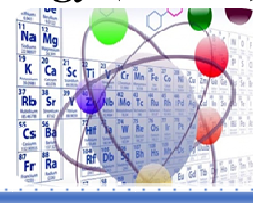


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## Adsorption Properties of Beta Carotene from Activated Carbon Derivatives of Oil Palm Empty Bunches

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### ABSTRACT

*This research aims to determine the adsorption ability of activated carbon and Fe-Cu modified activated carbon in the  $\beta$ -carotene adsorption process on Crude Palm Oil (CPO). Empty Palm Oil Bunches (TKKS) are used as a bio-sorbent for carbon production at a temperature of 500 °C. The synthesized carbon was activated using  $H_3PO_4$  and modified with Fe-Cu metal. CPO quality parameters such as Free Fatty Acids and Peroxide Number were analyzed to see the effect of adsorption on CPO quality. The  $\beta$ -carotene level in the CPO sample used is 472.1 ppm. The optimum conditions for using activated carbon in the  $\beta$ -carotene adsorption process are a mass variation of 8 grams with the  $\beta$ -carotene remaining after adsorption being 432.4 ppm, whereas by using Magnetic Activated Carbon, CPO  $\beta$ -carotene after adsorption remains at 426.1 ppm. Meanwhile, increasing the adsorption time causes the absorption of  $\beta$ -carotene to become greater. By using Activated Carbon the remaining  $\beta$ -carotene is 300.1 ppm after 120 minutes, whereas by using Magnetic Activated Carbon the optimum absorption time is faster and the amount of  $\beta$ -carotene absorbed is greater. The remaining  $\beta$ -carotene after absorption with Magnetic Activated Carbon was 288.7 after 90 minutes of adsorption. Apart from being able to absorb  $\beta$ -carotene, magnetic activated carbon is also better at reducing FFA and PV levels from CPO.*

Keywords: Adsorption, Palm Oil,  $\beta$ -carotene, Activated carbon

### 1. INTRODUCTION

More than 99% of the Crude Palm Oil (CPO) composition resulting from the clarification process is a lipid component, of which around 95% is in the form of oil/fat molecules (triglycerides) and the remainder is in the form of free fatty acid molecules. Meanwhile, other compositions, which total no more than 1%, consist of non-oil components such as water, phosphatides, carotene, aldehydes and other components in smaller quantities.<sup>1-3</sup>

CPO is natural source of carotenoids in the form of retinol (pro-vitamin A)<sup>4</sup>. Palm oil has a natural red pigment caused by carotenoid pigments which mostly consist of  $\beta$ -carotene. During the processing process, the red color in palm oil is always removed. The removal of  $\beta$ -carotene was carried out because consumers prefer the clear color of cooking oil rather than reddish cooking oil.<sup>2,5,6</sup>

The carotene content ( $\beta$ -carotene) itself is also a parameter for the quality of palm oil. There are several types of carotene, and  $\beta$ -carotene is the dominant type which is abundant in palm oil.<sup>7</sup>  $\beta$ -carotene is a minor component in palm oil. Therefore, the adsorption process is very suitable for separating materials with smaller concentrations from mixtures containing other materials with high concentrations. Various methods of recovering carotenoid components from palm oil have been carried out, including solvent extraction, transesterification, adsorption using synthetic resin, silica gel, chromatographic adsorption and membrane technology.<sup>8-10</sup>

Oil Palm Empty Fruit Bunches (OPEFB) has a cellulose content of 33.83% – 34.85%; hemicellulose 17.07% - 18.05%; and lignin 26.71% - 27.54%. With a fairly high cellulose content in OPEFB, it can be converted into active carbon using a carbonization and activation process.<sup>2,3,11-13</sup> The empty oil palm bunches that have been collected are prepared and used as activated carbon which is activated by  $H_3PO_4$  and modified by Fe-Cu metal. Modified activated carbon was applied for adsorption and desorption of  $\beta$ -carotene on CPO samples.

