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Physical Characteristics of Activated Carbon Derived from Durian Shell

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Durian shells are easily available agricultural by-products and its large quantities of generation make it a potential source for production of low cost activated carbon. This study was performed to determine the characteristics of activated carbon prepared from durian shell. Ultimate and proximate analysis for raw material was determined. The durian shell activated carbon was prepared from impregnating the sample in 5, 10, 20 and 30 % (v/v) concentration of phosphoric acid for 24 h, followed by carbonization at different temperatures in nitrogen atmosphere. The results showed that various treatment conditions affect the percentage of yield, surface area and pore structure. The highest BET surface area 1404 m^2/g was obtained at 30 % of acid concentration, 500 °C and 20 min of heating.

Key Words: Durian shell, Activated carbon, Phosphoric acid, BET surface area.

INTRODUCTION

Activated carbon has highly adsorptive efficacy and is mainly affected by its porous structure, the pore size and their distribution. Well-developed pore structure activated carbon is widely used as adsorbents, catalysts and catalysts supports. Commercialized activated carbon was proven to be effective for removing acid dye from industries[1]. Due to high production cost, the commercialized activated carbons are expensive and usually not economical for large scale applications.

Utilization of biomass from agricultural wastes as a raw material for production of activated carbons is steadily increasing especially in countries which are practicing agriculture as their main economic resources. Agricultural country like Malaysia has abundant of agriculture by-products which may caused many environmental issues. Agriculture residues such as coconut shell[2], rice husk[3], oil palm shell[4], rubber wood saw-dust[5], grain sorghum[6], corn cob[7] and jackfruit peel[8] are proven to be suitable precursor for activated carbon due to high carbon content and low ash content. Furthermore, production of activated carbon from agricultural by-products was more economically promising compared to conventional method[9].

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There are several methods that can be used for the preparation of activated carbons from biomass, these include chemical activation and physical activation techniques. Chemical activation is done by impregnating the raw material into chemical agents and followed by pyrolysis in inert atmosphere at high temperature. Chemical activation of lignocellulosic material using phosphoric acid has been carried out by many researchers. It is proven to be an effective activating agent. According to Patnukao and Pavasant[10], activated carbon prepared using phosphoric acid activation method produced high BET surface area and iodine adsorption. Physical activation comprise of two stage processes of carbonization of raw material in inert atmosphere and activation of the char at high temperature in the presence of carbon dioxide or steam[11]. Combinations of chemical and physical activation seem to be promising preparation of effective carbon adsorbents too[12].

Durian is a fruit of trees from the genus of *Durio* belonging to the family of Malvaceae which is native to Brunei, Indonesia and Malaysia. There is about 30 recognized *Durio* species with at least nine of which produce edible fruit. *Durio zibethinus* is the only species available in the international market. In Malaysia, about 376,273 metric tonne of durian are produced[13] in year 2008 and this may caused environmental problems if the durian wastes are not well managed.

There are a lot of literatures on preparation of activated carbon and its application from different materials but there is not much information on production and utilization of durian shell as activated carbon precursor. The objective of this study is to evaluate the physical characteristics of activated carbon prepared from durian shell at different activation temperature and phosphoric acid concentration.

EXPERIMENTAL

The durian shells were obtained from the markets in Serdang, Selangor. The shells were washed and cut into 1-2 cm particle size before being dried in an oven overnight to reduce the moisture content. The activation agent of choice was orthophosphoric acid of 85 % (Merck). Aqueous solution with concentration of 5, 10, 20 and 30 % (v/v) were prepared for the impregnation of the sample. Nitrogen gas with purity of 99.995 % in compressed gas cylinder was used to provide inert gas atmosphere during carbonization stage.

Ultimate and proximate analysis: The moisture content of the samples was determined by drying the sample in an oven at 135 °C for 2 h until a constant weight was obtained[14]. Ash content was determined[14] by dry-ashing in a furnace at 600 °C for 2 h. The analysis of C, H, N and S on the raw material was carried out using elemental analyzer (LICO-CHNS 932). The oxygen content was calculated by the difference.

