Preparation of activated carbon from palm kernel shell by chemical activation and its application for β-carotene adsorption in crude palm oil

A R Hidayu1′, M Z Sukor, N F Mohammad, O S J Elham, N I Azri, M A I Azhar and M J Jalil2

1Faculty of Chemical Engineering, Universiti Teknologi MARA, Johor Branch, Pasir Gudang Campus, Jalan Purnama, Bandar Seri Alam, 81750 Masai, Johor.  
2Faculty of Chemical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Permatang Pauh, Penang.  
*hidayurani@uitm.edu.my

Abstract. The losses of β-carotene in crude palm oil (CPO) during bleaching process in the industry of oleo chemical bring apprehension because β-carotene is the most important vitamin A precursor that can help to prevent night blindness, eye problems and skin disorders, and could enhance immunity and protects against toxins, colds, flu and infections. Yet, recovery of β-carotene can be done by adsorption using activated carbon. Accordingly, the study aimed to prepare activated carbon from palm kernel shell (PKSAC) by chemical activation and its application for β-carotene adsorption in CPO has been examined. Activation of palm kernel shell carbon was done chemically using Zinc Chloride (ZnCl2) at impregnation ratio of 1:1 mass basis for 24 hours and carbonization was done at 500 °C for 30 min, 60 min, 90 min respectively called as PKSAC30, PKSAC60 and PKSAC90. PKSAC are characterized using ultimate analysis, Fourier Transform Infrared (FTIR) analysis and scanning electron microscopy (SEM). The capability of PKSAC to adsorb β-carotene was studied using n-hexane as a solvent. β-carotene adsorption test was carried out in a lab-scale batch adsorption reactor. SEM and FTIR analysis result revealed the PKSAC has fibrous morphology and indicates that raw PKS was successfully converted to carbon after activation process and was proven by spectra of previous researchers. For adsorption testing, PKSAC90 give the highest percentage removal of β-carotene, 69%.

1. Introduction  
One of the richest source for carotenoids is in crude palm oil (CPO). Carotenoids are one of the components which are contribute to the orange-red color in CPO [1]. Carotenoids has β-carotene which is the most important vitamin A precursor in human nutrition as they can be transformed into vitamin A [2]. β-Carotene well known as a source to prevent night blindness, eye problems and skin disorders. It also could enhance the immunity and protects against toxins, colds, flu and infections. The importance of carotenoids in CPO has been attentive in recent years after some researches do some widely used for vitamin enrichment of margarine, nutrient preparation and pharmaceuticals. Besides, it was found that palm oil has 15 times more retinol equivalent than carrot and 300 times more than tomato [1]. Moreover,
Malaysia is one of the richest countries with palm oil where the palm oil industry has contributed substantially to the Malaysian agricultural sector and is a key driver in the Malaysian economy. However, during physical refining process of produce palm oil, approximately 20% of β-Carotene had lost after bleaching process and that is the reason why β-Carotene is should be adsorbed at first [3]. Since β-Carotene are expected to continually grow high in demands especially in food and health, their recovery from palm oil is important. Several methods have been explored to recover β-Carotene from CPO and one of the most promising technique is sorbent adsorption technology, particularly the usage of activated carbons.

Activated carbon one the most effective and useful adsorbents that used widely in industrial application such as for pollutant-gas adsorbent, water purification media, and catalyst support because of its pores with high specific surface area, adequate pore size distribution, variable characteristics of surface chemistry and relatively high mechanical strength [4-6]. Furthermore, activated carbon is widely used since most of its chemical and physical properties can be designed and adjusted according to the required applications [7]. This causes the demand for activated carbon is increasing day by day which made it high in cost and limited. This fact has prompted an interest into the production of low cost activated carbon. Recently, many researchers have been reported for preparing cheaper and readily available precursors activated carbon from agricultural wastes such as bamboo, bagasse, groundnut shells, peanut shells, coconut shells, palm kernel shell, coffee husks, tea industry waste because of their high mechanical strength and hardness [5]. For an example palm kernel shell (PKS) is a solid residue generated as a by-product of palm oil production and it is not being used optimally in the industry. Therefore, in this study, palm kernel shell (PKS) was chosen as a precursor for the production of activated carbon since it is having high carbon content and abundantly available in Malaysia and also has very low market value. This causes the demand for activated carbon is increasing day by day which made it high in cost and limited.