Carbon modification is useful for improving the performance of activated carbon in absorbing and removing certain pollutants. Previous reported that the addition of Fe-Cu in activated carbon can expand the surface of the activated carbon, making the carbon structure more regular and the distance between carbons more homogeneous, thereby increasing the activity and effectiveness of activated carbon.<sup>14-17</sup>

The use of metal ions from  $FeSO_4$  and  $CuSO_4$  as a method of modifying charged metals takes advantage of the reduction and adsorption characteristics of activated carbon. During this process, metal ions are adsorbed on the surface of the activated carbon, and then the reducing properties of activated carbon are used to reduce the metal ions to ions in the form of simple substances or low valence. Due to the strong binding capacity of metals or metal ions to the adsorbed substance, the adsorption capacity of carbon to the adsorbed substance is greatly enhanced.<sup>12,13</sup>

The results of the application were analyzed using a UV-Vis Spectrophotometer instrument to measure  $\beta$ -carotene levels and using the titration method to analyze free fatty acids and peroxide value. The CPO that was obtained was analyzed for free fatty acids, peroxide value, fatty acid composition and  $\beta$ -carotene content.

## **2. EXPERIMENTAL**

### *2.1. Chemicals, Equipment and Instrumentation*

Empty palm oil bunches and CPO (Crude Palm Oil) was taken from PT. Multi Agrindo Sumatra,  $CuSO_4$ ,  $FeSO_4$ , distilled water, KOH, KI, phenolphthalein indicator, and Whatman No.1 filter paper.

### *2.2. Preparation of OPEFB*

Oil Palm Empty Fruit Bunches was taken and collected from PT. Multi Agrindo Sumatra. The OPEFB that has been collected is washed using running water and dried under sunlight so that the water content is

reduced and the sample is dry. The dried OPEFB was chopped into small pieces then ground with a blender and sieved with a 200-mesh sieve.

### *2.3. Carbonization*

The OPEFB powder samples were heated in the furnace at a temperature of 500 °C for 2 minutes. The carbon formed is cooled to room temperature and placed in a closed container.

### *2.4. Activated Carbon (AC) Synthesis*

The carbonized OPEFB is then soaked in H<sub>3</sub>PO<sub>4</sub> for 24 hours. Filtered using Whatman filter paper and a vacuum filter then washed with distilled water until the pH is neutral. The precipitate was dried in an oven at 105 °C for 1 hour.

### *2.5. Modification Activated Carbon (MAC) Synthesis*

15 g of activated carbon was put into 150 mL of a mixture of FeSO<sub>4</sub> and CuSO<sub>4</sub> solutions in a 1:1 ratio. Then heated to a temperature of 60 °C for 3 hours using a magnetic stirrer, then cooled and filtered. The filtered results were placed in an oven at 105 °C for 24 hours.

### *2.6. Adsorption of β-carotene*

#### *2.6.1. Adsorbent dosage optimum of β-carotene Adsorption*

100 mL of CPO was put into five glass beakers, then add 4, 6, 8, 10 and 12 grams of Fe/Cu modified activated carbon into each beaker. Then the mixture was heated using a hot plate at a temperature of 60 °C and homogenized using a magnetic stirrer at a constant speed of 120 rpm for 120 minutes. The mixture was filtered using Whatman No. filter paper. 1. The filtrate is saved for analysis of β-carotene content.

#### *2.6.2. Determination of the Effect of Optimum Adsorption Contact Time on CPO*

Mixture of MAC and CPO with the optimum mass ratio that has been obtained into the glass beaker. Then the mixture was heated using a hot plate at a temperature of 60 °C and homogenized using a magnetic stirrer at a constant speed of 120 rpm for 30, 60, 90, 120 and 150 minutes. Then the mixture was filtered using Whatman No. filter paper. 1. The activated carbon from the filter was determined of β-carotene content.

