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RESEARCH ARTICLE

EFFECT OF ACTIVATION TIME ON CHEMICAL STRUCTURE AND QUALITY OF COCONUT SHELL ACTIVATED CARBON

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ABSTRACT

Preparation and characterization of the activated carbon from the coconut shell using the combination of both chemical and physical activations with the activator of KOH and CO₂ stream has been conducted. The research was aimed to study the mechanism of chemical change that occurred during the activation process by characterizing the charcoal after being chemically and physically activated. The coconut shell charcoal was immersed in the solution of KOH (0.5-2.0 M) for 12-24 h. It was then activated on the activation reactor at 800 °C with the stream of CO₂ 20 mL/min and with the variation of time 30-150 min. Characterization of the activated carbon included FT-IR, SEM and specific surface area BET analyses. FTIR analysis showed that the surface of the activated carbon had the functional group of O-H, C-H, C=C, and C-O. SEM analysis showed that the activated carbon had more porous structure. In addition, the pore diameter increased by the increasing of the activation time. The best activated carbon was obtained with the condition of KOH 2 M, immersion time of 24 h, activation time of 120 min. At such condition, the obtained activated carbon had properties of surface area BET of 451,14 m²g⁻¹, pore volume of 2,506 x 10⁻¹ cm³g⁻¹ and the averaged pore radius of 11,109 Å.

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INTRODUCTION

One of valuable products which could be prepared from the coconut shell is the coconut shell charcoal. The charcoal is obtained from the pyrolysis of the shell. The produced charcoal is potential to be further developed into activated carbon (Woodroof, 1970). The properties of the activated carbon are high number of pore and surface area as well as high adsorption capacity (Keneeth, 2002; Manocha, 2003). The preparation of the activated carbon consists of two steps, i.e. carbonization and activation. In the first process, the volatile materials will be removed. The second process was conducted to form the pores and increase the surface area (Kirk and Othmer, 1983). The main product of the carbonization is the charcoal with the side products of tar and liquid smoke. The obtained charcoal is usually not active enough as it has very low adsorption capacity. Therefore, activation process is required to improve the properties of the charcoal (Rodenas et al., 2005; Cuhadaroglu and Uygun, 2008). The activation is aimed to increase the pore by breaking the bond in the hydrocarbon framework or by oxidizing the molecules on the surface. Such property affects the adsorption capacity (Ahmadpour et al., 1998; Tsai et al., 2001; Kang

et al., 2006). The activation methods which are commonly applied in the preparation of activated carbon are chemical and physical activation. The chemical activation is breaking of chemical bonding in the organic molecules by using chemicals as the activator. Several activators which are commonly utilized are KOH, NaOH, ZnCl₂, KCl, H₃PO₄, HCl, etc (Sricharoenchaikul et al., 2008; Babel, 2004). The physical activated is the breaking of chemical bond by using heat, vapor and carbon dioxide. The activation process was expected to increase the quality of activated carbon as adsorbent. In this process, the charcoal is heated at high temperature (800-1000 °C) (ACS, 1996). In this study, the activation was conducted by combining both the chemical activation using KOH as the activator and the physical activation using carbon dioxide gas. The combination method was expected to increase the quality of the activated carbon. Therefore, it is required to study the chemical change during the activation process. This study was aimed to determine the chemical change on the activated carbon due to the effect of activation time. In addition, the application of the activated carbon would be also evaluated.

MATERIALS AND METHODS

The materials used are the coconut shell charcoal from the pyrolysis product from PT. Tropica Nucifera Industry, carbon dioxide (CO₂) gas, potassium hydroxide (KOH, p.a., Merck),

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hydrochloric acid (HCl, p.a., Merck), aquadest, universal indicator and Whatman 42 filter paper. The tools used are mortar, sieve 80 and 100 mesh (USA standard testing sieve), tube furnace-thermolyne (Sybron, type 21100), analytical balance (AND GR-200), hot plate, dessicator, pHmeter, vacuum filter, activation reactor, electric oven, magnetic stirrer, Fourier Transform Infra Red (FT-IR, Shimadzu Prestige 21), Scanning Electron Microscopy (SEM, JEOL JSM-6360) and Surface Area Analyzer (NOVA Ver. 2.2).

MATERIALS AND METHODS

Preparation of coconut shell

The coconut shell obtained from the pyrolysis was cleaned and grinded to give the powder. It was sieved using the sieve 80-100 mesh. The powder utilized for further process was that passed the 80 mesh sieve and retained on the 100 mesh sieve.

Chemical activation

The sieved charcoal was immersed in the solution of KOH with the variations of concentration (0.5-2.0 M) and time (12-24 h). The immersed charcoal was filtered under vacuum and heated on the oven at 120 °C for 2 h. The dried charcoal was then placed on the dessicator.

