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Effect of Chemical Treatment on Production of Activated Carbon from *Cocos nucifera L*. (Coconut) Shell by Microwave Irradiation Method

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Abstract

In recent years, activated carbon has attracted attention among researchers due to its special properties such as high porosity, highly adsorption and low cost. In this research, activated carbon has been successfully produced from the coconut shell by using the microwave irradiation method where zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) were implemented as the activating agents. The results showed that phosphoric acid has the most significant effect on the synthesized activated carbon properties. The optimum parameter for the power of microwave irradiation used was 380 W, impregnation ratio of activating agent to char was 3:1 for phosphoric acid, 2:1 for sodium hydroxide, and for 1:1 zinc chloride while concentration of each activating agents was 0.5 M with 10 minutes of activation time. All samples then were characterized by using, Moisture meter, FTIR-ATR, XRD and TGA in order to determine the functional groups, composition and element and weight loss of the activated carbon. This research could benefit the environment by recycling the agriculture waste into a new useful material as well as to keep the environment safe from pollution.

1. Introduction

In general, activated carbon is produced from the variety carbonaceous source of materials where for the production of activated carbon, the precursor must be organic materials that rich in carbon (Mochida et al., 2006). Activated carbon has high porosity and high surface area which make it a suitable candidate to be used as adsorbent.

Coal is the one of the great producer to produce activated carbon. However, the agriculture waste being the best choice to be converted into activated carbon because of its abundantly available and low cost (Prahas et al., 2008). Moreover, the local agriculture waste could reduce the ecological impact by converting it into activated carbon (Cobb, 2012). The sources and quality of the coal are the important things to guarantee the quality and consistency of activated carbon.

Chemical activation is mainly used for biomass precursor because it achieves the surface area and higher yield besides low operating and energy cost required (Gratuito et al., 2008). The chemical agent or dehydrating agent is used to functionalize the surface of native carbon into activated carbon (Abdullah et al, 2015). There are several advantages of chemical activation method as it could lower the activation temperature, increase the activated carbon yields and give well-developed micro porosity (Yorgun & Yıldız, 2015) lead to various applications such as catalyst (Abdullah et al, 2016) and water treatment (Lin et al, 2009).

In this research, the abundantly available coconut shells which have excellent natural structure and low ash content were used as precursor for preparation of activated carbon by using microwave irradiation method. Three different activating agents namely zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) were selected in order to determine the best activating agent for preparing the activated carbon. Moisture meter, Fourier Transfrom Infra-Red-Attenuated Total Reflectance (FTIR-ATR), X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) served as main investigative tools for characterization of the synthesized activated carbon from coconut shells.

2. Materials and Methods

2.1. Preparation of Raw Material

The coconut shells were obtained from market nearby. The coconut shells were dried under the sunlight directly for two weeks. After drying, the coconut shells were cleaned and washed with water to remove the impurities and followed by further drying for one week.

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Next, the coconut shells were put in the oven for 24 hours at 105°C. Then, the coconut shells were grinded into small pieces.

2.2. Preparation of Activated Carbon

The grinded coconut shells were filled in the crucible before were put in the furnace to undergo the carbonization process. The furnace was set up to temperature at 500˚C and then was held constant for one hour to allow the pyrolysis to take place with the absence of air until it becomes char. Then, the char was crushed into powder form by using mortar and sieved by using 250 micron siever. The powder then placed in airtight bags to prevent re-absorption of moisture from the atmospheric air. Chemical activation of the powdered precursor was done by NaOH, $ZnCl_2$ and H_3PO_4 with concentration of 50% w/w. The powdered coconut shell was initially impregnated with activating agents were put in the beaker and dried in the room temperature for 4 hours. Then, the impregnated samples were filtered and put in the oven at 105˚C for 24 hours for drying. Microwave assisted irradiation with nitrogen flow rate of 150 cm^3/min was used to further activate the impregnated samples where the microwave then was set at 380 W and 10 minutes of activation times. After that, the samples were rinsed copiously with hot distilled water and the pH of water was measured until it turned into pH 7. Finally, the samples were dried again in the oven at 80°C for 16 hours.

