Preparation and Characterization of Activated Carbon from Palm Kernel Shell

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Abstract. In this study, a high quality of activated carbon (AC) was successfully synthesized from palm kernel shell (PKS) via single step KOH activation. Several optimal conditions such as impregnation ratio and activation temperature were investigated. The prepared activated carbon under the optimum condition of impregnation ratio (1:1.5 raw/KOH) and activation temperature (800 °C) was characterized using \textit{Na}_2\textit{S}_2\textit{O}_3 volumetric method, CHNS/O analysis and Scanning Electron Microscope (SEM). \textit{Na}_2\textit{S}_2\textit{O}_3 volumetric showed an iodine number of 994.83 mgg\textsuperscript{-1} with yield % of 8.931 %. CHNS/O analysis verified an increase in C content for KOH-AC (61.10 %) in comparison to the raw PKS (47.28 %). Well-formation of porous structure was evidenced through SEM for KOH-AC. From this study, it showed a successful conversion of agricultural waste into value added porous material under benign condition.

1. Introduction
Activated carbon (AC) or activated coal has attracted the attention of many researchers due to its excellent properties such as thermo-stability, high performance, high adsorptive effect, large surface area and well-developed structure [1]. Commercially produced AC is prepared from solid carbonaceous materials such as nutshell, wood, lignite and petroleum pitch. However, in the aspect of industrial, production margin is the major challenge faced by industrialists. Thus, numerous studies had been done in order to discover new, inexpensive and renewable raw materials. This includes the use of agricultural waste with high carbon and low ash content [2]. Based on recent studies, raw materials which contain lignin, cellulose and lignocellulose can be used to produce high grade of AC in order to replace the current coal in the market. For example, olive kernel [3], coconut shell [4], tamarind seed [5], pistachio nut shell [6] and oil palm stones [7].

Statistically, there are about 4.98 Mty\textsuperscript{-1} of palm kernel shell (PKS) produced in Malaysia [8]. Being an inexpensive agricultural waste material, it gave an opportunity for researchers to convert this agricultural waste material into useful product. PKS contains 51.6% of C [9]. Generally, high carbon content produces high percentage of char and this increases the product yield. Therefore, it was believed that PKS will act as a good precursor in the production of AC.

In general, there are two widely used methods in the preparation of AC, namely; physical activation and chemical activation. For physical activation, it involves two steps which are carbonization and activation step which operates at 700 - 1100 °C in the presence of suitable activating agent such as carbon dioxide, steam, air or their mixture. For chemical activation, the precursor is mixed with certain amount of chemicals such as zinc chloride (ZnCl\textsubscript{2}), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) and potassium...
hydroxide (KOH) which acts as the activating agent. In chemical activation process, the carbonization (400 - 700 °C) and activation step are done simultaneously which thereby shortens the analysis time used, reduces the energy consumption and produces higher yield of product. Therefore, in this study, AC was synthesized from PKS via single step chemical activation using KOH as the chemical activating agent. To date, there are few studies reported on the synthesis of activated carbon from PKS using KOH, however, these works registered low surface area. For example, in a study by Rahim et al.[10], the prepared AC showed surface area of 391 m²/g and in a study conducted in Nigeria, the authors reported AC with only 155 m²/g at high activation temperature and time of 1000 °C and 30 min respectively [11]. Thus, this stimulates us to prepare high surface area AC from PKS via KOH activation by investigating the influence of several parameters such as activation temperature and impregnation ratio and characterized via elemental analyzer (CHNS/O analyzer), Scanning Electron Microscope (SEM) and by using Sodium Thiosulfate (Na₂S₂O₃) volumetric method (ASTM D4607).

2. Experimental Method

2.1. Materials and Reagents
PKS was collected from local oil palm plantation in Perak, Malaysia and used as the precursor. Potassium hydroxide (KOH, HmBG) was used as the chemical activator. Other chemicals used were iodine pearl (HmBG, 99%), sodium thiosulphate-5-hydrate (Na₂S₂O₅.5H₂O, HmBG, 99%), starch (C₆H₁₀O₅, HmBG), hydrochloric acid (HCl, Fisher, 37%), sodium carbonate anhydrous (Na₂CO₃, HmBG, 99%), potassium iodate (KIO₃, HmBG, 99.8%) and potassium iodide (KI, HmBG, 99.87%).

