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Preparation and Characterization of Activated Carbon from Rubber-seed Shell by Chemical Activation

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Abstract: The use of rubber-seed shell, an agricultural waste by-product as a raw material for the production of activated carbon with chemical activation using potassium hydroxide, KOH was investigated. In this work, the produced activated carbons were characterized by Nitrogen Adsorption Theorem and Scanning Electron Microscope instruments. The optimal activation conditions were found at temperature of 500°C and at activation time of 180 min. Result showed that the BET surface area, total pore volume and diameter of the activated carbon were 1288.52 $m^2\ g^{-1}$, 0.81 $cm^3\ g^{-1}$ and 2.49 nm, respectively. From the nitrogen adsorption-desorption isotherm and pore size distribution, it was found that vast majority of pores fall within range of mesopore, therefore indicating that activated carbon prepared from rubber-seed shell is an attractive source for liquid and gas adsorption applications.

Key words: Rubber-seed shell, activated carbon, adsorption, chemical activation, mesopores

INTRODUCTION

Recent production of biodiesel from refined rubber-seed oil by transesterification processes has generated large amount of solid wastes especially the rubber-seed shells. These solid wastes are left unutilized on the fields, causing significant environment and disposal problems (Wan Ngah and Hanafiah, 2008). One solution for this problem is to reuse this waste to produce activated carbon which is one of the most widely used materials due of its low cost and exceptional adsorption properties (Ioannidou and Zabaniotou, 2007). The use of activated carbon as an adsorbent has proven to be effective in a wide range of applications, including the removal of both organic and inorganic pollutants from industrial wastewater and municipal, purification and separation. Conventional methods such as coagulation (Stephenson and Sheldon, 1996), chemical oxidation (Salem and El-Maazawi, 2000), photocatalysis (Bukallah *et al*., 2007) electrochemical (Rao *et al*., 2001) and membrane separation (Cheung *et al*., 1997) have been examined. However, these methods are generally expensive; therefore has stimulated the interest in examining the feasibility of using cheaper raw materials which is effective and economic.

Either chemical or physical activation method is used to manufacture a wide variety of precursor materials. In chemical activation, the raw material is impregnated with an activating reagent like $ZnCl_2$, KOH, H_3PO_4 or their mixtures. In physical activation, a raw material is first carbonized and the resulting char is secondarily activated under the flow of gas such as steam, carbon dioxide, air or their mixtures (Hayash *et al*., 2002). The versatility of high surface area, porous structure and surface adsorption capacity which can be appropriately modified by physical and chemical treatments, are among the reasons for the use of such adsorbent. As for the properties, pore structure (in terms of surface area and pore volume) is an important characteristic of activated carbon. In general, activated carbon with both high surface area and porosity, allowing large capacity of adsorption, is desirable (Teng *et al*., 1997).

Many researchers have studied the production of low-cost adsorbents from renewable and cheaper precursors which are mainly industrial and agricultural by-products ranging from sawdust (Larous *et al*., 2005), rice husk (Wong *et al*., 2003), bamboo (Hameed *et al*., 2007), oil palm fibre (Tan *et al*., 2007), pecan shells (Shawabkeh *et al*., 2002), etc. and their findings are quite conclusive. However, very few literatures have been found on work involving the use of rubber-seed shells as precursor to produce activated carbon. Due to this reason, there is a need to perform research on this promising raw material for generating activated carbon capable of removing pollutants. The focus of this study was to evaluate the characteristics activated carbon prepared from rubber-seed shell using chemical activation method and KOH as the activating agent. Effect on

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operating variables such as activation time, temperature of activation and size of activated carbon produced will be studied.

MATERIALS AND METHODS

Material and pretreatment: The rubber-seed shell (*Hevea brasiliensis*) collected from a local rubber plantation estate in Malacca was used as starting material in this work. The activated carbon from rubber-seed shell was prepared by the procedure reported by Rengaraj *et al.* (1998). Initially, the materials were washed repeatedly with distilled water to remove earthy matter and then dried in an oven at 80°C overnight, crushed and sieved to a particle size of 500 μm^{-1} mm and stored in plastic containers for further use.

Carbonization and activation: For activation, about 10 g of the rubber-seed shell is impregnated with 100 mL of freshly prepared concentrated solution of KOH with impregnated ratio of 1:1. The impregnation ratio is defined as the ratio of dry weight of KOH is allowed to soak with the rubber-seed shell overnight, so the reagents are fully adsorbed into the raw material. The impregnated rubber-seed shell is then carbonized in the fixed bed activation unit to produce rubber-seed activated carbon. The furnace temperature was set at 500°C under nitrogen gas flow for 30 min. During carbonization, the carbonaceous material along with the impregnation agents turns black which turns into a dry powder during continued heating. The resulting activated carbon is then cooled to a room temperature before being washed with hot distilled water several times to remove any remaining KOH and then dried in the oven at 80°C overnight. The experiment was repeated with different activation time, temperature and size of rubber-seed shell as shown in Table 1 and 2. All produced activated carbon were placed in air tight containers, sealed with parafilm and stored in a desiccator.