2.3. Characterization of Activated Carbon

The percentage of the synthesized activated carbon was obtained by using the Equation 1 as below;

$$\text{Percentage Yield (\%)} = \text{(Weight final activated carbon)/(Weight of initial native carbon)} \times 100\% \qquad \text{Eq.1}$$

Moisture content was determined by using moisture meter where the amount of water bind to the activated carbon surface was determined. The surface organic functional groups of the synthesized activated carbon were studied by Perkin Elmer Spectrum ™ 400 FTIR-ATR Spectrometer. The samples were put into the FTIR-ATR spectrometer sample holder and the sprectra were recorded between 400 and 4000 cm-1.

Thermogravimetric analysis (TGA) was carried out in where a typical sample mass of 5 mg was heated from 30°C to 650°C at heating rate of 10°C/min with nitrogen flow of 20 mL/min. X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser X-ray diffractometer with monochromatized Cu K_α radiation (λ=1.5418 Å).

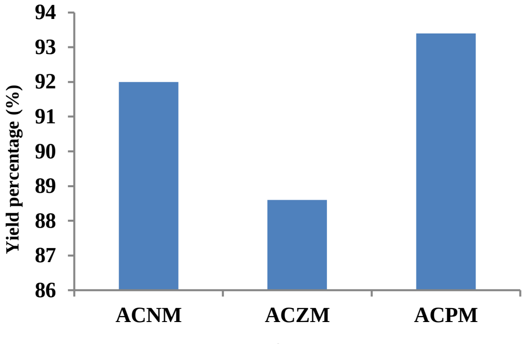
3. Results and Discussion

3.1. Yield Percentage of Activated Carbon

The yield percentage of each activated carbon with different activating agents were calculated and showed in the Table 1 and Figure 1. The yield of products are higher for activated carbon with phosphoric acid activated with microwave (ACPM), followed by activated carbon with sodium hydroxide (ACNM) and lastly the yield products was activated carbon with zinc chloride (ACZM). The higher yield product which might probably due to the formation of more micropores in the products as reported by Pradhan (2011).

Table 1: Weight before and after microwave process and the yield percentage of the products.

Sample	Weight Before Microwave (g)	Weight After Microwave (g)	Yield Percentage (%)
ACNM	5.00	4.60	92.0
ACZM	5.00	4.43	88.6
ACPM	5.00	4.67	93.4



ACNM - activated carbon with sodium hydroxide activated with microwave
ACZM - activated cabon with zinc chloride activated with microwave
ACPM - activated carbon with phosphoric acid activated with microwave

Figure 1. Yield percentage of synthesized activated carbon

3.2. Moisture Adsorbance

The moisture adsorbance content of the native carbon (NC), activated carbon impregnated with NaOH activated with microwave (ACNM), activated carbon impregnated with $ZnCl_2$ activated with microwave (ACZM) and activated carbon impregnated with H_3PO_4 activated with microwave (ACPM) were examined and results as shown in the Table 2. The temperature and time for test were fixed at 105°C and 5 minutes, respectively. The result showed that the ACNM has higher moisture content than AZNM and APNM. According to Gumus & Okpeku, (2015), the lower moisture content increases the rate of adsorption of contaminants.

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Table 2: Moisture Percentage (%)

Sample	Weight Before (g)	Time It Takes To Analyse Moisture (min)	Moisture Adsorbance (%)
NC	0.526	4.02	6.70
ACNM	0.532	2.55	14.66
ACZM	0.515	3.04	8.91
ACPM	0.527	2.51	9.89

3.3. XRD Analysis

Figure 2 and 3 show the X-ray diffraction (XRD) patterns of the activated carbon after and before the activation process that revealed that all these chars were amorphous. The broad peaks were identified at the 2Θ = 25° and 2Θ = 45° for all the graphs. The broad peak at the 2Θ = 45° became stronger after activation with activating agent NaOH, $ZnCl_2$ and H_3PO_4 which indicated that carbon tends to crystallize at an elevated temperature.

