Effect of Pre-carbonization Time on the Properties of Terminalia Catappa Fruit Shells-based Activated Carbon by Microwave Assisted KOH Activation

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Abstract: Activated carbons (ACs) had successfully been made from Terminalia Catappa fruit shells with variation of carbonization times and KOH assisted microwave activation. The carbonization times were varied for 2 hours, 3 hours and 4 hours, and then activated with ratio of mass of pre-carbonized and KOH of 2:1. The aim of this research was to study the characteristics of Terminalia Catappa fruit shells as ACs that were represented by yield, surface morphology, microstructures, surface area, and methylene blue adsorption. The yield of ACs was decreased with increasing of pre-carbonization time. The X-ray diffraction patterns indicated that all the activated carbons were in semicrystalline, with the presence of narrow peaks of 002 and 100 at 2θ around of 22^o and 41^o, respectively. The best of BET surface area of AC resulted from the carbonization time of 3 hours was 303 m^2/g. This surface area generated the highest methylene blue adsorption of 135.38 mg/g.

Keywords: Terminalia catappa fruit shells; Pre-carbonization time; KOH assisted microwave activation; Microstructures; Surface area

1. Introduction

Environmental protection has become the attention and focus of world since several decades ago because of rapidly changing technologies, industrial products and human generated waste that if improperly managed, could threaten public health and the environment. For this purpose, activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environment i.e. gas purification [1], reduction of organic pollutant [2], food processing [3], chemical and pharmacy industry [4], and waste water treatment [5,6] owing to their high surface area, pore structure, thermal stability, and low acid/base reactivity [7]. Thus an activated carbon has played an important role in the chemical, pharmaceutical and food industries.

Activated carbon, however is expensive which limits its large scale application. Various carbonaceous materials such as coal, lignite, nutshells, wood, and peat are used in the production of commercial activated carbon. A potential method to reduce its cost is to produce activated carbon from low-cost materials such as agricultural by-products, which has becomes attracted increasingly interesting research topics in recent years. Agricultural by-product are cheaper, readily available, environmentally friendly, renewable, and structurally porous. Many researchers have made efforts for

preparing activated carbons from agricultural by products such as pineapple peels [2], coconut shells [7], fibers oil palm empty fruit bunches [8], Jatropha hull [9], and cotton stalk [10].

Microwave irradiation assisted chemical activation has been successfully applied and regeneration for the activated carbon preparation [7-10]. Activated carbon is a good microwave absorber which receives microwave energy directly through dipole rotation and ionic conduction. Microwave heating has the advantages of high efficiency, rapid temperature rise, uniform temperature distribution and saving of energy over conventional thermal method and the treatment time can be significantly reduced [11]. Hence, it is expected that microwave radiation will be a viable technology for the modification of activated carbons.

In this study, the activated carbon is prepared from Terminalia Catappa fruit shells. The aim of this study was to prepare Terminalia catappa fruit shells based activated carbon using potassium hydroxide (KOH) as activating agents and heating carrier by microwave irradiation. The activated carbon was produced at the different of pre-carbonization times. The characterizations of activated carbons were performed using X-ray diffraction, scanning electron microscopy, N_2 adsorption–desorption isotherms, and adsorption of methylene blue.

2. Material & Methodology

2.1. Materials

Terminalia catappa fallen fruit used for preparation of activated carbon were collected from trees located in the region of University of Riau premises, Pekanbaru, Riau, Indonesia. The husk was removed from the fruit and their fruit shells were soaked in distilled water for a night. The fruit shells were crushed and then dried at the temperature of 100^{o}C for 24 hours. The dried shells were crushed into the size of 0.5 to 1 cm.

2.2. Preparation of Activated Carbon

Pre-carbonization of fruit shells were conducted in the electric oven at the temperature of 200^{o}C for different pre-carbonization time of 2, 3 and 4 hours. Pre-carbonized Terminalia catappa fruit shells were milled and then sieved to obtain grain with the size less than of 1 mm.

The pre-carbonized Terminalia catappa fruit shells was soaked in potassium hydroxide (KOH) solution with an impregnation (pre-carbonized: KOH) ratio of 2:1 (wt.%). The slurry was kept at room temperature for 24 hours and stirred to ensure the access of the KOH to the pre-carbonized Terminalia catappa fruit shells. The activation step was conducted in a tubular glass reactor placed in a microwave oven. The microwave output power was set at 630 Watt and 20 minutes of irradiation time was selected as the optimum heating period based on preliminary runs. After microwave irradiated, the activated carbon were washed for several times using distilled water and de-mineralized water to remove residual organic and mineral matters until the pH of the washing solution reached ~ 7, filtered and finally dried at 105^{o}C. Activated carbon with pre-carbonization time of 2, 3 and 4 hours were labeled as AC2, AC3 and AC4 respectively.