Preparation of activated carbon: Chemical activation method using phosphoric acid was used to activate the raw material. Ten gram of raw sample was impregnated in 100 mL of different concentration of phosphoric acid for 24 h. After impregnation, the wet samples were dried in oven for 12 h (*ca.* 85 °C) and subsequently activated in nitrogen atmosphere at 400, 500, 650 and 800 °C, respectively with heating rate of 5 °C/min. The soaking duration at final temperature was set at 20 min. The activated samples were cooled in a stream of gaseous nitrogen to room temperature. Then, the samples were washed at ambient temperature with distilled water until the filtrate reached approximately pH 6-7. The samples were then dried at 85 °C in an oven for overnight to make sure that they were moisture-free. Finally, the samples were kept in desiccators for further use.

Characterization of activated carbon: The activated carbon was degassed at 350 °C in a vacuum condition for at least 24 h. The porous structure parameters were determined from the nitrogen adsorption isotherm measured at -196 °C using an automatic Micromeritics ASAP 2010 volumetric sorption analyzer. The specific surface area was calculated using (Brunauer, Emmett and Teller) BET method. Total pore volume was determined by estimating the amount of nitrogen adsorbed at a relative pressure (P/P_o) of 0.95.

RESULTS AND DISCUSSION

Raw material analysis: The moisture content and ash content for the durian shell was 11.27 and 4.84 %, respectively. Ultimate analysis from Table-1 showed that durian shell has 39.3 % of carbon and 53.74 % of oxygen. High carbon percentage and low ash content suggested that durian shell can be potential activated carbon precursor. Similar result was obtained by using turkey manure as granular activated carbon precursor[15].

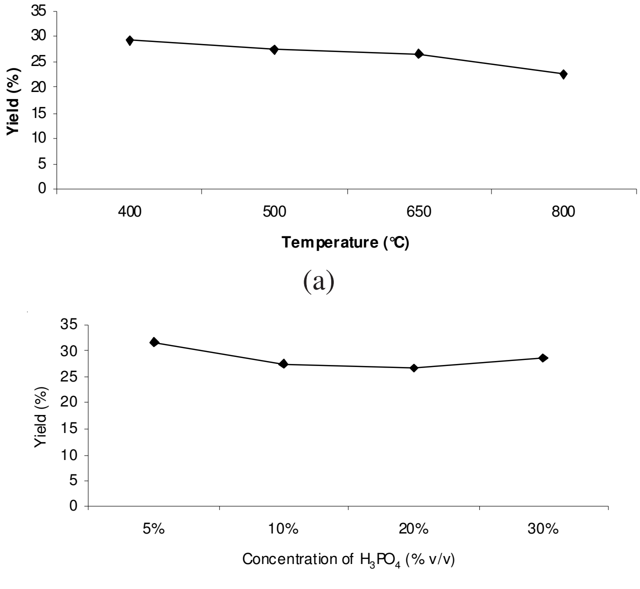
TABLE-1
PROXIMATE AND ULTIMATE ANALYSIS FOR DURIAN SHELL

Proximate analysis (%)		Ultimate analysis (%)				
Moisture content*	Ash content**	C	H	N	S	O
11.27	4.84	39.30	5.90	1.00	0.06	53.74

*Wet basis; **Dry basis.

Yield of activated carbon: Fig. 1 presents the percentage of yield obtained from the production of activated carbon derived from durian shell in different activation temperature and concentration of acid. Decreasing of yield was obtained as the activation temperature increased, range from 29.29 to 22.67 %. This trend is as expected because higher temperature will have higher tendency for the volatiles or hydroaromatic structure to be broken up and stripped from the raw material as gaseous products[16].

While varying the concentration of acid, the yield decreased from range of 31.64 to 28.73 %. As the concentration of the acid increased from 5 to 20 %, the percentage yield produced start to decline but the yield increased slightly as the acid concentration was increased from 20 to 30 %. Phosphoric acid as activating agent plays an important role in the increment of yield. The presence of phosphoric acid during activation enhances depolymerization, dehydration and redistribution of constituent biopolymers contributed to the conversion of aliphatic to aromatic compounds[8]. Furthermore, when pyrolysis occurred, cross-linking is further promoted with the increase in the carbon, reduces in tar formation, inhibition of shrinkage and develop-ment of extensive pore structure may cause increasing in the yield of the activated carbon[17].