As reported by Liou (2010) the peaks at 2Θ = 45° are due to the creation of pores by the decomposition of carbon along the direction of the graphic structures. This produces relatively well organized aromatic carbon that is more stable than amorphous like carbon. The sharp peak was produced due to better layer alignment which was characteristic of a crystalline structure. The absence of sharp peaks in the activated carbon suggest it was predominantly amorphous structure which is advantageous property for well-defined adsorbents (Das et al., 2015).

3.4. Functional Group Analysis of The Activated Carbons

Figure 4 shows the FTIR-ATR spectra of the activated carbons prepared using microwave heating with different activation agent. The sample of native carbon (NC), activated carbon impregnated with NaOH and activated by microwave radiation (ACNM), activated carbon impregnated with $ZnCl_2$ and activated by microwave radiation (ACZM), showed three major adsorption bands at 1900-2500 cm^{-1}, 1500-1600 cm^{-1} and 500-1200cm^{-1}. The bands at 1100-1200 cm^{-1} and 2100-2150 cm^{-1} showed the wide band with two maximum peaks.

The band around 1500-1700 cm^{-1} can be assigned to C = C stretching vibration mode of olefinic C = C bonds as reported by D. Das, (2015). The bands near 1700 cm^{-1} may indicate the C-H bonds of the phenyl ring substitution overtones (Dinesh, 2010). The peaks near 1570 cm^{-1} for AC and others were assigned to a conjugated hydrogen bonded carboxyl groups. At the peak around 1200 cm^{-1}, it was assigned as C – O vibration. In ACZM, at 1570.51 cm^{-1} there are C=C vibration and at 1153.27 cm^{-1} and 875.77 cm^{-1} the C – O and C – H vibration assigned.

For activated carbon impregnated with phosphoric acid and activated with microwave (ACPM), there were peaks near 1160 cm^{-1} (P=O) is characteristic of PO2 stretching. The region between 700 and 1000 cm^{-1} contain bands related to aromatic structure. For ACPM the presence of phosphoric species were detected at the band around 900 cm^{-1} – 1200 cm^{-1}. 1175cm^{-1} can be assigned to C – O stretching vibration in chain of C – O – P linkage. The adsorption patterns have almost same among each samples although the samples were prepared via different activating agents.

