4 exceeded 35%, all the impregnated sorghum grains became a blackened paste. In addition, when the concentration of H_3PO_4 was 50% or greater, more than half of the sorghum grains floated on the surface of the solution, and the rest remained immersed; after drying, the resulting sticky mass was very difficult to handle for activation. The samples were placed in small transparent bottles for impregnation and drying; their volume change was roughly estimated. With the 10% solution, the solid volume hardly changed; with the 20% solution, it increased slightly; with the 35% solution, it at least doubled; and with the 50% solution, it at least tripled. Hence, impregnating solutions of 10%, 20%, 35%, and 50% H_3PO_4, which covered different impregnation ratios and physical features, were selected to study the concentration effect on porosity development.

When sorghum was activated at 450 °C, smoke evolution ceased after about 8 min. It was presumed that the duration of this length sufficed to eliminate all the moisture and most of the volatile components from the precursor. Hence, activation durations were selected to be 10, 15, 25, and 35 min.

3.1.2. Influence of activation duration
A typical result for an acid concentration of 35% and an activation temperature of 450 °C is presented in Fig. 1. Note that when activation duration lengthened from 10 to 15 min, the surface area increased from 173 to 182 m^2/g, which amounted to only 5%. Increasing the activation duration to 25 and 35 min caused the surface areas to decrease to 163 and 119 m^2/g, respectively. The V_0/V did not change appreciably over the duration of 10–15 min, but dropped sharply thereafter. This indicates that the pore structure of the carbon developed over a duration of 10–15 min, and a longer duration caused some of the pores to enlarge or even collapse, thus reducing the surface area and increasing the mesoporosity. Activation duration of 15 min, therefore, was selected for subsequent experiments.

3.1.3. Influence of H_3PO_4 concentration
In chemically activating with phosphoric acid, it is well known that the impregnation ratio is one of the variables having a profound effect on the porosity of the
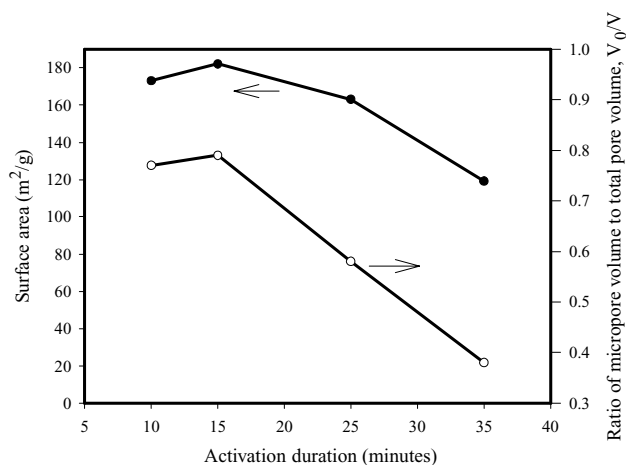

Fig. 1. Effect of activation duration: activation temperature of 450 °C and H_3PO_4 concentration of 35% for the one-stage process.

final carbons (Molina-Sabio et al., 1995, 1996). In this study, different X_p's were obtained by using the same volume of phosphoric acid solutions with different acid concentrations. A 24-h impregnation at room temperature followed by 12 h of drying at 100 °C allowed penetration of the acid into the interior of the sorghum and completion of the dehydration reactions. By adding 10 ml of acid solution to 3.5 g of sorghum and assuming that all the acid was well incorporated into the sorghum, the X_p's were calculated to be 0.11, 0.24, 0.45, and 0.71 for acid concentrations of 10%, 20%, 35%, and 50%, respectively.

The acid concentration and impregnation method affected the X_p as well as the structural and physical characteristics of the impregnated precursor. Derbyshire and coworkers studied the effect of phosphoric acid-promoted chemical and structural alterations of biopolymers on porosity development (Solum et al., 1995; Jagtoyen and Derbyshire, 1998). They found that lignin was altered significantly even at heat treatment temperatures as low as 50 °C and that a significant portion of the cellulose reacted by 100 °C. This clearly indicates that the precursors experience significant change prior to activation. As manifested by the aforementioned observations, there was a weakening of the structure of the sorghum grains, hydrolysis reactions, and an increase in elasticity during impregnation of sorghum with phosphoric acid and especially during subsequent drying. These phenomena were intensified as the phosphoric acid concentration increased.