Sample characterization

SEM: A Zeiss EVO-50 Scanning Electron Microscope (SEM) was used in this study. The structural of the raw material and the produced activated carbons were observed at magnification of 10-100,000 times with virtually unlimited depth of field. SEM images are very useful to obtain accurate adsorption details of adsorbent before and after the activation process.

Specific surface and porosity analyzer: The pore size distribution, specific surface area and porosity of the

Table 1: Preparation conditions and results of 1 mm rubber seed activated carbon

Sample	Act. time (min)	Act. temp (°C)	Specific surface area, S_{BET} (m^2 g^{-1})	Total pore volume, V_T (cm^3 g^{-1})	Average pore diameter, D (nm)
A1	30	500	1001.66	0.61	1.91
A2	30	600	988.15	0.58	2.11
B1	60	500	1086.42	0.61	2.27
B2	60	600	1080.92	0.61	2.30
C1	90	500	1091.13	0.65	2.32
C2	90	600	1095.16	0.63	2.38
D1	120	500	1133.07	0.68	2.40
D2	120	600	1142.25	0.62	2.38
E1	150	500	1198.56	0.71	2.45
E2	150	600	1117.03	0.73	2.45
F1	180	500	1288.52	0.81	2.49
F2	180	600	1192.10	0.75	2.46
G1	210	500	1116.74	0.76	2.45
G2	210	600	1125.61	0.75	2.41

Table 2: Preparation conditions and results of 500 μm rubber seed activated carbon

Sample	Act. time (min)	Act. temp (°C)	Specific surface area, S_{BET} (m^2 g^{-1})	Total pore volume, V_T (cm^3 g^{-1})	Average pore diameter, D (nm)
H1	30	500	1021.48	0.59	1.85
H2	30	600	1031.09	0.59	2.23
I1	60	500	1088.01	0.60	2.20
I2	60	600	1075.38	0.61	2.27
J1	90	500	1088.39	0.61	2.27
J2	90	600	1079.24	0.64	2.24
K1	120	500	1112.57	0.67	2.30
K2	120	600	1124.37	0.65	2.31
L1	150	500	1138.21	0.70	2.32
L2	150	600	1135.84	0.68	2.30
M1	180	500	1185.69	0.74	2.38
M2	180	600	1127.53	0.71	2.30
N1	210	500	1128.61	0.72	2.32
N2	210	600	1106.37	0.69	2.27

samples were determined by nitrogen adsorption-desorption isotherms characterized with Micrometrics ASAP 2020 apparatus, using N_2 as the adsorbate. Before such analysis, the samples were degassed under N_2 flow at 350°C for 2 h in a vacuum at 27°C. The specific surface area of the prepared activated carbons was estimated by the Brunauer-Emmett-Teller (BET) method using N_2 adsorption isotherm data. The micropore volumes were calculated from the amount of N_2 adsorbed at a relative pressure 0.1 and the mesopore volumes were calculated by subtracting the amounts adsorbed at a relative pressure of 0.1 from those at relative pressure of 0.95. The Barrett-Joyner-Halenda (BJS) model was used to calculate the pore size distribution (Rouquerol *et al*., 1999).

RESULTS AND DISCUSSION

Results of produced activated carbons: The preparation conditions, specific surface area (S_{BET}), total pore volume (V_T) and average pore diameter (D) of the resulting activated carbon at two different sizes are listed in Table 1 and 2. Results from Table 1 showed that the highest values of S_{BET} (1288.52 $m^2\ g^{-1}$), V_T (0.81 $cm^3\ g^{-1}$) and D (2.49 nm) were obtained at 500°C and activation time of 180 min. This is also true for 500 μm samples which yield S_{BET} (1185.69 $m^2\ g^{-1}$), V_T (0.74 $cm^3\ g^{-1}$) and D (2.38 nm), respectively when conducted at 500°C. Samples F1, F2, M1 and M2 show that S_{BET}, V_T and D are the highest when the activated time is 180 min but decrease with further increase in activation time. The optimum activation temperatures have been reported to be between 400-500°C, by most of researchers irrespective of operating parameters (Toles *et al*., 1998). At activation temperature of 400°C, the developing rudimentary of pores of activated carbon were formed by removing the low-molecular-weight volatile compounds from the matrix structure. Increasing the activation temperature to 500°C enhances the removal of molecular weight volatile compounds and further created new pores, resulting in the acceleration of porosity development of the activated carbon. However, when the activation temperature was increased to 600°C, excessive heat energy was given to the carbon resulting in the knocking and breaking of some porous wall, thus blocking the porosity formation. Hence, the pyrolysis at this activation temperature would yield decreasing surface area of the activated carbon. This can be explained by comparing samples F1 and F2 performed at different temperatures. Prolonged activation also may cause over activation, accelerating surface erosion more than pore formation. This can be observed by decreasing in S_{BET}, V_T and D after activation time of 210 min of two different activated sizes.

