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EFFECT OF KOH AND H_2SO_4 ACTIVATION AGENT IN MICROWAVE ULTRASONIC ACTIVATION PROCESS OF ACTIVATED CARBON

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ABSTRACT

Microwave ultrasonic (MW-ultrasonic) has considerable as one of the interest alternative method to enhance the performance of Bamboo Activated Carbon (BAC). In the present study, BAC was activated using two types of chemical agent which are KOH and H_2SO_4 in different of microwave (MW) power (100W, 300W, 500W) at retention time of 30 min and 60 min soaking time. While the carbonization process was conducted at temperature 400ºC, 600ºC and 800ºC. The BAC sample was analyzed using Field Emission Scanning Electron Microscope (FESEM) for morphology structure analysis, Fourier transform infrared spectroscopy (FTIR) for functioning group analysis, X-ray powder diffraction (XRD) for materials phase analysis and Brunauer, Emmett and Teller (BET) for active surface area determination. It is desired to produce BAC that has a higher active surface area for industrial application. The result showed that activation with KOH at microwave power of 300W gave active surface area of 922.72 m2/g. While with H_2SO_4 as activating agent the active surface area obtained was 1025.27 m2/g at MW power of 300W. The results indicated that MW-ultrasonic activation using chemical agents is capable to enhance active surface area for BAC.

Keywords: Microwave-ultrasonic; Chemical; Activation; Bamboo; Carbonization

INTRODUCTION

Microwave ultrasonic irradiation has become a fast emerging technique for surface modification of activated carbons. This is due to the less time and energy consumption as compared to the conventional method [1]. Microwave irradiation can initiate the

reaction of surface carbon atom with surrounding chemical, resulting in the modification of activated carbon surface chemistry [2]. Microwave ultrasonic irradiation offer a secure, quite, energy saving, fast, facile and controllable process which is suitable to be applied in activated carbon processing. Generally, activated carbon can be produced via activation and carbonization process. Activation process is conducted to produce high surface area of activated carbon which is desire in various applications. It can be achieved by physical or chemical approaches. Physical activation generally involved with carbon dioxide (CO_2) or steam as an agent to open the pore of activated carbon [3]. While chemical activation is a single step method of activated carbon in the presence of the alkali or acid [4]. The one-step activation process is desirable due to a lower energy consumption, capital expenditure, processing time that can significantly improve the process economics [5]. The present study was focused on the chemical activation using KOH and H_2SO_4 with microwave ultrasonic system. This technique give a better pores structure and active surface area formation of activated carbon due to the MW energy and ultrasonic frequency. The precursor used in this current study was bamboo residual which is a low cost materials and highly renewable materials. The aims of the present study is to determine a higher active surface area of BAC by varying microwave power using KOH and H_2SO_4 as activating agent.

EXPERIMENTAL

Materials

The chemicals used in this study were sulphuric acid (H_2SO_4) and potassium hydroxide (KOH) purchased from R&M Chemical, Inc. The bamboo precursor used for activated carbon processing was obtained from Forest Research Institute Malaysia (FRIM).

Activated Carbon Processing

Activated carbon (AC) in the present study was prepared by using bamboo residual. 50 g of bamboo residual was placed into a crucible. Then, chemical activation process was conducted by using H_2SO_4 and KOH with sample to chemical agent ratio of 1:4. The sample undergoes microwave (EMM2017x, Electrolux, Malaysia) activation with different energy power 100W, 300W and 500W for 30 min and continue soaked in 50oC for 60 min using ultrasonic homogenizer (ST-UB800D, SASTEC, USA). Then, the sample was washed with distilled water until the neutral pH was achieved. The sample was carbonized in the VT Furnace (Carbolite, Keison, UK) in various temperature with heating rate 40oC/min for 120 min. After the carbonization process, the sample was cooled in desiccator before undergoes analysis process. The BAC was produced according to the method reported by Mahanim et al., 2012 [6]. Process flow diagram is illustrated in Figure 1 and parameters involved in the present study was tabulated in Table 1.