The typical effect of acid concentration for an activation temperature of 600 °C and an activation duration of 15 min is illustrated in Fig. 2. It shows that while the surface area is substantially influenced by the phosphoric acid concentration in the impregnating solution, the V_0/V changes only slightly. The surface area increased from 156 to 528 m^2/g with an increase of acid

concentration from 10% to 35%; it decreased to 303 m^2/g when acid concentration increased to 50%. Therefore, 35% was determined to be the best concentration for porosity development. This behavior was different from earlier work with lignocellulosic precursors such as coconut shell, where surface area continued to increase with acid concentration up to 85% (Laine et al., 1989).

Observations from the impregnation and subsequent drying of sorghum indicated that the grains disintegrated and formed a paste-like substance with a phosphoric acid solution of 50% or above. The material was very sticky, and it clung to the screen basket when activated at high temperatures; this greatly increased the difficulty in handling it. In general, a phosphoric acid solution of 35% has been found to be ideal for producing activated carbons from sorghum.

3.1.4. Influence of activation temperature

An activation temperature of 450 °C has been determined to be the optimum for the highest surface area in the phosphoric acid activation of woods (Jagtoyen and Derbyshire, 1993) and coconut shell (Laine et al., 1989). Grain sorghum was not activated appreciably at temperatures between 300 and 400 °C. The typical influence of temperature for an acid concentration of 35% and an activation duration of 15 min is illustrated in Fig. 3. As can be discerned from the figure, the surface area displayed a sharp increase from 182 to 528 m^2/g with an increase of activation temperature from 450 to 600 °C, whereas V_0/V decreased sharply from 0.81 to 0.51 over this temperature range; then, a slight reduction of the surface area and V_0/V was seen when activation temperature was raised to 700 °C.

Based on the data in Table 2, the yield did not change substantially, but the average pore radius r_p was enlarged from 1.15 to 1.73 nm over the activation
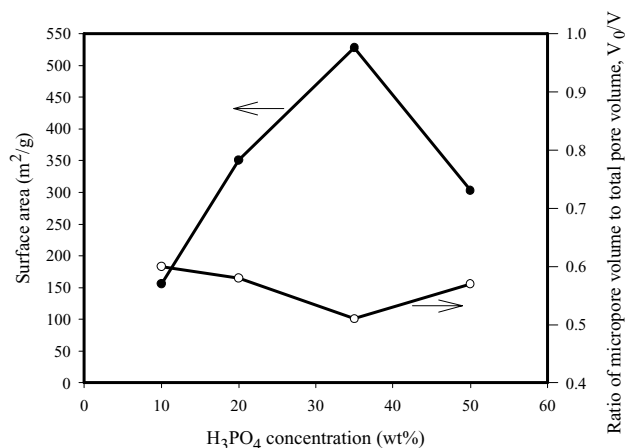

Fig. 2. Effect of H_3PO_4 concentration: activation temperature of 600 °C and activation duration of 15 min for the one-stage process.
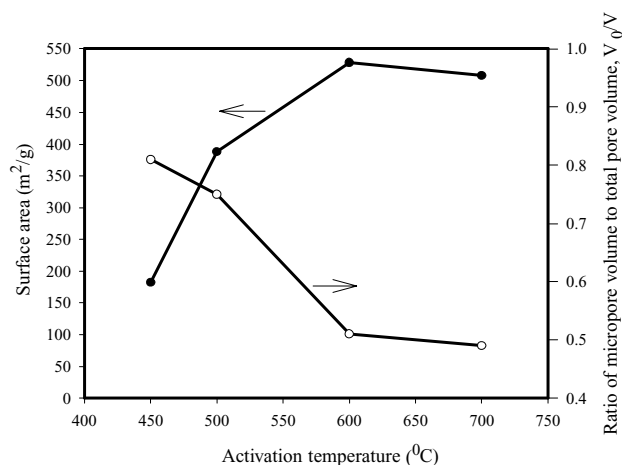

Fig. 3. Effect of activation temperature: H_3PO_4 concentration of 35% and activation duration of 15 min for the one-stage process.

Table 2
Properties of activated carbons

Activation temperature (°C)	Yield (%)	S_{BET} (m²/g)	V_0 (cc/g)	V_0/V	r_p (nm)
450	41	182	0.097	0.81	1.15
500	40	388	0.190	0.75	1.18
600	38	528	0.197	0.51	1.65
700	39	508	0.208	0.49	1.73

Activation duration of 15 min and phosphoric acid concentration of 35% for the one-stage process.

temperature range. Lower activation temperatures produced microporous carbons, but these carbons had relatively small surface areas; higher activation temperatures yielded mesoporous carbons with surface areas above 500 m²/g. The carbon with the highest BET surface area was obtained at an activation temperature of 600 °C; it was mesoporous.