(a)

(b)

Fig. 1. Effects of (a) activation temperature and (b) concentration of acid on the yield of activated carbon

Effects of activation temperature on pore characteristics: Activation temperature is an indispensable parameter in determining the physical structure of the activated carbon. Acid concentration used was 10 % and the soaking time was set at 20 min since soaking time does not have much effect on the development of pores[18]. The detail of pore characteristics was shown in Table-2 and Fig. 2 illustrate the development of pores corresponding to different activation temperature at 10 % of acid concentration and 20 min of soaking time. As can be seen in Fig. 2, the total volume and micropore volume increased as the temperature was increased from 400 to 500 °C. Further increase of temperature showed a reduction of micropore volume and total volume. However, in term of ratio for micropore volume to total volume (V_m/V_t), 0.46, 0.60, 0.61 and 0.76 was obtained at 400, 500, 650 and 800 °C, respectively. This increasing trend described that as the temperature increased, the pore become narrower because at low impregnation ratio and high temperature, there is possibility of volatilization enhancing new pores and increased porosity[19]. This is supported by the results of average pore diameter that reduced through the temperature range (Table-2).

TABLE-2
PORE CHARACTERISTICS OF ACTIVATED CARBON
DERIVED FROM DIFFERENT TEMPERATURE

Sample (°C)	S_{BET} (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)	Total volume (cm^3/g)	Average pore diameter (Å)
400	390	136	0.07	0.15	27.80
500	1024	404	0.21	0.35	25.35
650	789	308	0.16	0.27	24.43
800	926	427	0.23	0.30	22.50

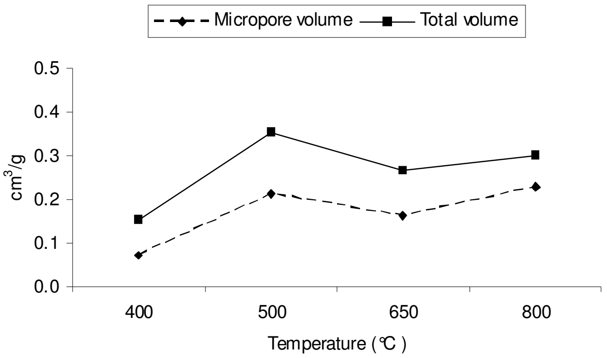


Fig. 2. Effects of temperature on pore evolution (10 % acid concentration)

Hysteresis loop was observed in all the nitrogen adsorption/desorption isotherm of the activated carbon produced from different temperature (Fig. 3). It explained that there is certain contribution of mesopores in their porous structure. Hysteresis loop is usually found in all the mesoporous carbons which are caused by pore connectivity effects[20]. From Table-2, the result of BET surface area shows a sharp increase from 390 to 1024 m^2/g with an increase of activation temperature from 400 to 500 °C and decreased to 789 and 926 m^2/g at 650 and 800 °C, respectively. At higher temperature, the burn-off rate is higher producing more ash and this may contribute to the reduction of surface area. Thus, the optimum temperature was obtained at 500 °C with highest BET surface area (1024 m^2/g), micropore volume (0.21 cm^3/g) and total volume (0.35 cm^3/g). For this reason, 500 °C has been selected for further study of the effects of phosphoric acid concentration on the development of pore.

Effects of phosphoric acid concentration on pore characteristics: Acid concentration or impregnation ratio is one of the important variables that influence the pore structure of the activated carbon. In this study, fixed volume of different acid concentrations was impregnated with the durian shell for 24 h. Assuming that all the acid was incorporated with the raw material, the calculated impregnation ratio, X_p was 0.7, 1.4, 2.8 and 4.2 for 5 %, 10 %, 20 % and 30 %, respectively. Impregnation ratio was defined as the amount of phosphoric acid incorporated with the sample[21]. The carbonization condition was set at 500 °C and 20 min of soaking duration.