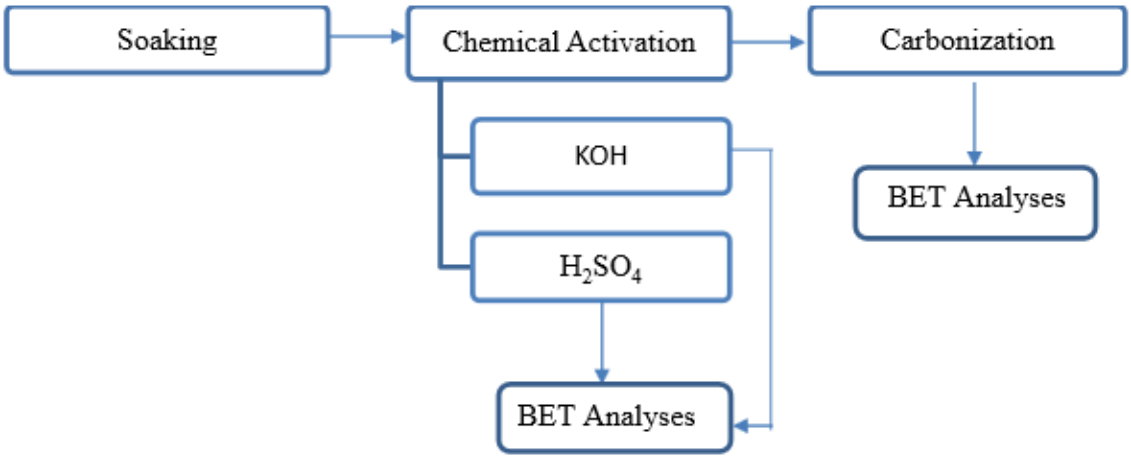

Figure 1: Flow diagram process

Table 1 Parameter for activated carbon samples

Sample	Description experimental	Chemical agent
AC1W	Soaking ultrasonic-MW (100W)	KOH
AC3W	Soaking ultrasonic-MW (300W)	KOH
AC5W	Soaking ultrasonic-MW (500W)	KOH
CIH4	Soaking ultrasonic-MW (100W)-carbanization (400°C)	KOH
C3H4	Soaking ultrasonic-MW (300W)-carbanization (400°C)	KOH
C5H4	Soaking ultrasonic-MW (500W)-carbanization (400°C)	KOH
C1H6	Soaking ultrasonic-MW (100W)-carbanization (600°C)	KOH
C3H6	Soaking ultrasonic-MW (300W)-carbanization (600°C)	KOH
CH3W8	Soaking ultrasonic-MW (300W)-carbanization (800°C)	KOH
CH5W8	Soaking ultrasonic-MW (500W)-carbanization (800°C)	KOH
C4A3	Soaking ultrasonic-MW (300W)-carbanization (400°C)	H_2SO_4
C8A3	Soaking ultrasonic-MW (300W)-carbanization (800°C)	H_2SO_4
C8A5	Soaking ultrasonic-MW (500W)-carbanization (800°C)	H_2SO_4
C1H24	Soaking ultrasonic-MW (100W)-carbanization (400°C)	KOH
C3H24	Soaking ultrasonic-MW (300W)-carbanization (400°C)	KOH
C3H26	Soaking ultrasonic-MW (300W)-carbanization (600°C)	KOH
C5H26	Soaking ultrasonic-MW (500W)-carbanization (600°C)	KOH
A100	Soaking ultrasonic-MW (100W)	H_2SO_4
A300	Soaking ultrasonic-MW (300W)	H_2SO_4
A500	Soaking ultrasonic-MW (500W)	H_2SO_4

Characterization of BAC

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR (Spectrum One, Perkin, USA) anaylses was conducted in order to identify chemical bonds in a molecule by producing an infrared absorption spectrum for functional group classification. The sample was put into the diamond mold and operated

using FTIR software. FTIR creates the absorbance spectra representing the unique chemical bonds and the molecular structure of the sample material. FTIR spectra were recorded between 4000 and 500 cm-1 by using AVATAR 360 Spectrophotometer.