3.1.5. Development of porosity

As mentioned previously, the porosity arose from the loss of volatile components and subsequent reorganization of the remaining structures. The end of the volatile evolution marked the formation of the basic pore structure; therefore, activation should not be continued beyond that point. An activation duration of 15 min was observed to be optimal for porosity development. Longer durations caused the pores to enlarge or even collapse, which increased the mesoporosity and decreased the surface areas of the resultant carbons (see Fig. 1).

Acid concentration had an effect on the amount and quality of the impregnation, and thus, had great influence on the porosity development. The nature of the resultant carbons' porosity was not substantially altered by the acid concentration, whereas the surface area was heavily dependent on the acid concentration (see Fig. 2). A solution of 35% H_3PO_4 was determined to be the best both for conducting impregnation and for the porosity development.

Activation temperature was seen to have remarkable effects on both surface area and the nature of porosity. Activation temperatures lower than 500 °C produced microporous carbons with small surface areas; temperatures higher than 600 °C yielded mesoporous carbons with high surface areas (see Fig. 3).

A noticeable transition from microporosity to mesoporosity occurs at activation temperatures between 500 and 600 °C (see Fig. 4). The indicators of this transition are the more open knees at low relative pressure and steeper branches at high relative pressure. If desorption isotherms are plotted along with the adsorption isotherms, hysteresis loops can be seen to develop at higher temperatures; this is also an indicator of a transition from microporous to mesoporous carbons. Based on the data presented in Table 2, it can be seen that the mi-
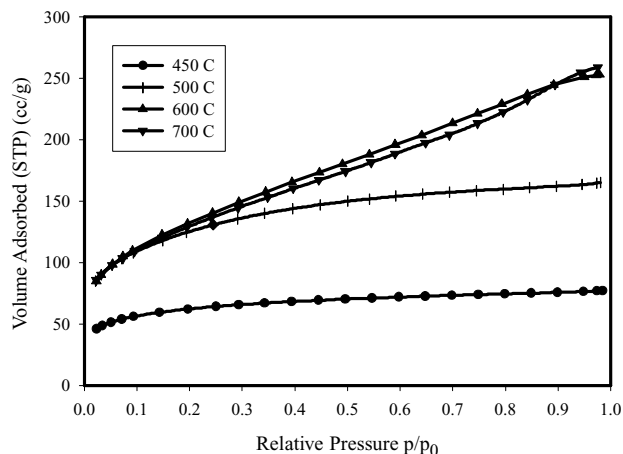

Fig. 4. Nitrogen adsorption (77 K) isotherms for activated carbons: H_3PO_4 concentration of 35% and activation duration of 15 min for the one-stage process.

cropore volume V_0 developed gradually from 0.097 to 0.208 cc/g with an increase in the activation temperature from 450 to 700 °C, but that V_0/V decreased dramatically from 0.81 to 0.49 over this same temperature range. The development of micropore volume started at about 450 °C, and increased rapidly to 0.19 cc/g at 500 °C; then it remained relatively constant until 700 °C. In constrast, mesopores developed at about 500 °C, and increased rapidly from 500 to 600 °C, causing V_0/V to decrease sharply from 0.75 to 0.51. SEM photographs (data not shown) indicated that there were no pores larger than 10 nm in these carbons. The development of micropores at lower activation temperatures and a shift to mesopore development at higher temperatures has also been observed for phosphoric acid activation of white oak (Solum et al., 1995). The BJH approximation of the PSD of the carbon with the highest surface area is displayed in Fig. 5.
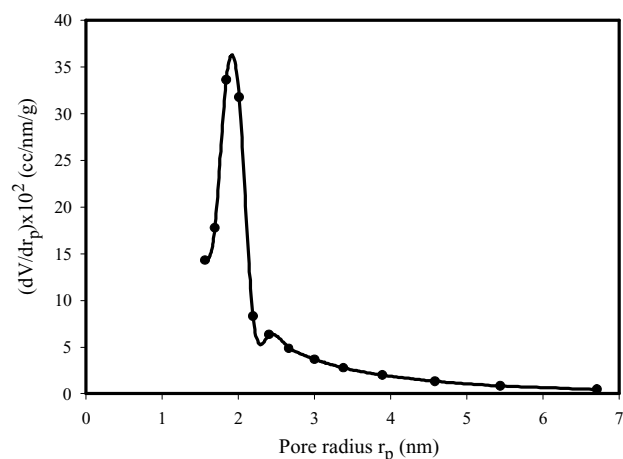

Fig. 5. Pore-size distribution of the activated carbon: activation temperature of 600 °C, activation duration of 15 min, and H_3PO_4 concentration of 35% for the one-stage process.