By comparing results between Table 1 and 2 where the particle size of the rubber-seed are in the range of 501-1 mm and 251-500 μm, respectively, the effect on characteristics of the produced activated carbon is not significant. This result show that the adsorption capacities does not determined by the initial particle size of the raw material. Instead, it is affected by the activation process parameters such as activation time and temperatures. Two promising rubber-seed activated carbon samples (E1 and F1) which have shown highest S_{BET}, V_T and D were chosen for further analysis. For comparison purposes, Sample A1 that has the lowest activation time was also chosen for further analysis.

N_2 adsorption and pore size distribution: Figure 1 shows the N_2 adsorption-desorption isotherms of the selected three activated carbons obtained at different activation time and temperature. The quantity of N_2 adsorbed is plotted against the relative pressure p/p_o (p = pressure, p_o = saturated vapor pressure) of N_2. Based on the IUPAC classification of adsorption isotherm (Mays, 2007), it can be seen that the N_2 adsorption isotherm of Sample A1 prepared at activation 30 min and 500°C corresponds to Type I. This indicates that the pores are microporous and the exposed surface resides almost exclusively within the micropores. Once filled by N_2 adsorbate, very few or no external surface left for additional adsorption. The amount of N_2 adsorbed on Sample E1 prepared at 150 min and 500°C shows an intermediate between Type I and II, associated with a combination of microporous and mesoporous structures. The N_2 adsorption isotherm on Sample F1 prepared at activation of 180 min and 500°C begin to change considerably, adopting Type III. At this condition, mesopores have been developed, as indicated

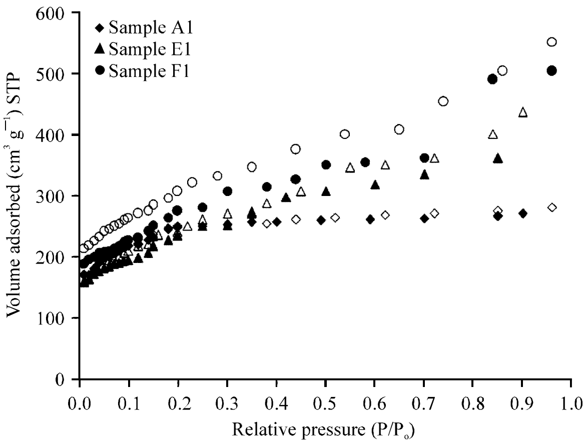

Fig. 1: Nitrogen adsorption-desorption isotherm, closed symbols: Adsorption, open symbols: Desorption

by the convex shape and increasing upwards which is often associated with the presence of slit-shaped mesopores (Lazaro *et al*., 2007).

Pore size distribution of the selected activated carbons (Sample A1, E1 and F1) is shown in Fig. 2. The pore structure of activated carbon is generally characterized in term of pore size distribution. One can see the activating temperature and time had significant effect on the pore structure of activated carbon prepared. At low temperature and time, the pore structure was mainly consisted of micropore. However, with the increase of carbonization temperature, the creation of mesopore increased. This increased the total pore volume of activated carbon. It was learned that the reaction rate between activating agent and carbon increased geometrically as the temperature rate and time increases. At high temperature, micropores were enlarged and the walls between pores collapsed and formed mesopores. Pore sizes are classified in accordance with the classification adopted by IUPAC that is, micropores (diameter (d)<20 Å), mesopores (20 Å<d<500 Å) and macropores (d>500 Å) (Mays, 2007). For Sample A1, the average pore diameter determined by BJS method was 19.1 Å indicating that a vast majority of the pores fall within the range of micropore while Sample E1 (24.5 Å) and F1 (24.9 Å) both showed that mesopores structure have been formed.