Activated carbons can be prepared via a physical or a chemical activation. In the physical activation, there are two steps which are carbonization step and activation step. The raw material is first carbonized under inert atmosphere and then activated at high temperature (400-1000°C) by steam or carbon dioxide. In the chemical activation, only one step is involved, where the raw material is impregnated with an activation agent (ZnCl₂, H₃PO₄, KOH, etc) and heated in an inert atmosphere. Chemical activation is preferable as it undergoes at moderate temperature (400-600°C) with higher surface area of activated carbon [8]. This chemical activation agent during the carbonization process will give an increasing in the carbon yield [9]. In this study, chemical activation is the chosen method for preparation of activated carbon due to the low activation temperature requirement and single step but produced higher surface area and better porosity compared to physical activation [4].

This research study is on the recovery of β-Carotene in CPO using activated carbon that was produced from biomass sources as an adsorbent. Hence, the goal of this study is to prepare activated carbon from PKS by the chemical activation with zinc chloride (ZnCl₂) using a muffle furnace. The physico-chemical properties of the PKSAC produced were analyzed using ultimate analysis, FTIR and SEM. In addition, the performance of PKSAC on the adsorption of β-Carotene in CPO were evaluated.

2. Experimental

2.1 Raw Materials
The palm kernel shell (PKS) sample (Figure 1) was selected for activated carbon preparation. PKS was obtained from a palm oil mill in Segamat, Johor. PKS sample was treated with distilled water several times to get rid of any unwanted dirt and impurities. Then, treated PKS sample was dried oven at 105 °C for 24 hours to remove moisture. The dried PKS was crashed with a grinder and sieved within a size of 250µm. The ultimate analysis was carried out to evaluate the volatiles and fixed carbon contents as well as to quantify the elemental composition, respectively.
2.2. Preparation of activated carbon
PKS was mixed with ZnCl₂ solution with the ratio 1:1 (mass basis) and was kept for overnight at room temperature. Then, the mixture was put into an oven and dried at the temperature of 110°C for 4 hours. The sample was later transferred into MF106 Muffler furnace at a temperature of 500°C and was kept at this temperature with various activation time 30, 60 and 90 minutes. Since this process was done in a Muffler furnace, a double crucible method is used where PKS sample were put into a small crucible with a lid covered. Next, the small crucible is put into another big crucible filled with raw PKS that are not grinded. This is to ensure minimum entrance of oxygen to the PKS sample [10]. After the activation process was completed, the PKS activated carbon (PKSAC) was soaked in 100 mL of 1 N hydrochloric acid (HCl) solution for overnight to leach out the activating agent. Then, the sample was filtered and rinsed by distilled water several times until the pH value obtains pH 6-7 in order to remove access chemical from adsorbent. Lastly, PKSAC sample was dried in oven (110°C) for 24 hours and stored in container. These activated carbons are referred to as PKSAC30 (PKSAC at 30 minutes), PKSAC60 (PKSAC at 60 minutes) and PKSAC90 (PKSAC at 90 minutes).

2.3. Characterization of activated carbon
The physico-chemical characteristics of the activated carbon from PKS using chemical activation were determined. Ultimate analysis was carried out using CHNS-O Analyzer (FlashEA,1112 Series) to determine carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) contents of the samples, whereas the content of oxygen (O) was calculated by in difference out of 100 from the value of C, H and N. [11]. Fourier Transform Infrared (FTIR) (Perkin Elmer Spectrum One) was used to determine the surface organic functional group. The IR spectrum was recorded from a wave number range of 500-4000 cm⁻¹ at a resolution of 4 cm⁻¹. The morphology of the raw PKS and PKSAC were determined using scanning electron microscopy (SEM Jeol).