2.2. Preparation of Raw Material
PKS was cut and dried under the sun for 2 days. Then, the sample was further oven dried at 80 °C for 12 h. Later, the dried sample was grinded and sieved to the size of 212 μm and kept in a closed container for further use.

2.3. Preparation of Activated Carbon using KOH
10 g of raw PKS was weighed and transferred into an empty crucible. 10 g of solid KOH was diluted in 20 mL of distilled water. The solution was added into the weighed PKS to make up ratio of 1:1 and stirred uniformly. Later, the mixture was oven dried for 24 h. Then, the carbonization of the raw material with activating agent in a furnace was carried out. The furnace was set at a constant temperature of 700 °C, activation time of 30 min and rate of 5 °C per min. After completion of carbonization process, the sample was washed with 3M of HCl and suction filtered, washed with hot distilled water until it reaches pH 7. Then, the sample was transferred into an empty petri dish and placed in an oven at temperature of 80 °C for 24 h. The dried sample was weighed and the percentage of yield was calculated using Equation (1).

\[ \text{Yield \%} = \frac{\text{Mass Final}}{\text{Mass Initial}} \times 100\% \quad (1) \]

where, Mass Final = Mass of product; Mass Initial = Mass of precursor used

Next, the dried sample was sieved (150 μm) and kept in a closed container for further use. Impregnation ratio (1:1, 1:1.5 and 1:2) and activation temperature (500-900 °C) were optimized in this study under KOH treatment to prepare AC of high yield %, high iodine number and well developed pore structure. The prepared AC was denoted as KOH-AC.
2.4. Characterization Analysis

Na$_2$S$_2$O$_3$ volumetric titration based on ASTM D4607 was used to determine the iodine number (IN) of char and KOH-AC. Ultimate analysis was done to determine the C, H, N, S and O element contained in the synthesized AC using the CHNS/O Analyzer (Thermo Scientific flash 2000) based on ASTM 3172. SEM analysis (S MINI CUP EX-54165 JMU) was conducted to visualize the surface morphology of the raw and KOH-AC.

3. Results and Discussion

3.1. Influence of Synthesizing Parameters

3.1.1 Influence of Impregnation Ratio (Raw:Activator)

The effect of impregnation ratio was studied at a constant temperature and activation time of 700 °C and 30 min respectively. The impregnation ratios used were 1:1, 1:1.5 and 1:2 and the results are presented in Figure 1.

![Figure 1. Effect of impregnation ratio on yield (%) and IN (mg g$^{-1}$) of KOH-AC.](image)

Based on Figure 1, the prepared AC showed decreased in yield as the ratio of raw material to KOH increased from 1:1 until 1:2. Moreover, iodine number (IN) value increased from 1:1 to 1:1.5 which indicated a well-developed porous structure. According to Marsh and Rodriguez-Reinoso, [12], this occurrence may due to the gasification of volatile matter as a result of reaction between KOH and the carbon in the precursor as shown in the Equations (2) and (3).

\[ 6\text{KOH} + 2\text{C} \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \quad (2) \]

\[ \text{K}_2\text{CO}_3 + 2\text{C} \rightarrow 2\text{K} + 3\text{CO} \quad (3) \]

Referring to the reaction equations, KOH was reduced to metallic potassium and K$_2$CO$_3$ as by-product. Then, carbon was further oxidized into CO which emits as volatile matter and leads to the formation of pore. In addition, the reaction was enhanced due to intercalation between metallic potassium and the graphene layer structure which breakdown into carbon particles [12]. This phenomenon explained on why the yield percentage decreased and IN increased at higher loading of activating agent. Reduction in the IN at impregnation ratio of 1:2 indicated that the wall of AC’s pore started to become thin and suddenly collapsed. Therefore, it reduces the amount of iodine which can
be absorbed. Thus, based on the IN value, impregnation ratio of 1:1.5 was selected as the optimized ratio for the subsequent optimization studies.

