



Physical Characterization of Activated Carbon Derived from Mangosteen Peel

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Mangosteen fruits have gained some great attention in fruit juice industry and the solid generated could be use as potential source for activated carbon production. In order to determine the potential of using mangosteen husk, the raw mangosteen peel was subjected to ultimate, proximate, biopolymer and thermogravimetric analysis. Furthermore, activated carbon derived from mangosteen peel was prepared by impregnating the sample with different phosphoric acid concentration (10, 20, 30 and 50 %) for 24 h with heating rate of 5 min together with activation duration for 20 min until the desired temperature 850 °C with presence of flushing of nitrogen gas. The sample was characterized by using micrometric ASAP 2010. The results revealed that acid concentration affect the surface area, yield of activated carbon and pore structures. The highest surface area with high micropore volume was obtained at 30 % acid concentration with 731 m²g⁻¹ and 0.33 cm³g⁻¹ respectively.

Key Words: Mangosteen husk, Phosphoric acid, Activated carbon, BET surface area.

INTRODUCTION

Activated carbon is porosity (space) enclosed by carbon atoms. It is an absorbent widely been applied in liquid or gas-phase application, as catalyst support, in food and beverage industries, pharmaceutical sectors and others due to the high porous texture and large adsorption capacity. The adsorption capacities of activated carbon depend not only on the surface area but other properties such as internal surface area, pore volume and pore size distribution also play important role as well^{1,2}. Earlier, activated carbon was produced by using precursor such as natural wood, coal and petroleum residue^{3,4}. However, the high demand of activated carbon and competitive price of this material together with high expense for regeneration of this material has enforced research toward utilization of various wastes. Waste is being considered as important feedstock since it is produced in large quantities and at the same time can reduced the disposal problem⁵. Among the wastes that have been extensively studied by researchers include coconut shell, coffee bean husk, durian shell, grain sorghum, apple pulp and others^{1,6-9}. Suzuki *et al.*¹⁰ stated at positive view that activated carbon prepared from agricultural by-products can be achieved at reasonable cost of US\$ 20 per kg and are comparable with commercial activated carbon.

Activated carbon can be prepared by employing physical or chemical activation or both. Physical activation involves

carbonization of sample followed by activation of obtained chars in the presence of activating agents such as air, steam or carbon dioxide^{6,11} meanwhile chemical activation involve impregnation of material with certain chemical reagents within certain duration followed by carbonization⁶. Chemical activation offer some advantages if compared to physical activation. It gives higher yield and usually can be carried out at lower temperature^{1,11,12}. Chemical agents that commonly used are zinc chloride, potassium hydroxide, sodium hydroxide, phosphoric acid and others¹³. However, phosphoric acid is preferred compared to zinc chloride due to environmental contamination¹⁴.

Mangosteen is one of the famous fruits in Malaysia and it is widely grown in Asian tropics. The weight of each fruits is approximately 55-75 g and only 25-30 % is considered as edible portion¹⁵. In Malaysia, approximately 29495 metric tones of mangosteen are generated in 2009 compared in 2003 which are only 18747 metric tones¹⁶. The fruit is gaining highly recognize recently by the grower and exporter. Furthermore, the rind or peel of the fruit posses hardened characteristics when exposed to air which make it as alternative candidate for activated carbon production.

Currently, there is no adsorption studies being conducted using mangosteen peel as adsorbents for activated carbon production. Therefore, this research is focussing mainly on assessed of mangosteen peel as absorbent and effect on

impregnation ratio of phosphoric acid in the development of porosity in activated carbon preparation.

EXPERIMENTAL

Sample preparation: Mangosteen peels used in this study were collected from Serdang supermarket. The pulps were removed from the fruits and peels were washed several times with distilled water to remove dirt, colour and impurities present in the material. Then, the peel were cut to obtain particle size of 1-2 cm and dried at 70 °C for 2 h to reduce the moisture content. The clean draw mangosteen peels was ensured to be completely dried to prevent formation of spores in the sample and was stored in desiccators for later use.

Raw material characterization

Ultimate, proximate and biopolymer analysis: The ultimate analysis consist of carbon, hydrogen, nitrogen, sulfur and oxygen was done by using Leco CHNS-932 elemental analyzer (Model Leco-Truspec®) while proximate analysis consist of ash and moisture were determined by using AOAC method¹⁷. Moisture content was determine by drying sample in oven at 135 °C for 2 h and ash by heating sample in muffle furnace at 600 °C for 2 h. Biopolymer analysis of cellulose, hemicellulose and lignin were analyzed by using fiber technology system 2010 instrument based on Van-Soest method.