Physical activation

The charcoal obtained from the previous step was placed in the activation reactor with the glasswool on the up and bottom side and the was activated at 800 °C with the variation of time (30-150 min) and was streamed with CO₂ 20 mL/min for 2 h. Then, the charcoal was immersed in the solution of HCl 1 M for 24 h. The charcoal was then washed with aquadest until neutral. It was then filtered and dried in the oven at 110 °C for 2 h.

Analysis of the activated carbon

Characterization of the activated carbon was conducted including the physical and chemical properties such as the functional group analysis using FTIR, surface structure using SEM, surface area using BET, total volume of the pore and average diameter of pore.

Analysis of fouriertransforlinfra red (FTIR)

Analysis of the structure of the activated carbon was conducted to determine the functional group of the material.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis was used to analyze the microstructure of the surface of the activated carbon either before or after the activation.

Analysis of surface area BET

Analysis of the pore structure and the surface area was performed using the Surface Area Analyzer NOVA Ver.2.2. The determination of the surface area was carried out using the BET method. In addition, by applying the BET equation the total of pore volume and the averaged the pore diameter could be determined.

RESULTS AND DISCUSSION

The IR spectra of the charcoal obtained from the pyrolysis without activation showed the presence of vibration at 3487-3417 cm⁻¹ as the stretching vibration of O-H group. The absorption was supported by the presence of band at 1381-1165 cm⁻¹ coming from the stretching vibration of C-O and the bending vibration of O-H from alcohol and carboxylic acid. The wave number of 1581-1527 cm⁻¹ represented the stretching vibration of C=C of the aromatic ring. The absorption at 802-748 cm⁻¹ showed the bending vibration of aromatic C-H. The IR spectra of the activated carbon which has been activated using KOH 2 M with the immersion time of 24 h at 800 °C with the variation of activation time (30, 60, 90, 120 and 150 min) were relatively similar with those of the charcoal without activation. However, the absorption intensity decreased and increased.

The shift on the wave number was also observed. The stretching vibration of O-H group from K.30 to K.60 spectra shifted to the lower wave number (from 3461 to 3410 cm⁻¹). The similar observation was also observed from K.120 to K.150 (from 3487 to 3456 cm⁻¹). It was predicted that the short activation time using KOH did not break the bond on the active sites of the activated carbon. These vibrations were supported by the absorption at 1442-1327 cm⁻¹ coming from the stretching vibration of C-O and the bending vibration of O-H of the alcohol and the carboxylic acid. The absorption at 2900-2990 cm⁻¹ represented the stretching vibration of aliphatic C-H from -CH₃ and -CH₂-. The absorption at these wave number was not observed for K.30 and K.150. In the case of K.30, The disappearance of the peak was probably due to the short activation time which led the chemical reaction via free radical mechanism. In the case of K.150, there was the bond breaking via free radical mechanism which was probably due to the long activation time or the high activation temperature (Demirbas, 2005). In addition, the band at 2337 cm⁻¹ came from the stretching vibration of C=O from carboxylic acid.

It was supported by the presence of peak at 1851 cm⁻¹ on K.120. The wave number of 1635 cm⁻¹ indicated the presence of the stretching vibration of aromatic C=C bond. The band at 802 cm⁻¹ showed the bending vibration of aromatic C-H. Based on those absorptions, it could be stated that there was no significant difference between the carbon before and after activation process using KOH. Several band shifted and there was no formation of new functional group on the surface of the activated carbon. The activation process using KOH make the result of aromatic formation C=C bond (1581-1635 cm⁻¹). It was indicated that the carbonization and activation of coconut shell charcoal into the activated carbon increased the aromatic compound (Pari, 2004). The produced activated carbon had O-H, C-O and C=C functional groups. The presence of O-H and C=O groups showed that the activated carbons were relatively polar and thus could be employed as the adsorbent. The charcoals before and after activation were then analyzed using SEM. It was showed that there was a change on the structure of the surface between the coconut shell charcoal without activation and the activated carbon after the activation, where the change of pore was mostly observed on the surface of the activated carbon. It was indicated that the pore of the activated carbon had relatively deep indentation.