Field Emission Scanning Electron Microscope (FESEM)
FESEM (Supra 40VP, Zeiss, Germany) was carried out using Zeiss Gemini Supra 40VP in conducive to examine the morphology of the sample and to analyze the composition, distribution and phase structure of residual bamboo. The sample must be electrically connected to the sample holder in order to prevent charging and distortion of the image.

X-Ray Diffraction Spectroscopy (XRD)
The pattern was recorded using Rigaku SA-HF3 Analytical from Japan at 40kV and 30 mA in the 2θ range of 10-80º with a scan rate of 5° min-1 and was powerful tool to analyze crystalline nature of materials.

Brunauer, Emmett, Teller (BET) test
Analyses used BET (Quantachrome, Autosorb-1, Florida) was used in order to determine the specific surface area of a variety materials by the BET Nitrogen adsorption technique. The adsorption process handled in 60 min by using quick single point and multipoint particular BET surface area determinations.

RESULT AND DISCUSSION

Functional group of BAC. Functional group analysis of BAC was analyzed using FTIR and the spectrum was revealed in Figure 2-5. In raw bamboo, it consist 3308.78 cm-1, 1599.98 cm-1, 1234.05 cm-1 and 1031.89 cm-1 peaks of wavenumber which identified as –OH stretching vibration and attributed to the C=C stretching vibration in the aromatic ring of lignin which is show in Figure 2. For Figure 3, it consist an activation of MW-utrasonic which conducted under KOH agent and it produced broad hydrogen-bonded O-H strecthing bands centered between 3400 and 3300 cm-1. C-O strech bond also occured at wavenumber 1300-1000 cm-1 and was grouped as esther because C=O was appeared in range of 1750-1735 cm-1 in sample AC1W, AC3W and AC5W. Figure 4 showed the analysis on functional group for alkali-base using KOH chemical agent. For sample C5H6, carboxylic acid C=O which produced –OH free occured at 1800-1700 cm-1 wavenumber. The C=C stretching bands for aromatic rings was appeared around 1600-1450 cm-1 outside the usual range. Besides, C=C for alkenes also appeared at the same of wavenumber frequency which produced from the sample that undergoes the carbonization process C1H4 and C5H4. For Figure 5, H_2SO_4 activation of acid consist many type of functional group. It consist a functional group which focus on wavenumber around 1200-1300 cm-1 produced from C8A5, C8A3 and C4A3 sample and it had identified as a sulfonic group -SO because it consist of the sulphur element. At 1735-1800 cm-1 C=O stretching vibration occurred. The possible group that occurred at 2850-3000 cm-1 were alkane C-H group. The weak bands also appeared in the range of wavenumber frequency 600-900 cm-1 which associated with out- of-plane bending mode of C-H or O-H group for both activations of acid and base,

H_2SO_4 and KOH respectively. From the results, a shiftment of functional group was occurred between activation processes of MW-ultrasonic before and after carbonized due to the adsorption of chemical activating agent.

