SHORT COMMUNICATION

ACTIVATED CARBON FROM DURIAN SEED BY H_3PO_4 ACTIVATION: PREPARATION AND PORE STRUCTURE CHARACTERIZATION

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ABSTRACT

Activated carbons have been produced from the natural biomaterial durian (Durio zibethinus) seed, using phosphoric acid (H_3PO_4) as the activating agent. The effects of impregnation ratio, activation temperature, heating rate on the carbon surface area, porosity and mass yield are presented. A two step process has been used, the first step was a low temperature impregnation at 150 °C using phosphoric acid and the second step was the carbonization at high temperatures, namely, 600 and 900 °C. The most outstanding carbon with the highest surface area of 2123 m^2/g was prepared using an impregnation ratio of 2, an activation temperature of 600 °C for 4 h and a heating rate of 1 °C/min.

Keywords: *activated carbon, durian seed, phosphoric acid activation*

INTRODUCTION

Activated carbons are the most versatile and commonly used adsorbents because of their extremely high surface areas and micropore volumes [1], large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration [2]. Precursors used for the production of activated carbons are organic materials that are rich in carbon, such as coal, lignite, and wood. Although coal is the most commonly used as precursor, agricultural by-products in certain condition are a better choice [1,3]. Many agricultural by-products such as coconut shell, grain sorghum, coffee bean husks, rubber wood sawdust, chestnut wood, and fruit stones, have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents [5]. Agricultural wastes are considered to be a very important feedstock because of especially two facts: they are renewable sources and low cost materials [4-5].

Activated carbons are generally obtained using two main steps, e.g. carbonization of the raw materials below 1000 °C in an inert atmosphere followed by activation of the resulting char in the presence of suitable oxidizing agents. In carbonization, most of the non-carbon elements like hydrogen and oxygen are being removed onto gaseous form by pyrolytic decomposition resulting in a carbon with fixed mass and a rudimentary pore structure. The following activation step is then employed to enlarge the diameter of fine pores and also create new pores so that the adsorptive power of the carbonization product is enhanced [3-6].

Activation can be carried out by chemical or physical means. Generally within chemical activation process, carbonization and activation take place simultaneously as facilitated by chemical activating agents, i.e. dehydrating agents and oxidants. On the other hand for physical activation, carbonization of a precursor occurs in priori followed by their activation at elevated temperature in the presence of suitable activating agents, i.e. carbon dioxide or steam. It has been noticed that chemical activation process normally takes place at a temperature lower than physical activation process [1]. The impregnation of precursor materials with chemical agents such as $ZnCl_2$ and KOH can inhibit tar formation while also reduce the volatile matter evolution resulting in high precursor to carbon conversion. Therefore, the development of a porous structure is improved with chemical activation process [1]. Among the chemical activating agents, zinc chloride ($ZnCl_2$) in particular is the most frequently used chemical in activated carbon preparation. Nowadays however, zinc chloride is less employed due to its environmental damage. In addition, activated carbons chemically activated with zinc chloride are not suitable in pharmaceutical and food industries due to its possibility to contaminate products. Another more favorable agent, H_3PO_4 has been claimed to be the most effective acid for activated carbons production.

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To obtain very specific materials with a given pore size distribution from low cost precursors at low temperature is considered a challenge. Thus, in this work, durian seed as precursors used for the production of derived activated carbons are produced and their characteristic properties have been determined. Preparation details including the effect of various parameters onto surface development and characteristics are also given because of their important roles in adsorption.

EXPERIMENTAL SECTION

Preparation of adsorbents

Durian seed collected from local durian processing industry was used as a precursor for preparing activated carbon. The contents of carbon, hydrogen, nitrogen and sulphur in the ultimate analysis were determined by an elemental analyzer (Vario EL III) and were found to be 47.32, 8.44, 0.26 and 0.04% (w/w) respectively. The ash content was determined by heating the raw material to 650 °C for 4 h and equaled to 1.95% by weight. The results indicated that this precursor is suitable for the preparation of activated carbon because of its high carbon content and low ash content.

The durian seed was dried at 100 °C in an oven for 12 h and subsequently crushed and sieved to a particle size fraction of 500–710 µm. About 10–20 g of the resultant durian seed was impregnated with 85% phosphoric acid to the desired acid to durian seed ratio, Xp, (weight of 85% H_3PO_4 used/weight of durian seed used). The mixture was then subjected to low temperature treatment at 150 °C in the muffle furnace under the flowing of nitrogen at atmospheric pressure for 2 h, and then final heat treatment at a temperature up to 600 °C or 900 °C for 4 h with different heating rates. After the heat treatment, the carbon was cooled to room temperature in the same flow of nitrogen. The excess phosphoric acid was washed off by hot deionised water until the pH of the wash water became 6 which is the pH of deionised water. After washing, the carbons were dried at 105 °C for further analysis and characterization. The following parameters were varied: Xp (1, 2, 4, 6); heating rate (1 and 5 °C/min); activation temperature (600 °C and 900 °C). Sample name, T600/R1/X2, means that the activated carbon was produced at 600 °C with a heating rate of 1 °C/min and with Xp = 4.