The yield of activated carbon was estimated according to eq. (1):

$$Yield\ (\%) = \frac{M_f}{M_o} x\ 100\% \quad (1)$$

where M_f is and M_o are mass of activated carbon and mass of sample before activation, respectively.

Methylene blue uptake at equilibrium, q_e (mg/g), was calculated by Eq. (2):

$$q_e = \frac{C_o - C_e}{W}\ V \quad (2)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium condition, respectively. V is the volume of the solution, and W is the mass of adsorbent used.

2.3. Characterization of Physical Properties of Activated Carbon

Some physical properties of activated carbon were characterized including the yield, microstructure, surface morphology, surface area and methylene blue adsorption. The characterization of microstructure, surface morphology and surface area were conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption/desorption isotherm at 77 K, respectively.

3. Results and Discussion

Influences of pre-carbonization time on the yield of activated carbon are show in Table 1. The yield of activated carbon decreased with increasing pre-carbonization time which could be attributed to the reaction between carbon and activation agent [12] and most aliphatic compounds were decomposed during pre-carbonization before it were converted into aromatic compound by acid treatment [13] . These results indicated that the pre-carbonization times were significantly influenced to the yield of activated carbon.

Table 1. Yield of activated carbon

Sample	Mass (g)		Yield (%)
	Before	After	
AC2	30	9.85	32.83
AC3	30	7.91	26.37
AC4	30	5.40	18.00

Figure 2 shows micrographs of AC2, AC3 and AC4 at the magnification of 1kX. Grains surface of activated carbon have a porous microstructure and there is an open large macropores (~ in units of microns) between grains with different size and randomly distribution throughout the sample but the grain surface of AC3 seem to be more rough than the other two AC2 and AC4, indicating the effect of changing the pre-carbonization time on the microstructure of the activated carbon. Smaller macro pores on the surface and inside the grains are not visible in the micrograph at this magnification.

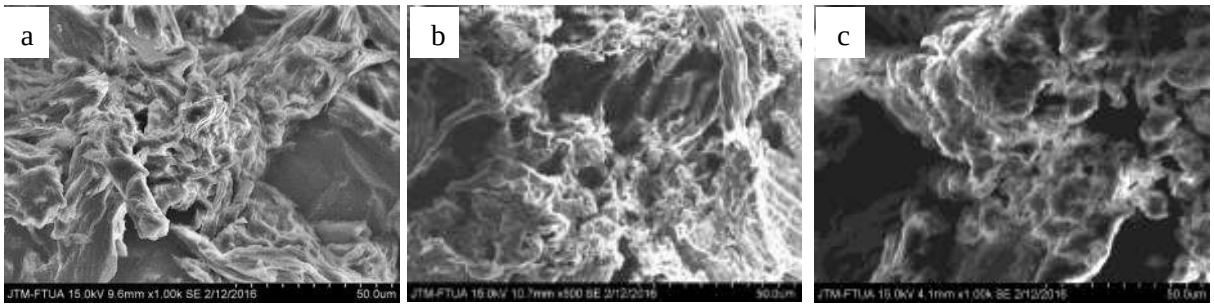

Figure 1. SEM micrographs of (a). AC2, (b). AC3 and (c). AC4

Table 2. Interlayer spacing and microcrystallite dimension of activated carbon

Samples	Interlayer spacing (nm)		Microcrystallite dimension (nm)		L_c/L_a
	d_{002}	d_{100}	L_c	L_a	
AC2	0.4067	0.2187	2.6365	1.1087	2.3780
AC3	0.4020	0.2195	3.1881	1.1002	2.8977
AC4	0.4055	0.2181	2.6828	1.1010	2.4367

X-ray diffractogram (Figure 2) of each activated carbon has two broad peaks at 2θ of about 22^o and 41^o respectively, corresponding to the diffraction peaks (002) and (100) which indicates that all activated carbon have turbostratic structure [14]. The values of microcrystallite parameters i.e. stack height (L_c), stack width (L_a), ratio of L_c/L_a, and interlayer layer spacing d correspond to the diffraction peaks (002) and (100) respectively, calculated from the X-ray data, are listed in Table 2. The ratio of

L_c/L_a has been reported to be proportional to the value of surface area [15], this suggests that AC3 has higher surface area than AC2 and AC4.