2.4. Adsorption of β-carotene from Crude Palm Oil (CPO)
Crude palm oil (CPO) contains β-carotene was collected from Sime Darby Kempas, Johor. β-carotene adsorption test was carried out in a lab-scale batch adsorption reactor. The batch adsorption reactor was made from a 250 mL conical flask equipped vacuum outlet, N₂ gas inlet, thermometer and stirrer hot plate referring to [3] with modification. CPO contains β-carotene was prepared by dissolving the sample in n-hexane. Then, 50 mL of the sample solution was put into conical flasks and readily set up for adsorption of β-carotene for PKSAC30, PKSAC60 and PKSAC90. In each experiment, 1wt% of PKSAC were used in the batch adsorption reactor. The adsorption process was conducted on a hot plate with temperature of 50°C and stirring at 150 rpm (under nitrogen atmosphere) with constant adsorption time; 10 minutes. The flask was plugged with a rubber stopper and wrapped with an aluminium foil to reduce the β-carotene degradation by oxygen and light.
After the adsorption process, the filtrate was separated from each adsorbent by centrifuge at 4500 rpm for 10 min. β-carotene filtrate content was analyzed according to PORIM Test Method, 1995, PORIM p2.6 (Method of test for palm oil and palm oil production – Determination of carotene content) [1] by using UV-Vis analyzer. The solution was then transferred to a cuvette and absorbance at 446 was measured using Lambda 25 UV/VIS Spectrometer, Perkin Elmer Precisely (Massachusetts, USA) that was calibrated previously. The carotene content was expressed as ppm β-carotene and was calculated later using an Eq. (1) with assumption as $a_b$ is negligible:

$$\text{β-carotene (ppm)} = 25 \times \frac{383}{100W} (a_s - a_b)$$  \hspace{1cm} (1)

Where,
- $25$ = is the volume used for analysis
- $383$ = extinction coefficient for carotenoid
- $a_s$ = absorbance of the sample
- $a_b$ = cuvette error
- $W$ = weight of the sample in grams

In that case, the efficiency of β-carotene removal in CPO using PKSAC can be calculated as Eq. (2):

$$\% \eta_{\text{β-carotene}} = \frac{\text{Concentration inlet} - \text{Concentration outlet}}{\text{Concentration inlet}} \times 100$$  \hspace{1cm} (2)

3. Result and Discussion
3.1. Characterization activated carbon of PKS
3.1.1 Ultimate analysis of the activated carbon
The ultimate of chemical activated carbon was summarized in Table 1. The chemical activated carbons were produced at 500°C and thus, most of the oxygen containing functional groups was removed from carbon skeletal. This was due to at high temperature, volatile matter content was removed [12]. From ultimate analysis, the changes of elemental composition (C, H, N and O) due to the pyrolysis process that cracked some of the organic functional groups and also volatiles evolution. It is clearly shown that activation processes increase the carbon content from 48.70 wt% to 58.43 wt% and also keep increasing as the activation time increase from 30 minutes to 90 minutes. This is attributing to the reaction of carbon via activation with ZnCl$_2$, since ZnCl$_2$ tends to increase the pore development in activated carbon structure and high carbon yield is obtained [13]. With this high carbon content, there is high possibility that the amount of active site may also be increased significantly.
Table 1. Ultimate analysis of raw PKS and PKSAC

| Sample       | C     | H     | N     | O*    |
|--------------|-------|-------|-------|-------|
| Raw PKS      | 48.70 | 6.61  | 0.71  | 43.98 |
| PKSAC30      | 50.35 | 6.07  | 0.95  | 42.63 |
| PKSAC60      | 55.46 | 4.48  | 0.17  | 39.89 |
| PKSAC90      | 58.43 | 3.98  | 0.79  | 36.80 |

*Oxygen by difference

3.1.2 FTIR analysis

The FTIR spectra of raw PKS and PKSAC were given in Figure 2. Based on the graph, only raw PKS shows the most complicated spectrum. A broad adsorption peak appeared at 3340.554 cm\(^{-1}\), corresponding to the stretching of O–H functional group and this indicates the presence of bonded hydroxide in the raw sample. The peak observed at 1605.00 cm\(^{-1}\) corresponding to the C=O stretching. This raw PKS sample also showed two important adsorption peaks at 1238.36 and 1033.19 cm\(^{-1}\) which corresponded to the stretching of C–O functional group [2].