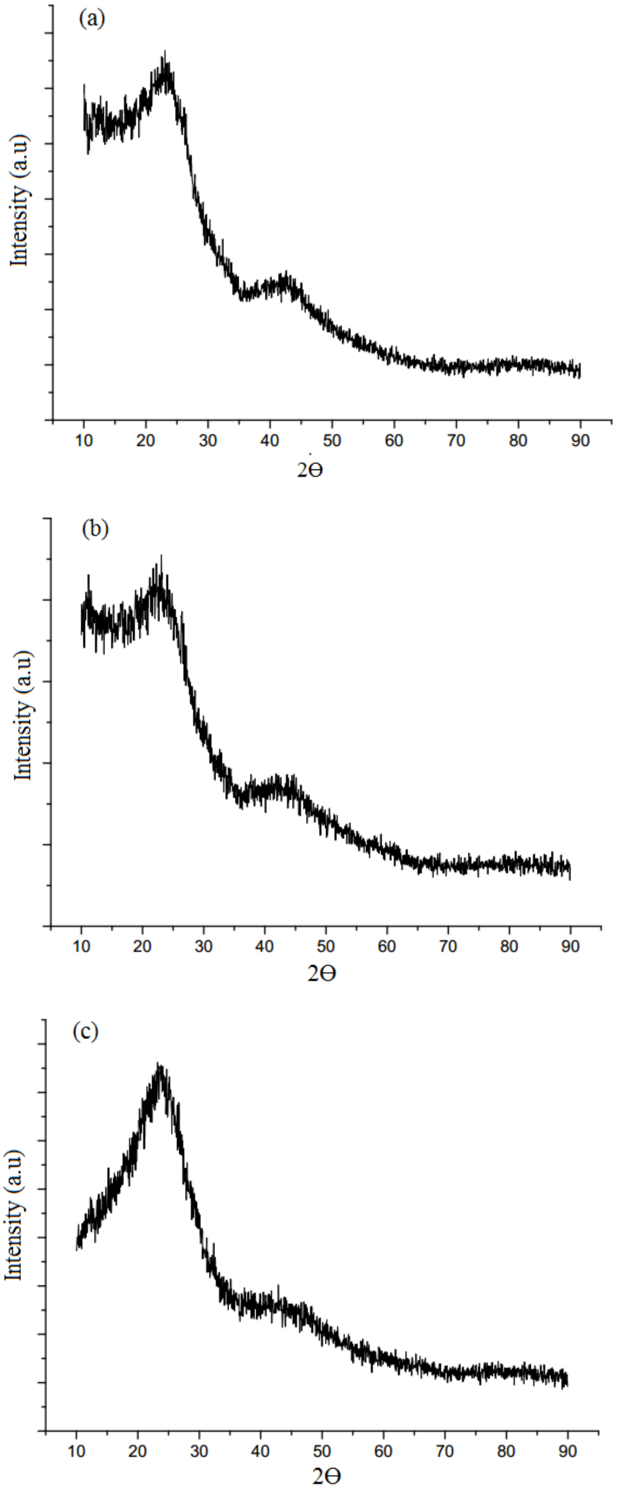

Figure 2: (a) Activated Carbon Impregnated with NaOH Without Microwave Process (ACNWM), (b) Activated Carbon Impregnated with $ZmCl_2$ Without Microwave Process (ACZWM) and (c) Activated Carbon Impregnated with H_3PO_4 Without Microwave Process (ACPWM).