Thermogravimetric analysis: The thermogram of raw mangosteen peel was obtained using Mettler-Toledo (TGA/STDA 851e) instrument to determine the decomposition behaviour of raw material. Approximately, 12.4930 mg of sample were placed in ceramic crucible and heated from 25 to 1000 °C at a heating rate of 5 °C per min under flushing nitrogen gas (50 mL/min).

Preparation of activated carbon using chemical activation: Ten gram of mangosteen peel was weighed and impregnated with 100 mL of different phosphoric acid concentration for 24 h in order to obtain different impregnation ratio. The impregnation ratio was calculated by assuming all the acid present in 100 mL of solution was taken up by the precursor. The impregnation ratio was expressed as gram of phosphorus per gram of dry precursor. By assuming that all the acid was well incorporated into the raw material, the impregnation ratio X_p 's was calculated to be 1: 1.4, 1: 2.8, 1: 4.2 and 1: 8.4 for acid concentration of 10, 20, 30 and 50 % respectively.

The wet impregnated samples were dried in an oven for 12 h at 85 °C and they were placed on a ceramic boat, which were then placed in the centre of a tube furnace. The furnace used in this study is programmable temperature controllers, which provided control of heating rate, temperature and heating time. The samples were heated at 850 °C with heating rate of 5 °C per min and continuous nitrogen flow of 150 cm³ min⁻¹ were supplied throughout the activation process. The samples were held at final temperature for 20 min before cooling down to room temperature. Then, the samples were washed with distilled water several times followed by 0.1 M NaOH solution until the pH of the filtrate reached approximately around pH 6-7. The wet samples were dried at 85 °C in oven overnight and weighed.

The yield of activated carbon is defined as the ratio of the weight of activated carbon to the original material with both weights on a dry basis.

Activated carbon characterization

Physical characterization of prepared activated carbon: In the process of characterization of prepared activated carbon, the sample was degassed at 200 °C for few hours to eliminate impurities and dehydrate the sample. The specific surface area and pore size distribution of the prepared activated carbon were determined by using automatic Micromeritics ASAP 2010 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.

Scanning electron microscope: The scanning electron micrograph was done to identify the surface morphology of raw and activated carbon by using JEOL JSM 6400. Activated carbons that have good quality based on the results from physical characterization were selected for SEM analysis. Samples were dried for few hours before sticking the sample onto the stub using double-sided tape and were coated with gold coating. The stub was place into the vacuum chamber of SEM instrument. The morphology scanning were performed using different magnifications to obtain clear images.

RESULTS AND DISCUSSION

Raw material characterization: The results of ultimate, proximate and biopolymer analysis of raw mangosteen peel is tabulated in Table-1. The ultimate analysis consist of carbon, hydrogen, oxygen, nitrogen and sulfur are C-39.1 %, H-5.5 %, N-1.0 %, O-54.37 %, S-0.03 %, respectively. The results of ultimate analysis are very similar to activated carbon prepared from durian shell with C-39.3 %, H-5.9 %, N-1.0 %, O-53.74 %, S-0.06 %¹⁸. Proximate analysis gave 22.8 % of moisture and 9.9 % of ash conclusively. The high carbon content and reasonable ash content together with low inorganic matter derived from mangosteen peel revealed the potential of using this precursor since that is the important criteria in selecting material for activated carbon production. The differences of elemental analysis of this material compared to other material that successfully converted to activated carbon are given in Table-2. The chemical composition of mangosteen peel consist of cellulose, hemicellulose and lignin are 6.61, 12.15 and 48.63 % respectively. The fraction of lignocellulosic composition in the precursor mainly influences the pore distribution in activated carbon produced. In addition, the porosity development in activated carbon mainly depends on the nature of precursor together with method employed for activated carbon production¹¹. Ncibi *et al.*¹⁹, stated that the presence of high lignin content derived from the raw precursor can be considered as capable precursor in activated carbon production. Apart from that, the hardness posses by mangosteen peel after exposure to air indicate the suitable of precursor in production of granular activated carbon.