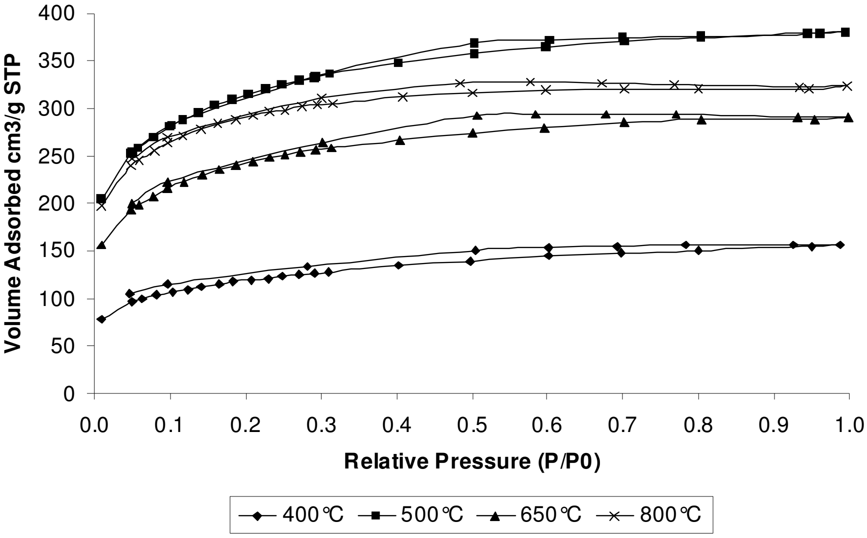


Fig. 3. Adsorption/desorption isotherm of nitrogen at -196 °C on activated carbon prepared from different temperature

The effect of acid concentrations on the development of pore structure is very significant as shown in Fig. 4. As the concentration of acid increased, the total pore volume increased and the micropore volume also increased from 5 to 10 % but started to decreased from 20 to 30 % of acid concentration. This indicated that the pore of the carbon are widen as the acid concentration increased because reaction between raw material are more intensive due to more phosphoric acid being incorporated into the raw material subsequently led to pore enlargement[22]. Similar result was reported that low impregnation ratio produced mainly micropore and increased of impregnation ratio has widen the micropores to mesopores[18]. Table-3 displayed the pore characteristics of activated carbons from varied acid concentrations. The BET surface area is influenced by the amount of acid concentration. It is noted here that the surface area increased drastically from 350 m^2/g at 5 % to 1024 m^2/g at 10 % and continue to increase to 1404 m^2/g at 30 % of acid concentration. Many studies have proven that BET surface increasing accordingly to the phosphoric acid concentration up to a certain level of concentration[6,8,23].

TABLE-3
PORE CHARACTERISTICS OF ACTIVATED CARBON DERIVED FROM DIFFERENT ACID CONCENTRATION

Sample (%)	S_{BET} (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)	Total volume (cm^3/g)	Average pore diameter (Å)
5	350	232	0.12	0.14	25.95
10	1024	404	0.21	0.35	25.35
20	1390	171	0.09	0.69	32.61
30	1404	112	0.05	0.79	33.07

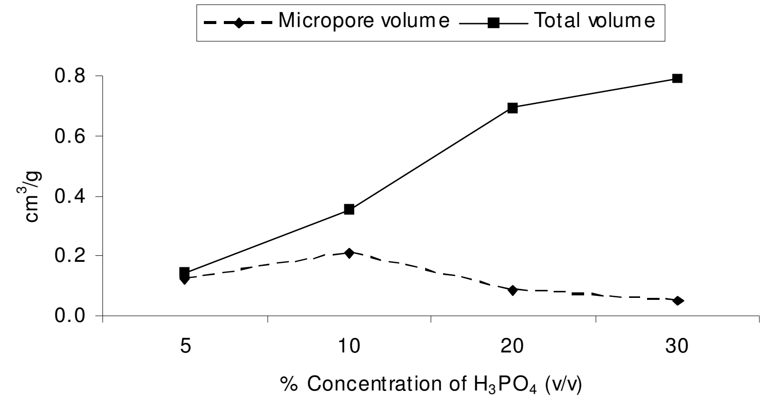


Fig. 4. Effects of acid concentration on pore development

A typical effects of acid concentration on the nitrogen adsorption/desorption isotherms is illustrated in Fig. 5. A transition of micropores to mesopores was observed in the isotherms. The hysteresis loop has become larger at the carbons produced at 20 and 30 % compare to the carbons from 5 and 10 %. The ranges of the average pore diameter are from 25.950 to 33.067 Å, which are classified as mesopore carbon according to the classification of pores proposed by IUPAC[24]. Therefore, 30 % (v/v) of phosphoric acid concentration was generally determined to be the best concentration for the development of high surface area mesoporous carbon from durian shell.