Unlike raw PKS, FTIR spectra of PKSAC (AC30, AC60, and AC90) illustrate less absorption peaks since most of functional groups were disappeared. According to previous researches, the functional groups from the raw material spectrum were released as volatile materials when heat was supplied to the sample during activation process [14,15]. This proved that the activation process has taken place successfully. Although the samples were prepared via various time activation, there was a similarity in the adsorption patterns. Moreover, all PKSAC shows apparent decrease in the broad C–O peak around 1250 – 1000 cm\(^{-1}\) and C=C absorption band around 1650 – 1500 cm\(^{-1}\). Samples activated for PKSAC60 and PKSAC90 showed clearer peaks reduction than PKSAC30. The decreasing bands suggest that activation time influenced the prepared samples. This indicates that higher 60 minutes’ activation time is favourable than 30 minutes’ activation time.

![Figure 2. FTIR spectra of raw PKS and PKSAC](image-url)
3.1.3. SEM analysis

SEM images for raw PKS and PKSAC were depicted as in Figure 3 (a)-(d). It can be observed that there were distinct images obtained between PKS and PKSAC micrographs where on raw PKS, the sample showed a more integrated surface indicating the raw PKS particles were much connected to each other. The raw PKS’s image also showed no pores except for a few occasional cracks and void due to the surface of raw PKS being rough and dented. In contrast, after chemical activation with ZnCl₂, pores network with different size and shapes were formed as shown as in Figure 3 (b), (c) and (d) but with many small cavities randomly scattered among the pores. This is because, during the activation process, most of the volatile matter were released and the reaction of carbon with activating agent produced a large number of micropores and mesopores which significantly increased the surface area of activated carbon and resulted in good adsorption capacity [16].

Figure 3 (b), (c) and (d) display the morphologies of PKSAC30, PKSAC60 and PKSAC90. With increasing of activation time, more pores were be created and this probably makes the surface area of ACs increased thus, resulting in high adsorption capacity. This may be due to longer activation time, the development of porosity was higher because some of volatile compounds which were still attached in the inner part could evaporate more and also bring out the substance in the pore to be dispersed to outside of the particles [17].

![Figure 3. SEM image (a) Raw PKS (b) PKSAC30 (c) PKSAC60 and (d) PKSAC90](image)

3.3 Adsorption of β-carotene by activated carbon

The adsorption efficiency increased with increasing of the activation time from 30 to 90 minutes with 45%, 55%, and 69% respectively as shown in Figure 4. This may be caused by the fact that when the activation time is long, more porosity will be created because some of volatile compounds which were still attached in the inner part could evaporate more and dispersed from the substance [18]. As a result, more molecule of β-carotene can be attached to the carbon surface of PKSAC and finally increased the efficiency of adsorption. The effect of activation time of PKSAC30, PKSAC60 and PKSAC90 give increasing result in adsorption efficiency of β-carotene which related to porosity of PKSAC [3]. Based
on previous researchers, this is due to the high porosity of adsorption sites in the adsorbent [19]. As stated in Figure 4, PKSAC90 exhibits the highest removal of β-carotene concentration at 69%. This conclude that activation time affect the increases of adsorption of β-carotene in CPO.

![Figure 4. Percentage Removal of β-carotene (%)](image)

### 4. Conclusion
This study showed that PKS can be used as raw material with ZnCl$_2$ as the activating agent for the production of activated carbon by varying the activation time. The properties of the activated carbon were characterized in term of ultimate analysis and FTIR. FTIR results indicated that all the raw PKS was successfully converted into carbon and had potential as an adsorbent for adsorption of β-carotene. According to the SEM image, the PKSAC shown its porosity compare to raw PKS. Based on the result, PKSAC90 shows the highest adsorption efficiency at 69% of percentage removal of β-carotene compared to others. This is due to high porosity in the adsorption sites of PKSAC. Thus, β-carotene adsorption using PKSAC adsorbents had made the percentage removal increased with the increasing chemical activation time (30, 60 and 90 minutes).