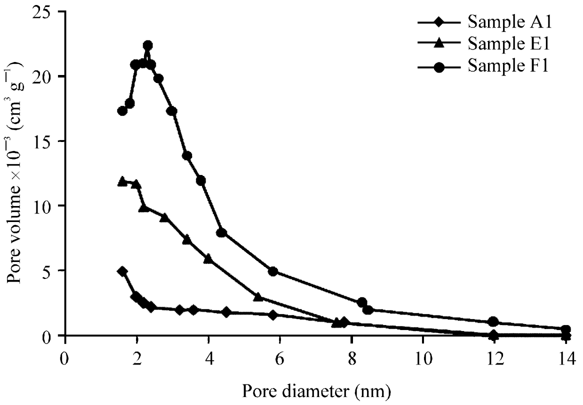

Fig. 2: Pore size distribution of rubber-seed activated carbons

SEM: The microstructure of the raw rubber-seed shell and the selected three activated carbons prepared at different temperatures and activation time are shown in Fig. 3. For

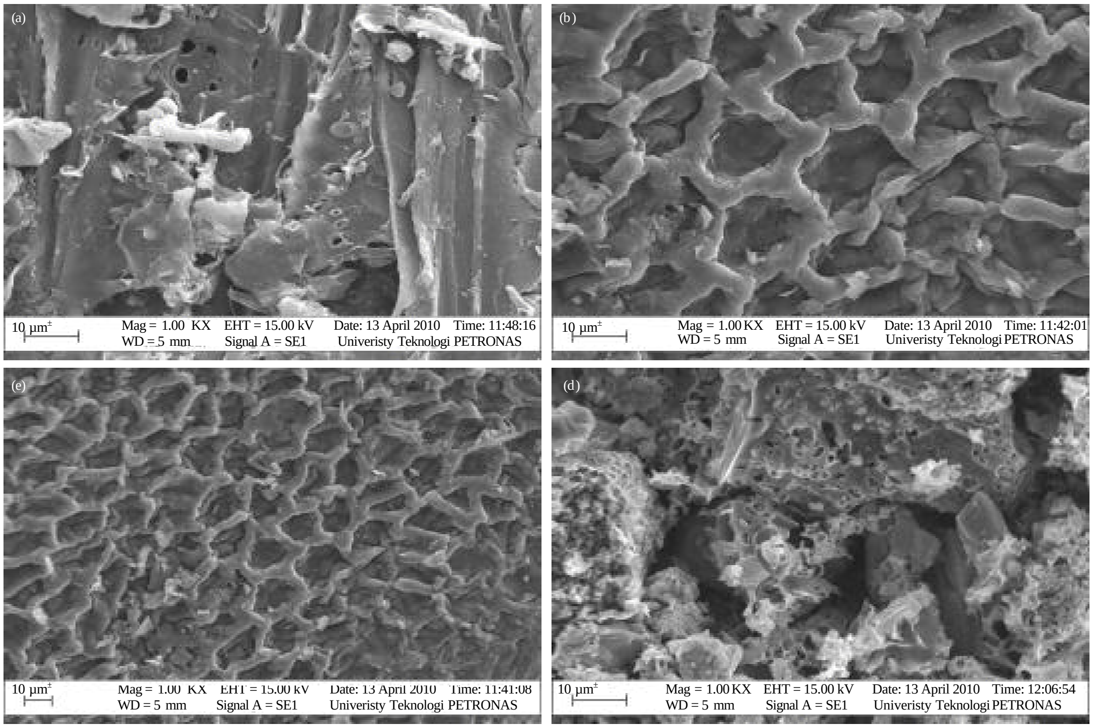

Fig. 3(a-d): SEM of the three selected samples, (a) Fresh rubber-seed shell, (b) Sample A1, (c) Sample E1 and (d) Sample F1 the raw rubber-seed shell material, the micrograph showed clearly the canal structure which is good texture for preparing activated carbon, because activating agents can easily contact with the inside surfaces. From the SEM micrographs, it can be seen that morphological characteristics are much different between raw material and the three activated carbons. The SEM images reveal the nature of its surface. Sample A1 shows good canal structure for the raw material. That means the carbonization and activation are taking place but still at early stages. Many large pores were clearly found on the surface of the activated carbon. The well-developed pores has led to the large surface area and porous structure of the activated carbon. The surface in sample E1 shows that the canal structure has been partially broken which means activation process occurred and the surface was eroded by longer activation time than sample A1, the S_{BET} of Sample E1 is much higher. Sample F1 shows the most well-developed porous structure among the three activated carbons. This justified that sample F1 has the highest S_{BET}, V_T and D compared to other samples.

CONCLUSION

Rubber-seed shell, an agricultural waste, is a potential source for the preparation of high quality activated carbon by chemical activation with KOH. Activation conditions have significant influence on porous properties. The activated carbon with huge specific surface area, pore volume and average pore diameter is obtained at the activation temperature of 500°C and activation time of 180 min. In addition, the characterization studies reveal its adsorption capacity, the micropore and mesopore are both developed that made the activated carbon suitable for adsorption application. It is concluded that the activated carbon prepared from rubber-seed shell could be exploited for commercial applications in the tertiary level treatment of portable water as well as industrial effluents.

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