3.2. Two-stage process

3.2.1. Formation of the first-stage char

When sorghum was carbonized at 300 °C for 15 min, the char yield was 52%. After the carbonization, the sorghum grains expanded to disintegration; this precluded the possibility of producing granular activated carbon by the two-stage process. Adsorption experiments demonstrated that the char only had a surface area of 1 to 2 m^2/g. SEM photographs (data not shown) revealed that the char had a rough surface, and that macropores did not exist.

3.2.2. Influence of H_3PO_4 concentration

The first-stage char was ground to approximately 100 mesh and then impregnated with a specified phosphoric acid solution for 24 h. The mixture, which was paste-like, was dried in an oven at 100 °C for 12 h prior to activation at a selected temperature. By adding 10 ml of acid solution to the char obtained from 4.0 g of sorghum and assuming that all the acid was well incorporated into the char, the X_p's based on the first-stage char were calculated to be 0.19, 0.40, 0.76, and 1.19 for acid concentrations of 10%, 20%, 35%, and 50%, respectively; the X_p's based on the original dry precursor were 0.10, 0.21, 0.40, and 0.62, respectively.

The following is discernable from Fig. 6. The surface area was substantially influenced by the phosphoric acid concentration in the impregnating solution, whereas the V_0/V did not change greatly and remained above 0.80. The surface area increased from 561 to 1522 m^2/g with an increase of acid concentration from 10% to 35%; it decreased to 1381 m^2/g when acid concentration was increased to 50%. Consequently, 35% was determined to be the optimal concentration for the development of porosity.
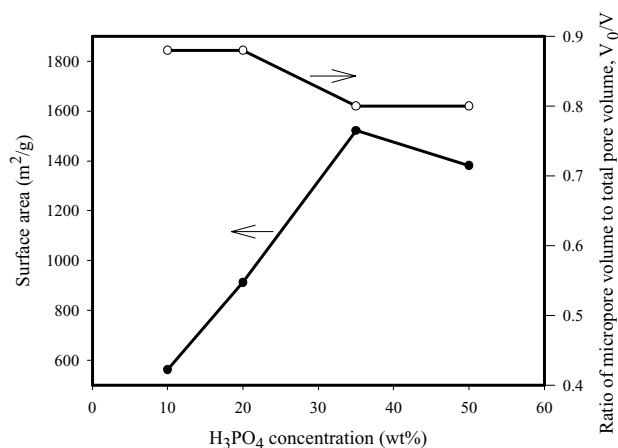
3.2.3. Influence of activation temperature

It is shown in Table 3 that the optimal temperature for porosity development is 500 °C. The surface area increased from 975 to 1522 m^2/g when the activation temperature was elevated from 400 to 500 °C; then, it decreased to 1431 m^2/g when activation temperature was further elevated to 600 °C. The V_0/V had a slight tendency to decrease with an increase in activation temperature, but remained above 0.80. As can be seen from Fig. 7, the adsorption isotherms for these carbons are of Type I, which is characteristic of highly microporous carbons.

3.2.4. Development of porosity

As in the one-stage process, acid concentration greatly influenced the surface area but not the nature of the porosity. A solution of 35% H_3PO_4 was determined to be the best for porosity development, and the carbons produced were essentially microporous with V_0/V above 0.80 (see Fig. 6).

Activation temperature also exhibited a significant influence on the surface area of the resultant carbons, but did not change their microporous nature within the temperature range 400–600 °C (see Table 3). An

Table 3
Properties of activated carbons

Activation temperature (°C)	Yield (%)	S_{BET} (m^2/g)	V_0 (cc/g)	V_0/V	r_p (nm)
400	29	975	0.517	0.92	1.06
450	29	1348	0.636	0.85	1.09
500	29	1522	0.688	0.80	1.10
600	26	1431	0.669	0.81	1.09

Activation duration of 15 min and phosphoric acid concentration of 35% for the two-stage process.