Thermogravimetric analysis: Fig. 1 represent the thermogravimetric (TG) and differential thermogravimetric (DTG) curve of the raw mangosteen peel conducted under

nitrogen flow. Mangosteens are classified as lignocellulosic material since it is composed of lignin, cellulose and hemicellulose that make up the total composition around 67 %. The decomposition reaction of pyrolysis in the material can be articulated by following reaction²⁰:



Ultimate analysis ^a (%)	
Carbon	39.1 \pm 4.30
Hydrogen	5.50 \pm 0.30
Nitrogen	1.00 \pm 0.20
Sulfur	0.03 \pm 0.02
Oxygen*	54.37
Proximate analysis ^a (%)	
Moisture ^b	22.8
Ash	9.90
Volatile matter	12.9
Fixed Carbon*	54.4
Biopolymer analysis ^a (%)	
Hemicellulose	12.15
Cellulose	6.61
Lignin	48.63

*Estimated by differences, ^avalues on dry basic, ^bvalues on wet basic

Description	Ref. 12	Ref. 1	Ref. 7	This work
Raw material	Jackfruit peel	Cassava peel	Apple pulp	Mangosteen husk
Carbon content	35	59.31	49.6	39.1
Oxygen content	-	28.74	38.2	54.37
Ash content	4	0.30	2.60	9.90

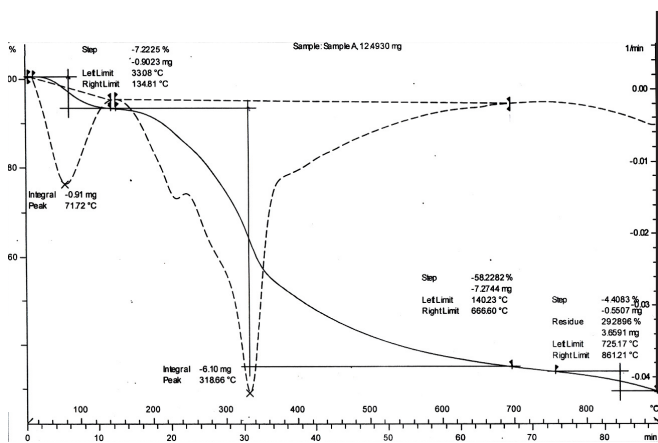


Fig. 1. Thermogravimetric/differential thermogravimetric curve of raw mangosteen peel

The decomposition behaviour of mangosteen peel occurs in four stages. The first stage occurred at 80 °C, second at 270 °C, third around 320 °C and fourth and finally at 700 °C. The first stage might be due to moisture released from the material with mass loss (22 %). The second stage and third stage correspond to hemicelluloses and cellulose degradation which occur around

200-400 °C²¹. As seen in Fig. 1, the last stage involves degradation of lignin, which occurs throughout the whole range of temperature²¹. In addition, difficulty arises in comparison of thermal degradation of one material to another due to different chemical composition (cellulose, hemicelluloses and lignin fraction), heating rate, temperature, inorganic substances present in the sample are the factors affecting the thermal behaviour²². The thermal decomposition of the mangosteen peel was completed around 700 °C due to no significant weight loss was observed. However, in this study activation temperature selected for activated carbon preparation was 850 °C, which was 150 °C higher than 700 °C to ensure complete decomposition of organic compounds and liberation of volatiles.

Activated carbon characterization

Effect of acid concentration on yield of activated carbon: The yield of activated carbon prepared at different phosphoric acid concentration is displayed in Fig. 2 in terms of percentage. The yield of activated carbon can be elaborated as a ratio of the weight of resultant activated carbon to the original precursor, mangosteen. The yield of activated carbon prepared at different phosphoric acid concentration is in the range of 30.73-35.09 %. The pattern showed that the activated carbon yield decreased from 32.18 to 30.73 % when the ratio of phosphoric acid increased from 10 to 20 % concentration. However, at higher phosphoric acid concentration 30-50 %, the yield was observed to increase. Chemical activation commonly increases the yield of activated carbon and phosphoric acid as an activating agent plays an important role during carbonization by promoting depolymerization, dehydration and redistribution of chemical composition followed by conversion of aliphatic compounds to aromatic compounds and thereby enhances the yield of activated carbon¹².