### Acknowledgements
This research was supported by Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Pasir Gudang.

### References
[1] Akhmazillah A and Sarmidi M R 2010 Extraction of Heat Treated Palm Oil and Their Stability on β-carotene During Storage J. of Sci. and Tech. 2, 1 p. 45–54.
[2] Ahmad A Chan C and Abd Shukor S 2008 Recovery of oil and carotenes from palm oil mill effluent (POME) Chem. Eng. J. 141, p. 383–386.
[3] Ulfah M Raharjo S Hastuti P and Darmadj P 2017 Adsorption of β-carotene in isopropyl alcohol with decolorized activated carbon as model for β-carotene adsorption in crude palm oil Indones. J. Chem. 17, 1 p. 105–112.
[4] Jung S -H Oh S -J Choi G -G and Kim J -S 2014 Production and characterization of microporous activated carbons and metallurgical bio-coke from waste shell biomass J. Anal. Appl. Pyrolysis
[5] I. Ozdemir L Şahin M Orhan R and Erdem M 2014 Preparation and characterization of activated carbon from grape stalk by zinc chloride activation Fuel Process. Technol. 125, p. 200–206.

[6] Rashidi N A and Yusup S 2017 Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption J. Clean Prod. 168, p. 474–486.

[7] Hidayu A R and Muda N 2017 Impregnated Palm Kernel Shell Activated Carbon for CO2 Adsorption by Pressure Swing Adsorption Indian J. of Sci. and Tech. 10, 2 p. 1-6.

[8] Demiral H Demiral I Karabacakoğlu B and Tümsek F 2010 Production of activated carbon from olive bagasse by physical activation Chem. Eng. Res. Des. 89, 1 p. 206–213.

[9] Chong Lua A and Yang T 2004 Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell J. Colloid Interface Sci. 274, p. 594–601.

[10] Ahiduzzaman Md. and Sadrul Islam A K M 2016 Preparation of porous bio char and activated carbon from rice husk by leaching ash and chemical activation SpringerPlus 5, p. 1-14.

[11] Shiung S S Liew R K Wong Y M Yuh Yek P N Ling Ma N Lee C L and Chase H A 2017 Microwave-assisted pyrolysis with chemical activation , an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent J. Clean. Prod. 162, p. 1376–1387.

[12] Hidayu A R and Muda N 2016 ScienceDirect Preparation and characterization of impregnated activated carbon from palm kernel shell and coconut shell for CO2 capture Pro. Eng. 148, p. 106–113.

[13] Gong T and Zhang X 2018 The effect of carbonization temperature, carbonization time and impregnation ratio on the properties of activated carbon produced from Arundo donax Water Res. 268, 3 p. 225–234.

[14] Yacob A 2008 Comparison of various sources of high surface area carbon prepared by different types of activation Malaysian J. Anal. Sci. 12, p. 264–271.

[15] Hidayu A R Mohamad N F Matali S and A. S. A. K. Sharifah A S A K 2013 Characterization of activated carbon prepared from oil palm empty fruit bunch using BET and FT-IR techniques Proc. Eng. 68, p. 379–384.

[16] Tang Y -B Liu Q and Chen F -Y 2012 Preparation and characterization of activated carbon from waste ramulus mori Chem.Eng. J. 203, p. 19-24.

[17] Gratuito M K B Panyathanmaporn Chumnanklang T R A Sirinuntawaittaya N and Dutta A 2008 Production of activated carbon from coconut shell: Optimization using response surface methodology Bioresource Technology 99, p. 4887-4895.

[18] Tani D Setiagi B Trisunaryanti W and Syoufian A 2015 Effect of activation time on chemical structure and quality of coconut shell activated carbon Int. J. of Applied Chem. 11, 1 p. 73-83.

[19] Ahmad A L Chan C Y Abd Shukor S R and Mashtah M D 2009 Adsorption kinetics and thermodynamics of β-carotene on silica-based adsorbent Chem. Eng. J. 148, 2-3 p. 378–384.