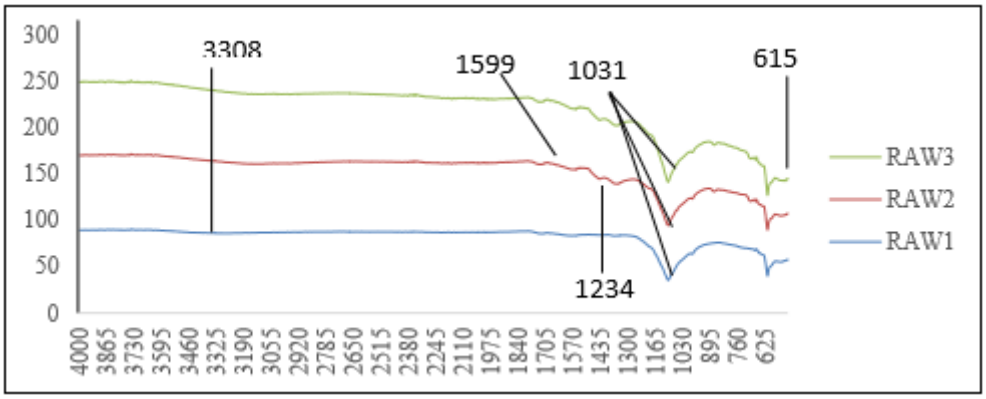

Figure 2: FTIR analysis for raw bamboo

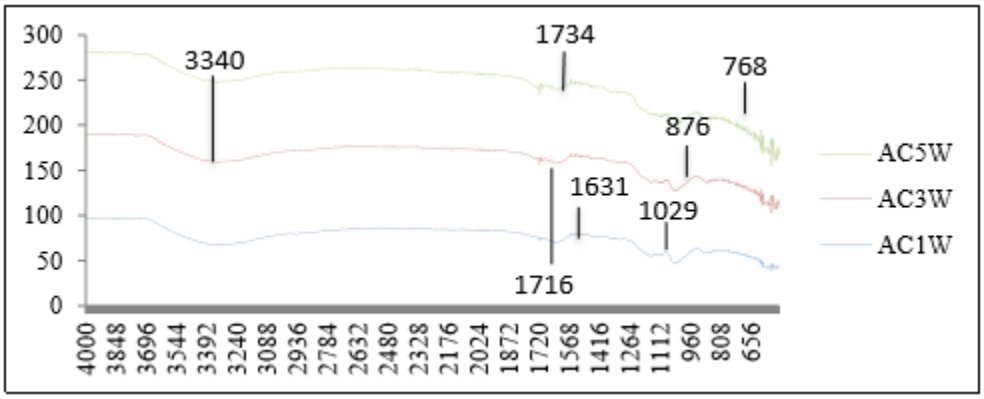

Figure 3: FTIR analysis result for KOH after MW-ultrasonic activation

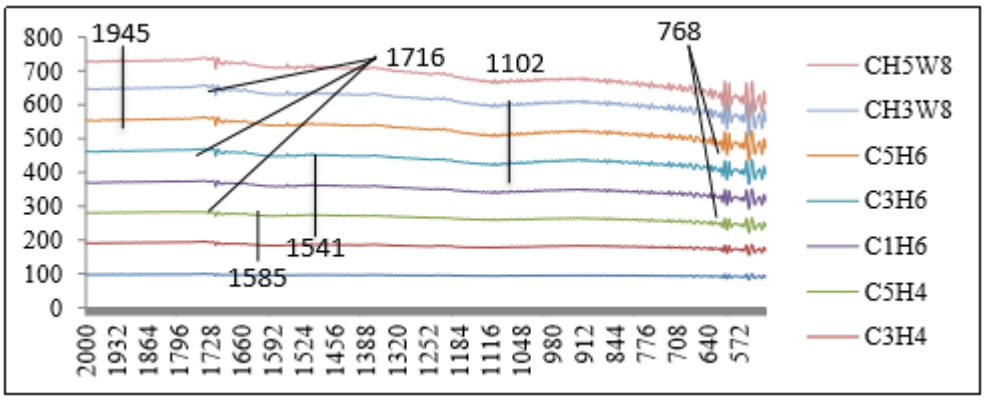

Figure 4: FTIR analysis result for KOH after carbonization

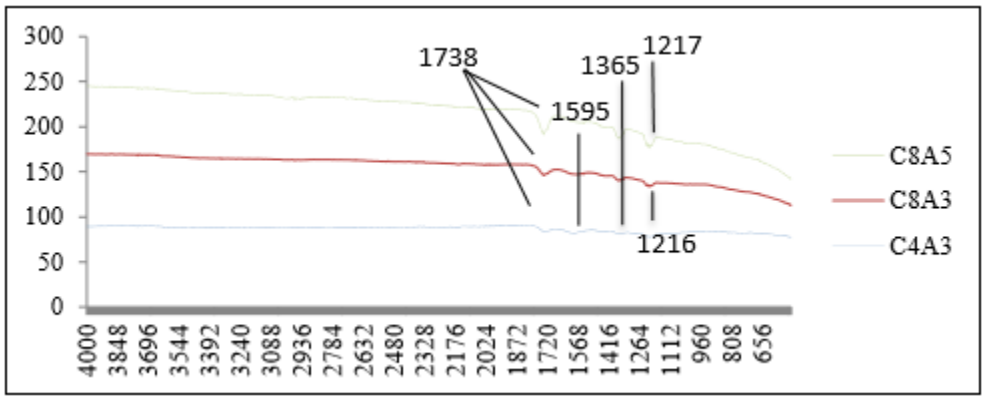

Figure 5: FTIR analysis result for H_2SO_4 after carbonization

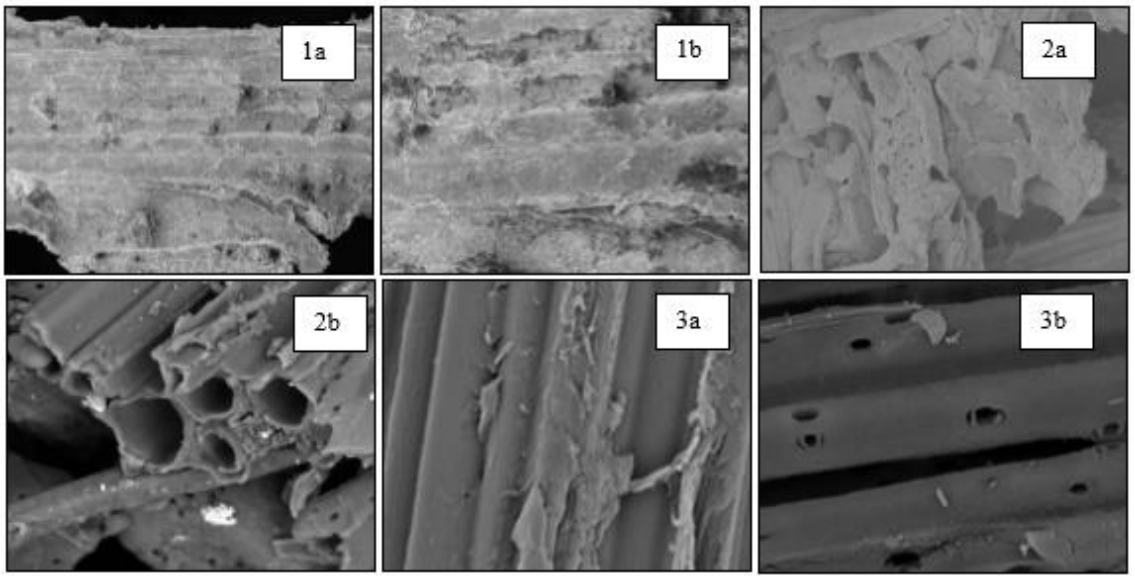

Figure 6: (1a),(1b) Raw bamboo; Mag: 500x,1000x; (2a) Activation of MW-ultrasonic of KOH; (2b) BAC of KOH; (3a) Activation of MW-ultrasonic of H_2SO_4; (3b) BAC of H_2SO_4

Surface Morphology of BAC.

FESEM analysis was conducted to study the morphology structure of activated carbon before and after the activation of MW-ultrasonic and carbonization process. The physical and chemical properties of activated carbon morphology were characterized using Zeiss Gemini Supra 40VP model. Figure 6 showed a different type of BAC morphology after MW-ultrasonic activation and carbonization process of activated carbon using different type of chemical agent. From the results, the development of pore structure was observed before and after the activation process of BAC. Figure 2a, showed the morphology of BAC after activation using MW-ultrasonic of KOH. The structure consist of the micropores with the size less than 2nm. The pores development was enhanced after carbonization process and it showed at Figure 2b. For H_2SO_4

chemical activation, the development of the pores for activated carbon was illustrated in Figure 3a and 3b. According to the results, the structure of the activated carbons are smooth with the present of the cavities. This might be due to the devolatilization of carbonaceous matters that allows the release of reaction gases from the core of particles to the outer surroundings [7].