Characterization of textural properties

The textural properties of the adsorbents were performed by determining the nitrogen adsorption/desorption isotherms at -196 °C using a Quantachrome Autosorb 1. The samples were degassed under vacuum at 200 °C for 6 h before measurements were made. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation (S_{BET}) and α_s method (S_α) using the standard as data reported by Katsumi Kaneko from the adsorption data of N_2 at -196 °C [7]. The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of P/P^0 = 0.97 and the average pore diameter was calculated from $D_p = 4\ V_p/S_{BET}$. Pore size distribution was estimated using the α_s method (for micropore analysis) and the Barrett-Joyner-Helenda (BJH) model (mesopore analysis). For microporous adsorbents, α_s method was employed to analyse the micropore volume (V_{micro}) and mesopore volume ($V_{meso} = V_p - V_{micro}$). For mesoporous adsorbents, the α_s method was employed to analyse the micropore volume and the BJH method was employed to estimate the mesopore volume. BJH method was also applied to estimate the pore size distribution of the adsorbents.

SEM images were recorded using JEOL JSM-6400F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during SEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere using a current of 6 mA for 3 min. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 20.00 kV.

RESULT AND DISCUSSION

Characteristics of durian seed activated carbon

T600/R1/X2 seemed to be a mixed-type of I + II of the BDDT classification [8]. This indicates that the carbon is mainly micro and mesoporous in character with a minor presence of wider pores where capillary condensation occurred. T600/R1/X4 and T600/R1/X6 exhibited type II behaviour of the BDDT classification which is indicative of the multiplayer adsorption process due to the nonporous surfaces. The hysteresis loop in the N_2 adsorption/desorption isotherm indicates the presence of mesopores. Other biomaterials converted into active carbons include; sugar beet pulp activated with carbon dioxide with surface areas 200–900 m^2/g [9]; palm shell activated with potassium carbonate with surface areas 248–1170 m^2/g [10] and rice bran activated with sulphuric acid with surface areas 200–700 m^2/g [11]. These BET values are lower than the durian seed activated carbons produced in the present study.

Different methods can be employed to analyze the surface area and pore size distribution of porous solids. Although, the BET model has some limitations for the surface area assessment, it is still used as a standard procedure for surface area determination as it

Table 1. Experimental conditions, yield, BET surface area (S_{BET}), total surface area ($S\alpha$), micropore volume (V_{micro}), mesopore volume (V_{meso}) and average pore diameter (D_p) of phosphoric acid activated carbon from durian seed.

Sample	Yield (%)	S_{BET} (m^2/g)	$S\alpha$ (m^2/g	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_p (nm)
T600/R1/X1	35.98	1559	1791	0.738	0.056	2.04
T600/R1/X2	38.85	2123	2147	0.586	0.904	2.80
T600/R1/X4	39.37	1410	1430	0.265	1.385	4.89
T600/R1/X6	38.03	1399	1422	0.140	1.801	5.32
T600/R5/X1	46.82	1129	1362	0.544	0.076	2.20
T600/R5/X2	44.58	1337	1403	0.342	0.738	3.27
T600/R5/X4	40.70	1198	1248	0.225	1.316	5.05
T600/R5/X6	40.57	1305	1338	0.209	1.598	5.39
T900/R5/X1	21.73	1474	1651	0.705	0.111	2.21
T900/R5/X2	17.00	1628	1659	0.374	0.997	3.38
T900/R5/X4	16.27	1356	1381	0.297	1.256	4.39
T900/R5/X6	15.57	697	694	0.156	0.727	4.18

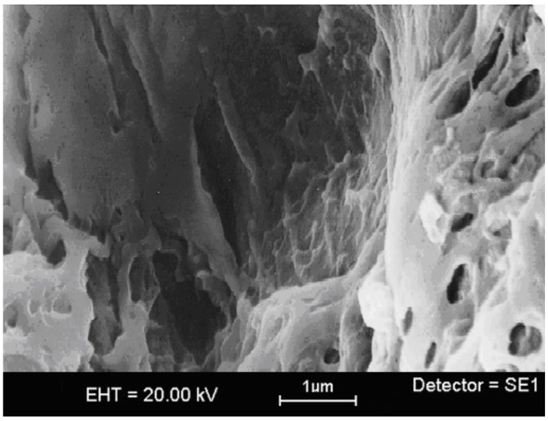

Fig 1. SEM images activated carbons at T600/R1/X2

can give an accurate assessment of surface area in many types of adsorption isotherms if there is no significant primary micropore filling contribution and the structure of the completed monolayer does not vary from one surface to another [1]. The α_s method can provide more accurate assessment of higher surface area instead of the BET method by comparison between the test isotherm and the reference isotherm. Therefore, the surface area obtained from α_s method can be used to check the surface area obtained from the BET method.