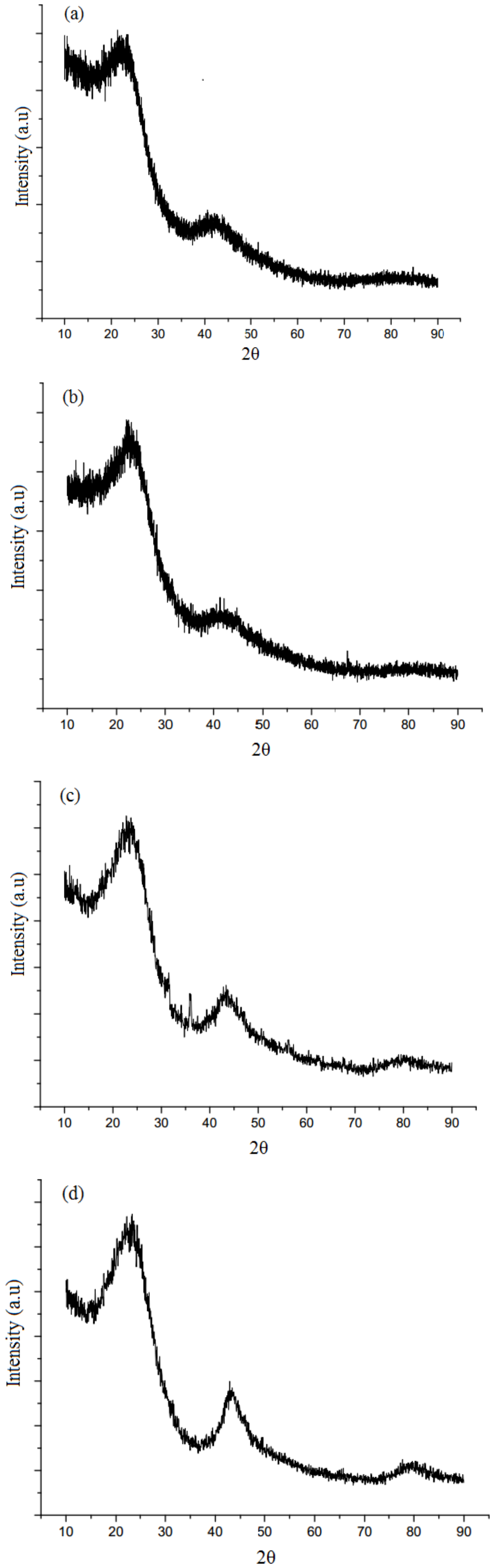

Figure 3: (a) Native Carbon (NC). (b) Activated Carbon Impregnated with NaOH Activate with Microwave (ACNM), (c) Activated Carbon Impregnated with $ZnCl_2$ Activate with Microwave (ACZM) and (d) Activated Carbon Impregnated with H_3PO_4 Activate with Microwave (ACHM).

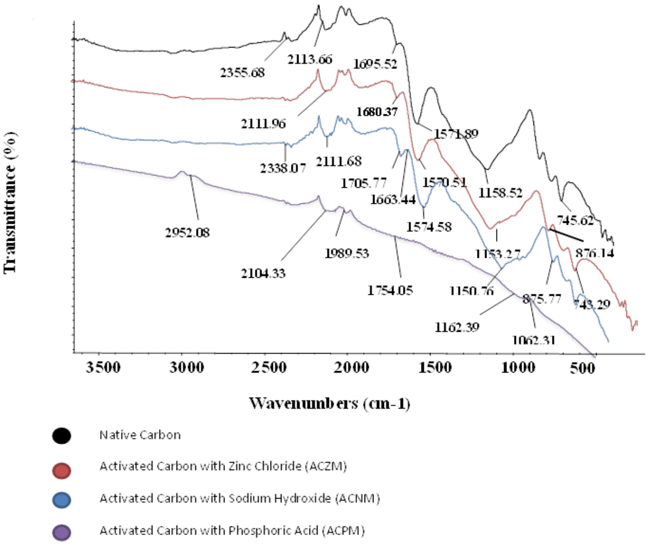

Figure 4 FTIR- ATR Spectra for Activated Carbon

3.5. Thermogravimetric Analysis

Figure 5 showed the TG and DTG curves for weight loss versus temperature of sample of native carbon (NC), activated carbon with phosphoric acid (ACPM), activated carbon with sodium hydroxide (ACNM) and activated carbon with zinc chloride (ACZM) at the impregnation ratios prepared. The TG curves indicated that the initial weight loss was begun at 30 °C. It could be noted that the maximum loss of weight at the temperature around 100 °C. The constant line from 100 °C until 600 °C implied the constant ash that was left over before it started to lose weight for the last time at 600°C.

It was observed that weight loss for activated carbons were around 11.41% - 12.0% compared to 14.2548% for the native carbon when the temperature was raised from 30°C to very high temperature 650°C. Hence, the activated carbon is suitable to be applied as adsorbent since it has high thermal stability compared to native carbon.

Native carbon and ACHM have two stages of reaction where the first stage decreasing slope was maximum as the organic matter decomposes releases the gaseous volatiles. For native carbon and ACHM, the temperature range 30°C - 110°C and 30°C - 130°C while for the stage two, with further rose in temperature the downward slope again increased rapidly for both cases. In the stage two, the temperature range from native carbon was 191.17°C – 649.13°C and ACHM was from 142.57°C – 649.45°C. The ACNM and ACZM involved three stages of reaction. For the first stage, the decreasing slope was maximum and for ACNM the temperature range was from 30.90°C – 138.58°C while the temperature range for ACZM was 31.07°C – 151.05°C. At stage two, the decreasing was a bit slowly from the range 137.61°C – 384.38°C for ACNM and 151.55°C – 347.27°C for ACZM where at this stage the chemical activating agents start to

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melt or decompose. At the last stage, the downward slope again increased rapidly for ACNM which range from 384.38°C – 649.63°C while downward slowly for ACZM ranging from 374.75°C - 649.84°C as the temperature rose. At this stage, it is expected that severe erosion happened when the char reacts with activating agents causing the pores to open.