Table 1. The IR absorptions of the coconut shell charcoal before and after activation using KOH with the variation of time

Charcoal from pyrolysis	Wave number, cm ⁻¹					Vibration
	Charcoal after activation using KOH Variation of time (min)					
	30	60	90	120	150	
3749	-	-	3749	3749	3749	Stretching vibration of O-H from hydroxyl group
3487,17	3464,1	3410,1	3441,0	3487,3	3456,4	Stretching vibration of C-H from CH ₃ and CH ₂ group
2831	-	2970,3	2939,5	2931,8	-	Stretching vibration of C=O from carboxylic acid group
2377,72	2337,7	2337,7	2337,7	2337,7	2337,7	Aromatic C-H bond
-	-	-	-	1851,66	1928	Stretching vibration of C=O from aromatic carbonyl group
1581,6	1635,6	1581,6	1635,6	1635,6	1635,6	Stretching vibration of C=C from aliphatic double bond
-	1442,7	1381,0	1381,0	1327,0	1404,1	Stretching vibration of C-O and bending vibration of O-H from alcohol and carboxylic acid
1165	1118,7	1165,0	1111,0	1095,5	1095,5	Stretching vibration of C-O-C from 6-membered ring ether
802,39	810,1	516,9	964,4	956,6	956,6	Bending vibration C-H aromatic

Additionally, the distance of the pore got closer by the increasing of the activation time. The activated charcoal was more porous, which showed that the activation process could open and form the new pore in the activated carbon. The SEM images of the activated carbon with the zoom of 1,500-10,000x showed that the increasing of activation time led the decreasing of the particle size. This showed that the carbonization and the activation processes led the breaking of the carbon chain. In the other word, the small size of the activated carbon gave higher surface area.

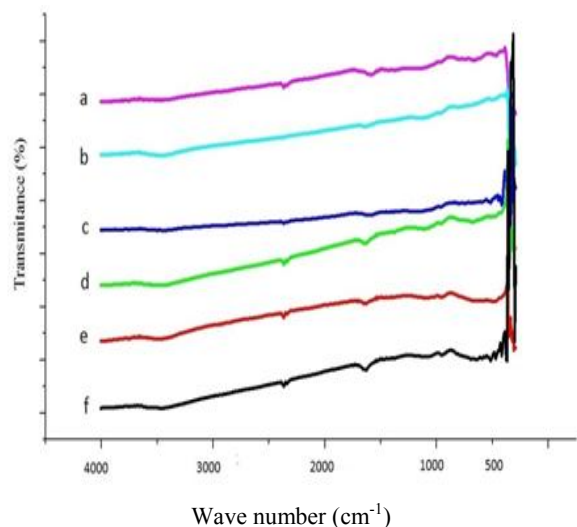


Fig.1. IR Spectra of the coconut shell charcoal: (a) before activation; and after activation using KOH for: (b) 30; (c) 90; (d) 120 and (e) 150 min

Analysis of the activated carbon using Scanning Electron Microscope (SEM)

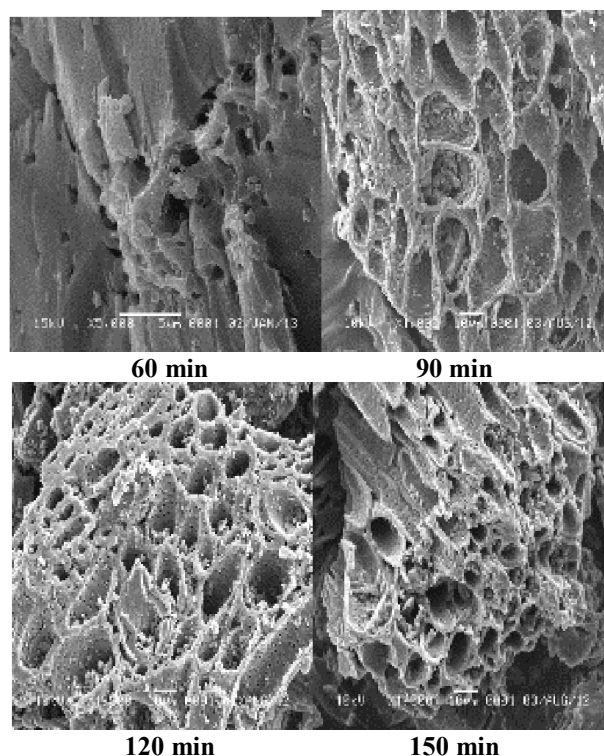
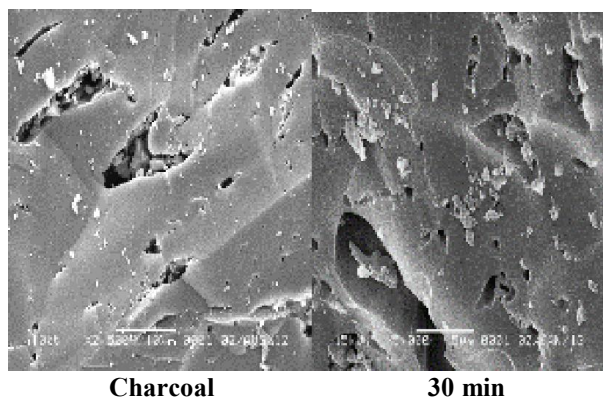