3.1.2. Influence of Activation Temperature

At a constant impregnation ratio and activation time of 1:1.5 and 30 min respectively, the effect of activation temperature was studied at 500 - 900 °C and the results are compared in Figure 2.

![Figure 2. Effect of activation temperature on yield (%) and IN (mg g⁻¹) of KOH-AC.](image)

Referring Figure 2, it can be observed that the yield % decreased tremendously as the temperature was increased (500 – 900 °C). On contrary, IN increased as the temperature increased from 500 - 800 °C. This phenomenon was due to the rapid gasification of volatile matter as the activation temperature increases [13]. Moreover, it can be seen that the yield % reduced and IN increased drastically starting at 700°C. Based on Marsh and Rodriguez-Reinoso, [12], KOH started to react above 700°C after the formation of char. During activation, the metallic potassium vibrated on the PKS surface and caused some of the pores started to develop. Moreover, the use of high activation temperature caused a vigorous collision of K⁺ ion on the AC surface and carbon structure was rapidly disintegrated. Thus, disintegration resulted in an increase in the removal rate of volatile matter and the creation of porous structure. The IN dropped significantly at 900 °C as the carbon structure was breakdown into powder which caused more pores to collapse [6]. Based on the highest IN of 994.83 mg g⁻¹, 800 °C was selected as the best temperature. Thus, to conclude, the optimized condition was set at impregnation ratio of 1:1.5 and impregnation temperature of 800 °C.

3.2. Sample Characterization

3.2.1. Ultimate Analysis

The composition of carbon, hydrogen, nitrogen, oxygen and sulphur in both raw and prepared AC were determined through the ultimate analysis. The results of the analysis are shown in Table 1. Referring Table 1, it showed a reduction in the hydrogen and oxygen content. This is due to during the activation process at high temperature, oxygen containing functional groups will be removed from the
carbon skeletal due to the released of volatile matter [14]. In addition, the enlargement of porous structure also increases the removal rate of volatile matter and resulted in the reduction of hydrogen and oxygen content in the final product.

| Table 1. Ultimate analysis of PKS and KOH-AC. |
|-----------------|------|------|------|------|------|
| Sample          | C    | H    | N    | S    | O    |
|                 | wt.% |      |      |      |      |
| PKS             | 47.28| 5.32 | 0.00 | 0.00 | 47.40|
| KOH-AC          | 61.10| 1.40 | 0.00 | 0.00 | 37.50|

As a result of the released of volatile matter, it results in the increment in the carbon content of KOH-AC and this is useful in producing AC with high yield. The absence of sulphur showed that the synthesized KOH-AC is eco-friendly which further proved that PKS is a good precursor for the fabrication of AC.

3.2.2. Morphological analysis
The surface morphology of the PKS and the KOH-AC was investigated by SEM and the images are shown in Figure 3.

![Figure 3. SEM images of (a) raw material and (b) KOH-AC at x250; (c) raw material and (d) KOH-AC at x2600.](image)

Referring Figures 3(a) and (c), it can be clearly observed that there were no pores formation except for some occasional cracks on the surface. However, in Figures 3(b) and (d), there were many pores
development occurred and was clearly observed. The pore formation might have contributed to the high \( \text{IN of 994.83 mgg}^{-1} \). At temperature of 800 °C with KOH as the chemical activating agent, it resulted in the creation of more pores and a substantial removal of volatiles compound during the carbonization and activation step [6]. Therefore, the formation of pore on the AC surface shown in Figures 3(b) and (d) was due to the intercalation of KOH and the dehydration of volatile matter.

4. Conclusion
In this work, highly porous activated carbon with \( \text{IN of 994.83 mgg}^{-1} \) was successfully synthesized from Palm Kernel Shell (PKS) under the optimal condition of impregnation ratio (1:1.5 raw/ KOH) and activation temperature of 800 °C. Through the SEM analysis, a smooth surface morphology was spotted for the raw material and a large number of pores were developed for KOH-AC. This study provides a facile method for the conversion of waste PKS into high quality AC.

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