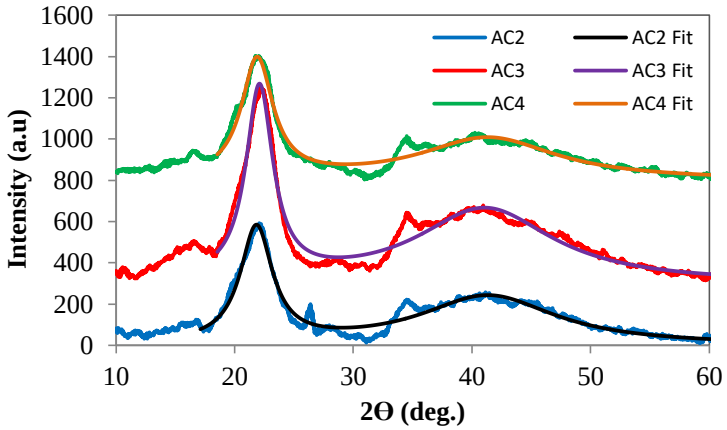

Figure 2. XRD patterns of activated carbon

The XRD pattern as shown in Figure 2 are indicates strongly that the pre-carbonization produces the char consisting of relatively well-organized aromatic carbons with sp^2 bonding character, which are more stable than amorphous-like carbons of sp^3 bonding character [16].

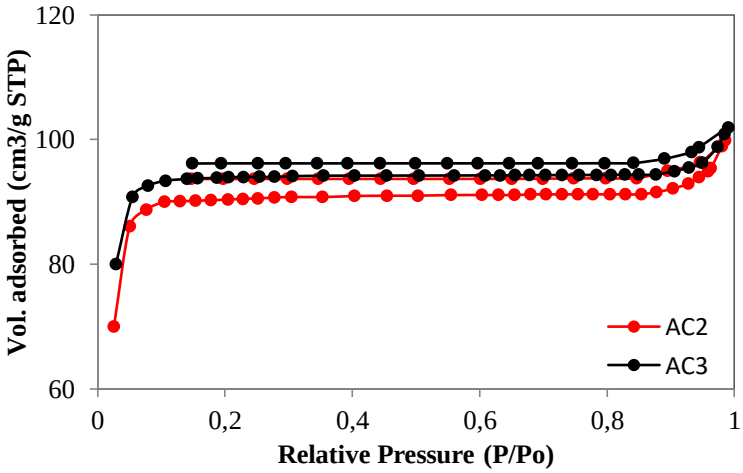

Figure 3. Nitrogen adsorption/desorption isotherm of AC2 and AC3

Figure 2 represents the nitrogen adsorption/desorption isotherms at 77 K of AC2 and AC3. Both of AC2 and AC3 shapes of the adsorption isotherms are quite similar to each other. The isotherms of the activated carbons prepared at pre-carbonization time are of Type I, indication of the microporous character [17]. The BET surface areas and pore diameters of the two types of activated carbons, calculated from the adsorption isotherms of Figure 3, are listed in Table 3. The higher of BET surface was obtained at the pre-carbonization time of 3 hours with values of micro surface area (S_{Micro}) and meso surface area (S_{Meso}) of 265 and 38 m^2/g, respectively. The higher of BET surface area of AC3 was predicted by the higher value of stack height (L_c). The pore diameter of AC2 and AC3 were slightly decreased with increasing pre-carbonization time.

Table 3. Porosity data obtained from N_2 adsorption-desorption for AC2 and AC3

Sample	Surface Area (m^2/g)			Diameter (nm)
	S_{BET}	S_{Micro}	S_{Meso}	
AC2	279	251	28	3.0732
AC3	303	265	38	3.0659

The methylene blue adsorption capacity on the activated carbon is listed in Figure 4. As can be seen, the AC3 showed the higher adsorption capacities than AC2 and AC4, which is deals with the

BET surface area and values of L_c. The adsorption capacity of AC2 for methylene blue was about 39% and 27% higher than that of AC2 and AC4, respectively.

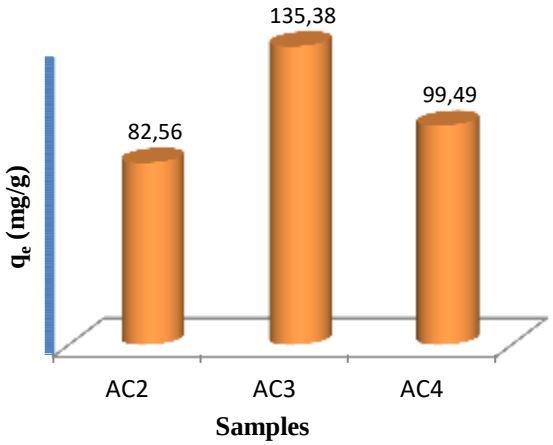

Figure 4. Methylene blue adsorption on activated carbon

4. Conclusion

It had indicated that KOH was a suitable activating agent for the preparation of activated carbon from Terminalia catappa by microwave irradiation. The effects of the pre carbonization time, on the yield, the physical properties and the methylene blue adsorption properties of activated carbon were investigated systematically. The optimum condition was pre-carbonization time at 3 hour with the stack height (L_c), BET surface area, and methylene blue adsorption on AC3 of 3.1881 nm, 303 m^2/g, and 135.38, respectively.

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