Fig. 6. Effect of H_3PO_4 concentration: activation temperature of 500 °C and activation duration of 15 min for the two-stage process.
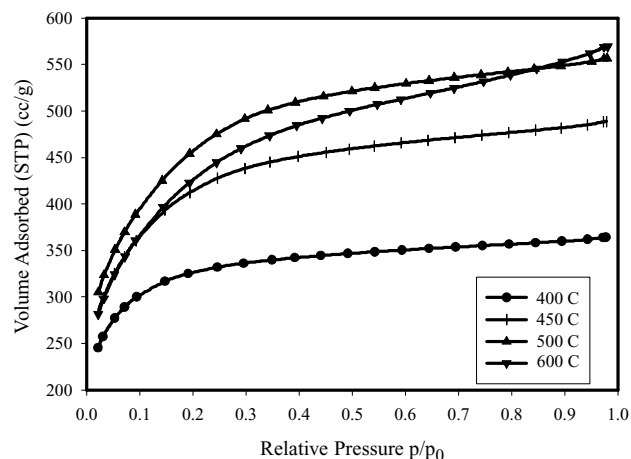

Fig. 7. Nitrogen adsorption (77 K) isotherms for activated carbons: H_3PO_4 concentration of 35% and activation duration of 15 min for the two-stage process.
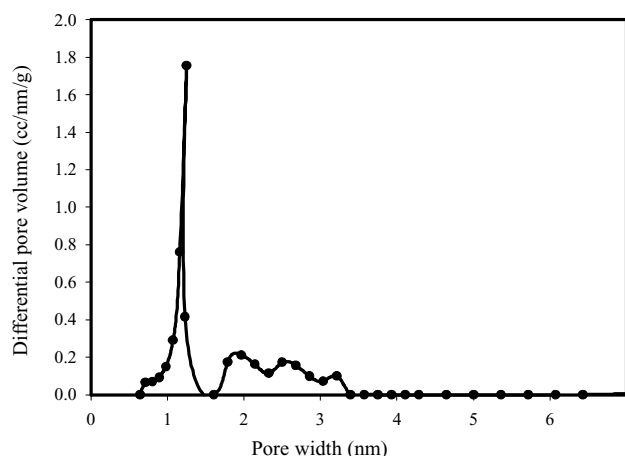
Fig. 8. Pore-size distribution of the activated carbon: activation temperature of 500 °C, activation duration of 15 min, and H_3PO_4 concentration of 35% for the two-stage process.

activation temperature of 500 °C was determined to be optimal for porosity development.

Increasing the activation temperature from 500 to 600 °C caused a slight broadening of the micropore-size distribution (see Fig. 7). The indicators for this are the more open knee at low relative pressure and a slightly steeper branch at high relative pressure. The PSD of the carbon with the highest surface area, approximated by the DFT method, is depicted in Fig. 8.

3.3. Comparison of the one-stage and two-stage processes

In both the one-stage and two-stage processes, acid concentration had a similar effect on the surface area and V_0/V of the resultant carbons: surface area was highly dependent on the acid concentration, but V_0/V was little influenced. The activation temperature greatly influenced the surface area of the carbons derived from both the one-stage and two-stage processes. In the one-stage process, activation temperature also exhibited a substantial effect on the V_0/V of the carbons; in the two-stage process, the V_0/V of the carbons remained above 0.8 within the activation temperature range 400–600 °C. The surface area of the carbons obtained from the two-stage process were found to be much higher that those from the one-stage process; this clearly demonstrates that the two-stage process enhances the porosity development.

It was also noticeable that both the V_0 and V_0/V were much larger for the carbons derived from the two-stage process than those from the one-stage process. The two-stage process produced microporous carbons within the range of the activation temperature from 400 to 600 °C and the range of the acid concentration from 10% to 50%; the one-stage process produced microporous carbons with small surface area at low activation temperatures only and produced mesoporous carbons with surface area above 500 m^2/g at high activation temperatures.

Carbon yields were within the ranges between 38–41% and 26–29% for the one-stage and the two-stage process, respectively (see Tables 2 and 3). The yield was observed to be about 12% lower with the two-stage process than with the one-stage process. However, the surface area of the carbon with the highest porosity from the two-stage process was about three times as large as that from the one-stage process. These results appear to imply that the two-stage process is superior to the one-stage process for the production of microporous activated carbons from sorghum using phosphoric acid activation.

4. Conclusions

Activated carbons can be produced from grain sorghum with phosphoric acid activation. Two preparation processes, i.e., the one-stage and two-stage processes, were investigated. It has been found that both the surface area and the nature of porosity are greatly influenced by the processing modes. Generally speaking, the one-stage process produces carbons with moderate surface areas and high mesoporosity, whereas the two-stage process yields carbons with very large surface areas and high microporosity.

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