Composition structure of BAC

BAC sample was analyses using XRD analysis to determine the graphitic nature of AC. The sample of AC was recorded on X-ray diffractometer (40kV and 30 mA) in the 2 range of 10-80° with a scan rate 5° min-1. From the XRD results in Figure 8, it shown the present of the graphite structure in the AC sample. Figure 7 showed one reflection at 2θ of 71.686° due to the (1 0 4) diffraction peaks which is far from the graphitic carbon in XRD patterns of BAC at high temperature (800°C with MW-ultrasonic 500W) in H2SO4. In Figure 8, the different of diffraction peaks was produced in different type of activation on BAC samples. The degree of order in the carbon structure was related to the intensity of the (0 0 2) diffraction peaks [8]. Isotropic pitch with broader(0 0 2) peaks would have more microstructural defects and noncrystallite carbons atoms. While crystallites of anisotropic AC would have larger size and good tropism if (0 0 2) peaks show narrow and sharp shape [9]. Diffraction peaks (1 0 2) and (1 1 0) revealed the graphitic nature of samples as a result from a low crystallite order of the carbon samples.

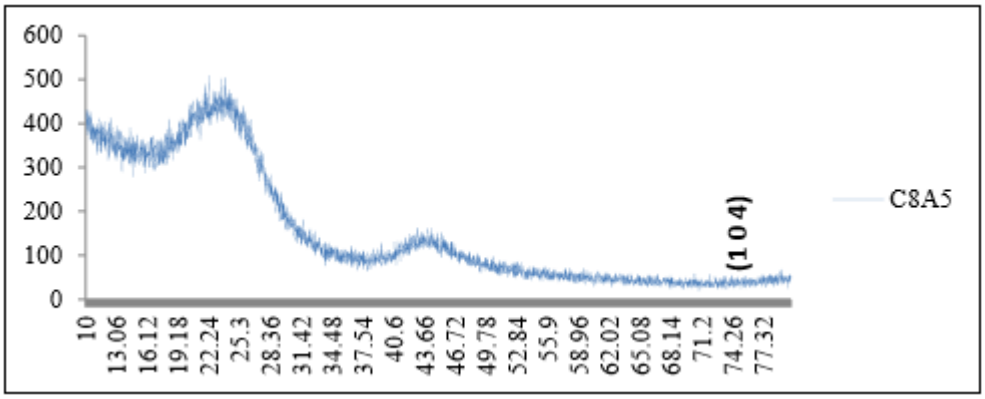

Figure 7: XRD patterns examined of activated carbon samples on H_2SO_4 chemical agent

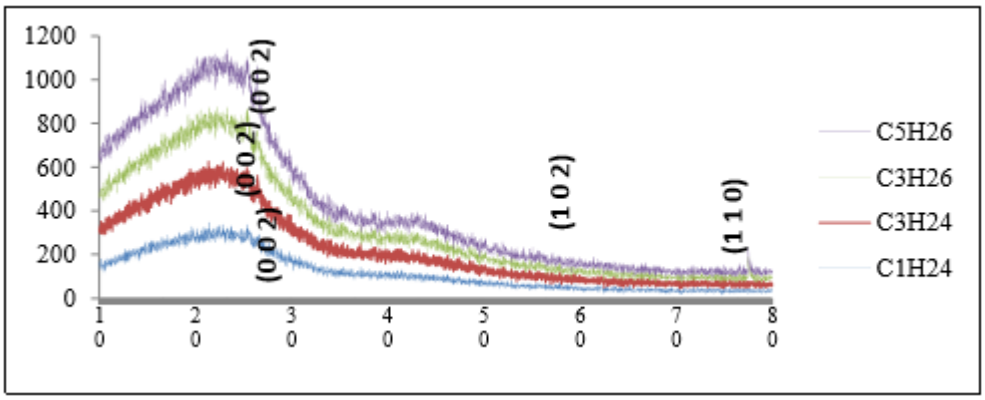

Figure 8: XRD patterns examined of activated carbon samples on KOH chemical agent

Active surface area of BAC.