Fig. 2. SEM image of the coconut shell charcoal before and after activation using KOH 2 M for 24 h at 800 °C, with the variation time of 30-150 min

Poresize distribution of the activated carbon

The pore size distribution gives the description of the poresize of material. The analysis was conducted toward the charcoal before and after the activation. For the comparison, the same analysis was also carried out toward the activated carbon purchased from Merck. Based on Figure 3, the variation of time from 30 to 150 min gave similar pattern. The activated carbon had smaller pore diameter than the charcoal without activation (Table 2). This showed that the treatment with the activator could unify the pore size. In addition, the pore volume of the activated carbon was higher than that of the unactivated carbon. In order to determine the pore homogeneity, the calculation of pore size distribution was carried out. The determination of the distribution used the method of Barrett-Joyner-Halenda (BJH). Based on Figure 3, the patterns were relatively same, i.e. they had one peak. It was indicated that the formed activated carbon had good uniformity.

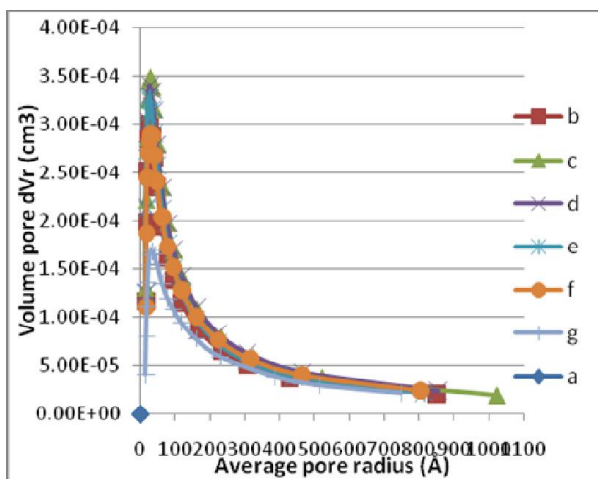


Fig. 3. Pore size distribution of the activated carbon before (a) and after activation with the variation time of (b) 30; (c) 60; (d) 90; (e) 120; (f) 150 min and (g) the activated carbon from Merck

Determination of surface area BET of the activated carbon

Table 2. Determination of specific surface area, total volume of pore and averaged pore radius of the activated carbon

Sample	Specific surface area (m^2g^{-1})	Total volume of pore ($\times 10^{-1} \text{cm}^3\text{g}^{-1}$)	Averaged pore radius (Å)
Charcoal	15,451	0,217	26,478
K8-2-24-30	387,712	2,168	11,185
K8-2-24-60	396,221	2,190	11,053
K8-2-24-90	402,697	2,308	11,463
K8-2-24-120	451,141	2,506	11,109
K8-2-24-150	445,096	2,508	11,268

The surface area, the pore size and the pore volume are important properties of material as the adsorbent. As displayed on Table 2, the surface area of the activated carbon with the activation time of 30 to 60 min increased from 387.71 to $451.14 \text{ m}^2\text{g}^{-1}$ and decreased to $445.10 \text{ m}^2\text{g}^{-1}$ (150 min). It was predicted that the increasing of activation time led the heavier volatile compound to be evaporated and got out from the pore. Thus, the new pore was formed and it could increase the surface area, pore volume and could decrease the pore diameter. It was observed that with the activation time of 150 min gave the decrease on the surface area ($445.096 \text{ m}^2\text{g}^{-1}$), which was probably because knocking had occurred at such condition and the break of the structure on the pore wall was also occurred, thus inhibit the formation of the pore (Allwaret al., 2008). The pore volumes of the activated carbon with the variation time of 30, 60, 90, 120 and 150 min were $2,168 \times 10^{-1}$; $2,190 \times 10^{-1}$; $2,308 \times 10^{-1}$; $2,506 \times 10^{-1}$; and $2,508 \times 10^{-1} \text{ cm}^3\text{g}^{-1}$, respectively. These values were higher than the volume of the unactivated carbon, $0,217 \times 10 \text{ cm}^3 \text{ g}^{-1}$.

Conclusion

Chemical and physical activation of coconut shell using the activator of KOH with the variation of activation time affected the character of the activated carbon. It could be seen from the morphology of the surface structure, where the more porous surface was formed and the surface area increased by the increasing of the activation time. The best activated carbon was obtained with activator of KOH 2 M, immersion time of 24 h, at 800°C and the activation time of 120 min. All the

activated carbon prepared with the variation of activation time has the same pattern, where the pore diameters were lower and the pore volume was higher than those of unactivated carbon. The activated carbon had the BET surface area of $451,14 \text{ m}^2\text{g}^{-1}$, pore volume of $2,506 \times 10^{-1} \text{ cm}^3\text{g}^{-1}$ and the averaged pore radius of $11,109 \text{ \AA}$.

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