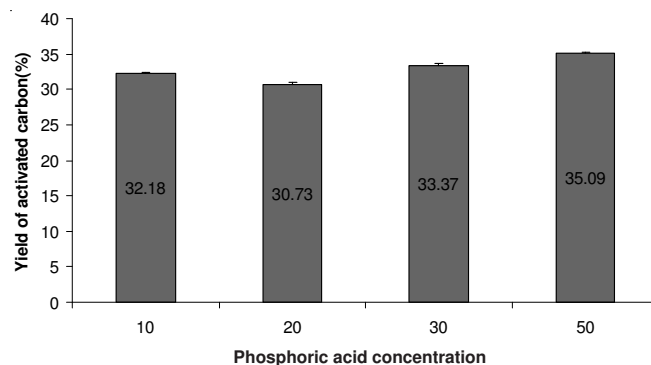


Fig. 2. Yield of activated carbon obtained at different acid concentrations. The error bars represent the mean \pm standard error where n = 3

Effect of acid concentration on pore development: Impregnation ratio is one of the important variables in controlling the frame of pore networks. A series of activated carbon with different phosphoric acid concentrations were prepared and evaluated in order to study the effect of impregnation ratio. The pore characteristics obtained for all the prepared activated carbon were tabulated in Table-3. As shown in Table-3, initially the surface area of raw mangosteen peel was found to be 0.66 m² g⁻¹ only, which did not even exceed 1 m² g⁻¹. After carbonization, the raw material impregnated with different concentrations of phosphoric acid, all the activated carbons produced

TABLE-3
PORE CHARACTERISTICS OF RAW MATERIAL AND ACTIVATED CARBON WITH DIFFERENT ACID CONCENTRATION

Sample (%)	S_{BET} (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)
Raw material	0.6598	-0.19	-0.000113	0.00014	3.68
AC-10	143	125	0.07	0.07	9.91
AC-20	667	564	0.30	0.32	9.62
AC-30	731	627	0.33	0.35	9.76
AC-50	756	569	0.30	0.34	9.18

showed significant changes and extensively produce higher surface area compared to the raw precursor. This proved that chemical activation offer advantages by creating larger surface area. In the context of surface area, the low impregnation ratio 1:1.4 or 10 % acid concentration, the surface area is $143 \text{ m}^2 \text{ g}^{-1}$, which is not in the range of activated carbon synthesized that generally used in industry. Basically, the range of activated carbon was between $700\text{--}1500 \text{ m}^2 \text{ g}^{-1}$. Apparently, the surface area increased four fold higher when the acid concentration was raised to 20 % concentration with $667 \text{ m}^2 \text{ g}^{-1}$ or about 79 %. The surface area continued to increase when the acid concentration was increased to 30 % by having $731 \text{ m}^2 \text{ g}^{-1}$. However, only slight increment was observed which was about $64 \text{ m}^2 \text{ g}^{-1}$. There is no significant change in term of surface area between the activated carbon prepared at 30 and 50 % acid concentration since the differences in surface area was only $25 \text{ m}^2 \text{ g}^{-1}$. The surface area of prepared activated carbon should not be the only parameter taken in account to evaluate the properties of activated carbon. Therefore, the pore texture of activated carbon prepared at different impregnation ratios were further examined.

Fig. 3 shows the nitrogen adsorption-desorption corresponding to activated carbon obtained from activation of mangosteen with different phosphoric acid concentration meanwhile Fig. 4 displayed the total volume and micropore volume present in the sample at different phosphoric acid concentration. The shape of adsorption isotherm will provide the qualitative information on the adsorption process and extent of the surface area available to the adsorbate. The shapes of isotherms of all prepared activated carbon are similar even with different impregnation ratio. According to IUPAC classification²³, all the activated carbon prepared followed type 1 isotherm

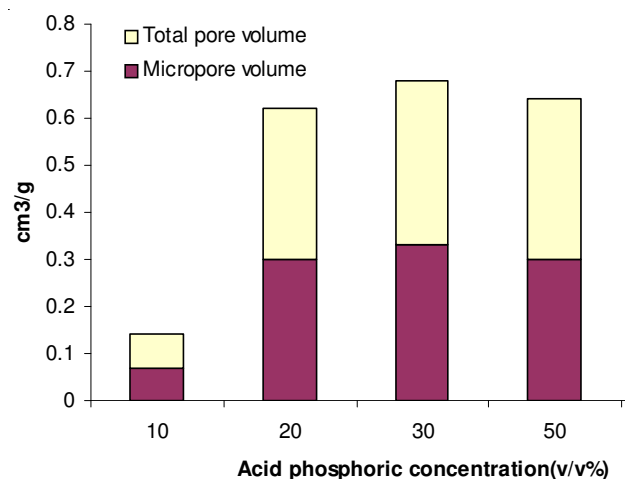


Fig. 3. Distribution of pore volume in activated carbon assessed at different acid concentration