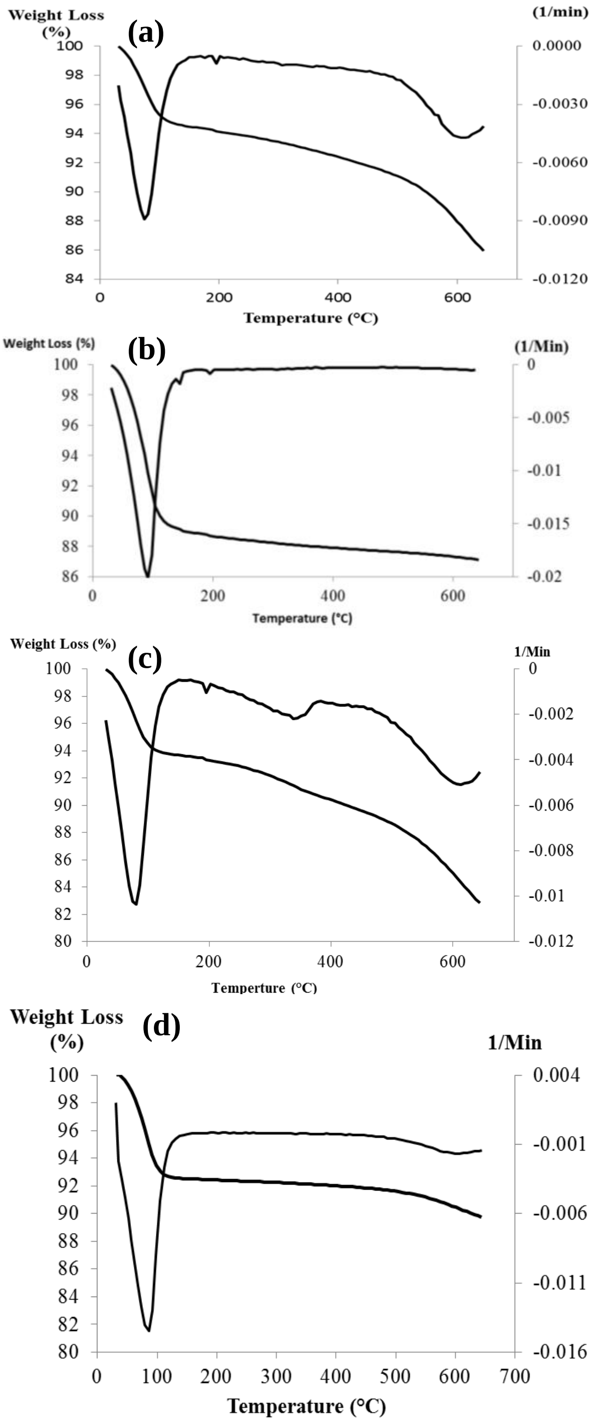

Figure 5: TGA/DTG results of (a) native carbon, (b) activated carbon with phosphoric acid, (c) activated carbon with sodium hydroxide, and (d) activated carbon with zinc chloride.

By analyzing both graphs , it was observed the activated carbon has very high resistant to weight loss compared to char, which range temperature rise was same from 30°C - 650°C. Thus the activated carbon can be subjected till 650°C without much significant weight loss of adsorbent.

4. Conclusion

Coconut shell based activated carbon was successfully synthesized by chemical activation method using H_3PO_4, NaOH and ZnCl2 followed by microwave irradiation method. The results indicated that the highest yield of products was observed for ACPM compared to ACNM and ACZM while the highest moisture content was discovered for ACNM. XRD patterns showed that all samples were amorphous and FTIR-ATR spectra revealed the surface functional groups that related to ACPM, ACNM and ACZM were detected for all samples. The thermogravimetric analysis study exposed that the thermal stability was very good up to 650°C.

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