For the pore size distribution analysis, the BJH method has been widely used for mesopore analysis, however, it is limited to only mesopores due to ambiguity of the meniscus in the Microporous region [12]. Therefore, the α_s method was also employed to estimate the micropore volume. The as method is a comparison plot in which the amount adsorbed against standard data determined on a non-porous reference material and is a common and safe method to determine the micropore volume. The surface area can be estimated from the slope of first linear section connecting to the origin and the micropore volume can be determined from the intercept of the second linear section.

Based on the observations on the shape of the adsorption isotherm, the α_s theory was used to determine micropore volume and mesopore volume of T600/R1/X1 which is a microporous carbon. The mesopore volume can be calculated from the subtraction micropore volume from the total pore volume because the macropore volume is negligible for a Type I isotherm which has a distinct plateau and the total pore volume can be determined accurately at a certain predetermined P/P^0 (i.e. 0.97).

The α_s method and the BJH method were applied to estimate the micropore volume and mesopore volume of T600/R1/X2, T600/R1/X4 and T600/R1/X6 which are mesoporous activated carbons. The α_s method is not used to estimate the mesopore volume as there is no distinct plateau on the adsorption isotherm which indicates the presence of non-porosity or macroporosity in the activated carbon. The surface area, micropore volume, mesopore volume, average pore size and the preparation conditions of phosphoric acid activated carbons are summarized in Table 1.

Scanning electron micrographs of the surface morphology of sample of the activated carbons are given in Fig 1. This figure shows the external surfaces of the activated carbons prepared at T600/R1/X2. From this figures, it is obvious that the activated carbon has cavities on their external surface. It seems that the cavities on the surfaces of carbons resulted from the evaporation of the activating agent in this case is phosphoric acid during carbonization, leaving the space previously occupied by the activating agent.

Effect of impregnation ratio

The effect of impregnation ratio was studied using carbons activated at 600 °C for 4 h at four different impregnation ratios ranging between 1 and 6. The heating rate is 1 °C/min. The results show that the surface area increased initially, reached maximum at

Xp = 2 and then decreased. The total pore and mesopore volume increased with the increase in impregnation ratio but the micropore volume decreased with the increase in impregnation ratio. At Xp = 1, the activated carbon is microporous, and developed into mesoporous when Xp increases.

The porosity developed is due to the formation of phosphate linkages such as phosphate and polyphosphate esters which can serve to connect and crosslink biopolymers. These linkages expand the structure of the durian seed and phosphate compounds retained in the expanded structure and hinder the shrinkage at high temperature treatment. Activated carbons prepared from pecan shell using phosphoric acid activation showed a maximum BET surface area of 900 m^2/g at an impregnation ratio of 1.5 [13].

Effect of activation temperature

The effect of heating temperature was studied using carbons activated at 600 °C and 900 °C. The heating rate is 5 °C/min and the impregnation ratio used is 2. It was found that the yield of activated carbon prepared at 900 °C is around 20% which is 20% lower than the yield of activated carbon prepared at 600 °C. It was due to (i) the loss of most of the volatile matter, (ii) the loss of phosphate compounds, and (iii) the resultant carbon volatilization once the formerly protecting phosphate compounds are lost. Under high activation temperature and high impregnation ratio, the porosity and surface area decreased sharply as a considerable portion of phosphate compounds volatilise when the temperature is above 800 °C. Although, it was found the volatilization can produce new pores and increased porosity at high activation temperature, this enhancement may be limited only to the activated carbon with low impregnation ratio [13]. During the production of activated carbons from cassava peel, increasing temperature from 450 °C continually increased surface area development from 972 to 1378 m^2/g [14].

Effect of heating rate

Carbons were activated at 600 °C for 4 h at two heating rates which are 1 and 5 ºC/min. The results showed that a slower heating rate can enhance the development of microporosity and hence enhance the development of surface area. The increase in surface area at a lower heating rate may probably be due to the longer contact time for the phosphoric acid and the biopolymer to react before the contraction temperature is reached. There are very few references in the literature referring to durian seed derived activated carbons despite the encouraging results reported in the present paper. Previous work reporting surface area values only for durian seed carbons, include surface area values around 400–500 m^2/g [15], steam activation produced values of 1038 m^2/g [16] but with alkaline potassium hydroxide, surface area values of 1413 m^2/g [17]. The last value is the highest value reported. In the present study using phosphoric acid, most surface areas were greater than 1000 to over 2000 m^2/g with mass recovery yields of 35–47% w/w.

CONCLUSION

A series of activated carbons has been produced using durian seed as a raw material. A two step process has been used, the first step is a low temperature impregnation at 150 °C using phosphoric acid and the second step is the carbonization at high temperatures, namely, 600 and 900 °C. Heating rate, impregnation ratio and activation temperature are all sensitive conditions for the surface area development. For carbon producing at 600 °C, decreasing the heating rate can increase the surface area. Increasing the impregnation ratio can increase the surface area initially and then decrease the surface area. For carbon production with a heating rate of 5 °C/min, increasing activation temperature can increase the surface area when the impregnation used is less than 4. The most outstanding carbon with the highest surface area of 2123 m^2/g was prepared using an impregnation ratio of 2, an activation temperature of 600 °C for 4 h and a heating rate of 1 °C/min.

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