which are microporous solid. An absence of hysteresis loop indicates the absence of mesoporosity and can suggest that the carbon prepared consist mostly of micropores with only small portion of mesopores, which can be concluded that porosity remain restricted in micropore which occurred at high impregnation ratio²⁴. However, the enhancement of nitrogen uptake can be observed as phosphoric acid concentration increased. As seen in Fig. 4, the total pore volume and micropore volume increased in correlation with acid concentration. In term of ratio of micropore volume to total volume ($V_{\text{mic}}/V_{\text{tot}}$) for 10, 20, 30 and 50 % are 1.00, 1.07, 1.06 and 1.13, respectively.

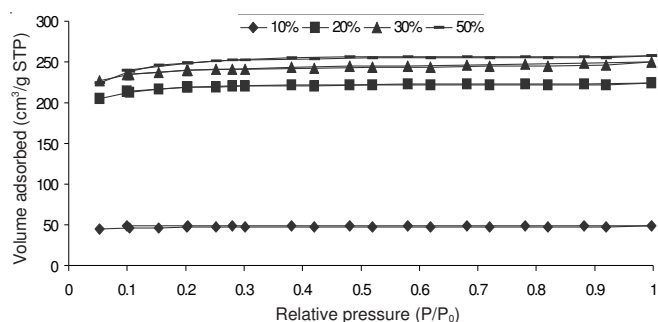


Fig. 4. Adsorption-desorption isotherms of activated carbon assessed at different acid concentration

Conclusively, based on cost consumption and chemical recovery, the optimum acid concentration selected was 30 %. The acid concentration based on highest surface area ($731 \text{ m}^2/\text{g}$), micropore volume ($0.33 \text{ cm}^3/\text{g}$) and total volume ($0.35 \text{ cm}^3/\text{g}$).

Examination of scanning electron microscope: The surface morphology of raw mangosteen peel and selected activated carbon prepared with acid treatment was observed using scanning electron microscope. Fig. 5 illustrates the morphology of raw precursor. The surface of raw precursor is hard and poorly developed. In addition, the evidence for the material is poorly developed can be assigned through the poor or negligible BET surface area (Table-3). Compare to raw precursor, the activated carbon prepared with acid activation followed by carbonization and activation shows completely

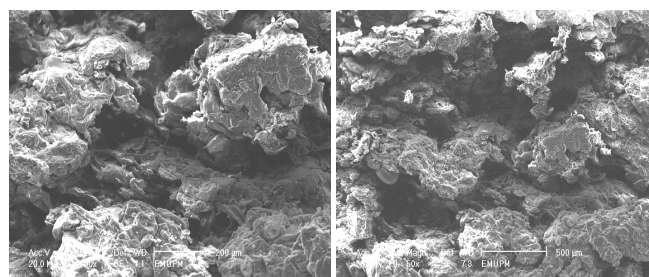


Fig. 5. SEM images of raw material at different magnification

smooth and clear appearances (Fig. 6). The heat treatment during carbonization creates formation of pores in the activated carbon by removing all the volatile compounds and impurities present in the material. Apart from that, washing process with sodium hydroxide is important in activated carbon production since it involves in creation of pores and makes the pores accessible.

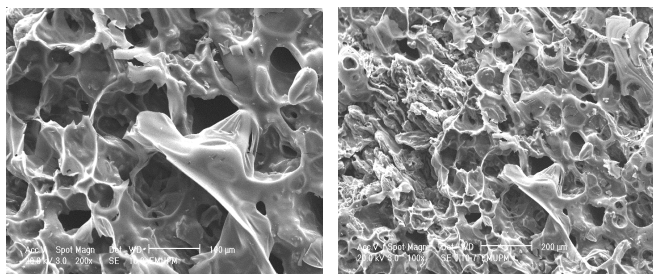


Fig. 6. SEM images of activated carbon prepared at 30 % acid concentration at different magnification

Conclusion

Mangosteen peel can be used as precursor for activated carbon preparation due to presence of high carbon content and reasonable ash content. The carbonization/heat treatment of raw material creates formation of pores in the sample. In correspond to thermogram, the suitable activation temperature for preparation of activated carbon is higher than 700 °C. All the activated carbon prepared with different phosphoric acid from mangosteen consists of micropores. The 30 % acid concentrations is the most suitable for activated carbon production. However, further studies by employing different parameters need to be carried out to assess the optimum condition for activated carbon production.

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