The BET surface areas corresponding to the different type of chemical activation with a different MW-ultrasonic power and temperature (KOH; H_2SO_4;100W,300W,500W; 400°C,600°C,800°C) were showed in Table 2. The BET surface area of activated carbon is important because like other physic-chemical properties, it may vigorously affect the combustion behavior and reactivity of the activated carbon [10]. In KOH activation, higher temperature in carbonization process, 800°C gave a high value of active surface area which is 922.72 m2/g. On the other hand, H_2SO_4 gave 1025.27 m2/g of active surface area at 600°C of carbonization temperature. The higher surface areas are probably due to the opening of the restricted pores. The percentage of micropore followed the increase of carbonization temperature [11]. The overall results for KOH and H_2SO_4 was tabulated in Table 2. For MW-ultrasonic activation in KOH, the BET value was 4.59 m2/g, 80.04 m2/g and 106.65 m2/g with the increasing of power-frequency 100W, 300W and 500W respectively. Nevertheless, the BET value for H_2SO_4 MW-ultrasonic activation was disorderly with the increase of power-frequency activation. According to Table 2, KOH produced a higher active surface area as compared to H_2SO_4 after activated using MW-ultrasonic system. This shows that MW-ultrasonic activation had increased the pore structure of BAC. A higher of active surface on activated carbon was designed in the present study that will contributed to the charges of energy storage in supercapacitor application [12]. The value of MW-ultrasonic active surface area in KOH was higher than MW-ultrasonic in H2SO4 becaused the molecule of potassium was smaller than molecule of H_2SO_4. On the other hand, after carbonization process, H_2SO_4 activating agent produced higher on active surface area value from BET analyses becaused the pore development after carbonization was increased from mesoporous to microporous which assisted by acid activation.

Table 2: Effects of MW-ultrasonic activation and different of carbonization temperature on the pore characteristics of activated carbons

	Active surface area [m^2/g]	Total pore volume [cm^3/g]
KOH		
MW-ultrasonic activation [W]		
100	4.59	$1.5x10^{-2}$
300	80.04	$6.4x10^{-2}$
500	106.65	$7.4x10^{-2}$
Carbonization temperature [°C]		
800	922.72	$4.7x10^{-1}$
400	2.88	$2.0x10^{-3}$
H_2SO_4		
MW-ultrasonic activation [W]		
100	1.97	$5.0x10^{-3}$
300	11.51	$1.3x10^{-2}$
500	6.07	$2.0x10^{-3}$
Carbonization temperature [°C]		
600	1025.27	$4.9x10^{-1}$
400	478.14	$2.2x10^{-1}$

The results of the present study was summarized in Table 3.

Table 3 Analysis data for the effect of MW-Ultrasonic activation on BAC before carbonization

Chemical agent [alkali/acid]	Sample	Power MW [watt]	MW retention time [min]	Soaking time ultrasonic [min]	FTIR	BET [m^2/g]		XRD		FESEM
						run	value	run	graphite	
KOH	AC1W	100	30	60	✓	✓	4.59	✓	x	✓
	AC3W	300	30	60	✓	✓	80.04	✓	x	✓
	AC5W	500	30	60	✓	✓	106.65	✓	x	✓
H_2SO_4	A100	100	30	60	✓	✓	1.97	✓	x	✓
	A300	300	30	60	✓	✓	11.51	✓	x	✓
	A500	500	30	60	✓	✓	6.07	✓	x	✓

From the results, it can be identified that chemical activation using KOH encourage to the development of pores as compared to acid activation, H_2SO_4 in the MW-ultrasonic activation.

CONCLUSION

Chemical activation of KOH and H_2SO_4 with an integration of MW-ultrasonic was an effective of activation process that have better in morphology, physical and chemical properties of activated carbon. Based on the results, its showed chemical activation agent and MW-ultrasonic activation had enhanced the performance of BAC.

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