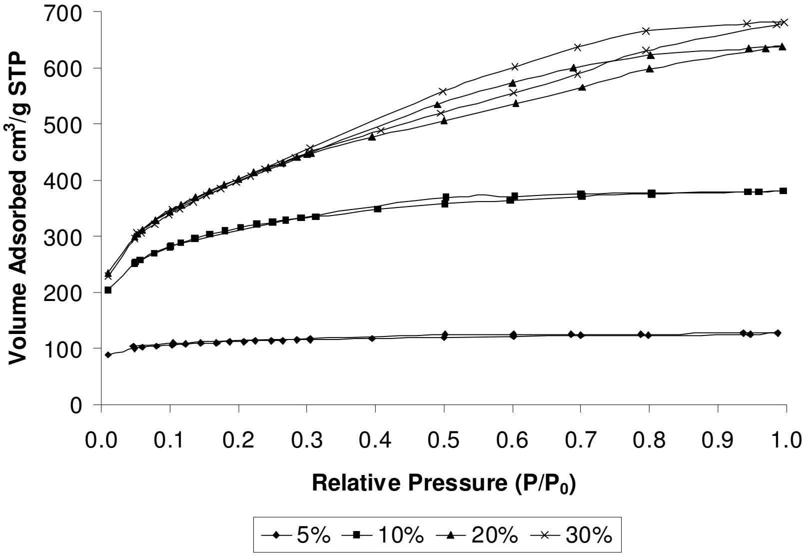


Fig. 5. Adsorption/desorption isotherm of nitrogen at -196 °C on activated carbon prepared from different acid concentrations

The comparison of the characteristics of activated carbon produced in this work with other types of raw materials and activating agent as in Table-4, shows that durian shell has the highest yield of activated carbon produced among all the other agricultural wastes. Chandra *et al.*[25] also reported that durian shell can be activated by KOH. However, higher BET surface area was obtained by activation of durian shell with phosphoric acid. Incorporating with phosphoric acid produces a dehydrating effect on the material during carbonization while KOH does not act as dehydrating agent and it is believed that activation consists in a redox reaction, oxidizing carbon to CO or CO_2 to create porosity[21]. Thus, phosphoric acid is a better activating agent compared to KOH for durian shell. Durian shell is a good raw material for preparation of activated carbon because with only short interval of heating duration, low heating temperature and reasonable acid fraction, it produced high BET surface area compared to other studies. This suggested that lower temperature and shorter heating duration can lower the cost of production as well.

TABLE-4
COMPARISON OF PREPARATION AND CHARACTERISTICS OF ACTIVATED CARBON FROM THIS WORK WITH OTHER STUDIES

Description	This work	Ref. 25	Ref. 26	Ref. 10	Ref. 27
Raw material	Durian shell	Durian shell	Palm shell	*Eucalyptus* bark	Hazelnut bagasse
Activation temperature (ºC)	500	400	800	500	700
Heating duration (min)	20	60	120	60	120
Impregnation ratio (sample:acid)	1: 4 with H_3PO_4	1:2 with KOH	1:1 with K_2CO_3	1:1 with H_3PO_4	1:3 with KOH
Yield (%)	28.73	n/a	18.86	26	n/a
BET surface area (m^2/g)	1404	991.82	1170	1239	1642

n/a – data not available.

Conclusion

Activation temperature and concentration of acid have significant influence on the physical characteristics of the activated carbon prepared from durian shell. The carbon with highest surface area (1404 m^2/g) was obtained by 30 % concentration of phosphoric acid, activation temperature of 500 °C and 20 min of heating duration. The activated carbons produced showed the mesopores carbon characteristics. Therefore, activated carbon prepared from durian shell has the potential to become a low cost effective adsorbent.

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