## **3. RESULTS AND DISCUSSION**

The modification process does not affect the structure of the active carbon, because in this process the metal itself only functions to increase the surface area of the pores without any chemical reactions between the active carbon bonds. The added Fe-Cu metal can fill the pore structure in activated carbon. The presence of Fe and Cu has an effect on increasing the crystallinity of activated carbon which has the potential to increase the stability of active carbon.<sup>14</sup>

Determination of the optimum mass of activated carbon was carried out to find out how much adsorbent mass was used to absorb the most β-carotene contained in CPO. The β-carotene adsorption process on CPO uses several mass variations to determine the optimal adsorbent mass for absorbing β-carotene. The mass

variations used are 4 g, 6 g, 8 g, 10 g and 12 g, both activated carbon and Fe-Cu activated carbon use the same mass variations. The levels of  $\beta$ -carotene absorbed in each adsorbent mass can be seen in the following picture.

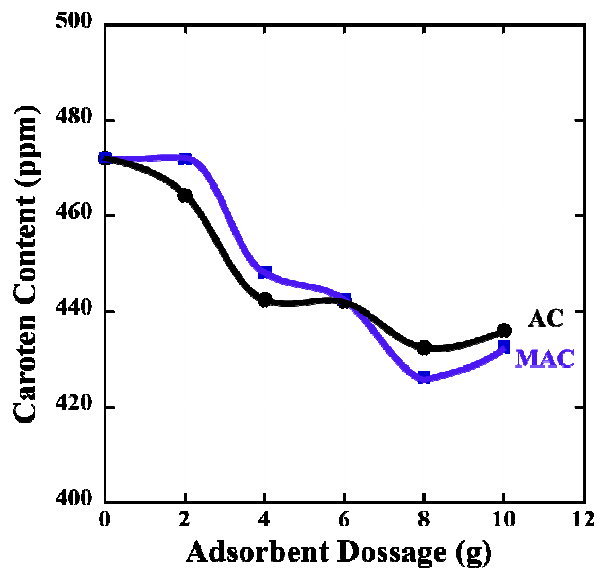


Figure 1. Adsorption of  $\beta$ -Carotene Mass Variations

In Figure 1 it can be seen that the optimum mass of active carbon for adsorbing  $\beta$ -carotene is 8 grams and 10 grams for Fe-Cu activated carbon. The optimum conditions for using activated carbon in the  $\beta$ -carotene adsorption process are a mass variation of 8 grams with the  $\beta$ -carotene remaining after adsorption being 432.4 ppm, whereas by using Magnetic Activated Carbon, CPO  $\beta$ -carotene after adsorption remains at 426.1 ppm.

The concentration of adsorbed  $\beta$ -carotene decreased at a mass of 6 grams and increased at a mass of 8 grams of activated carbon and a mass of 10 g of Fe-Cu activated carbon absorbed the most  $\beta$ -carotene compared to the mass of other adsorbents, which means the adsorbent experienced a saturated absorption capacity at optimal time. The decline in  $\beta$ -carotene levels again after the optimum mass is achieved is possible because the adsorbent has reached its saturation absorption capacity, thereby reducing the adsorption capacity of the adsorbent.

Contact time can also affect performance and absorption capacity so that it will affect the effectiveness of an adsorbent. The  $\beta$ -carotene adsorption process on CPO uses several time variations to determine the optimal adsorbent contact time for the absorption of  $\beta$ -carotene after obtaining the optimal mass.<sup>15-17</sup>

In Figure 2 it can be seen that by using Activated Carbon the remaining  $\beta$ -carotene is 300.1 ppm after 120 minutes, whereas by using Magnetic Activated Carbon the optimum absorption takes less time and the amount of  $\beta$ -carotene absorbed is greater. The remaining  $\beta$ -carotene after absorption with Magnetic Activated Carbon was 288.7 after 90 minutes of adsorption. At the 60th minute, less  $\beta$ -carotene was absorbed on the Fe-Cu activated carbon, this is because the adsorbate may still react with the pores of the adsorbent, then when the adsorption time increases, the adsorbate reacts with the Fe and Cu in the adsorbent, which can be seen in the 90th minute Fe-Cu activated carbon was able to absorb far more  $\beta$ -carotene compared to activated carbon.

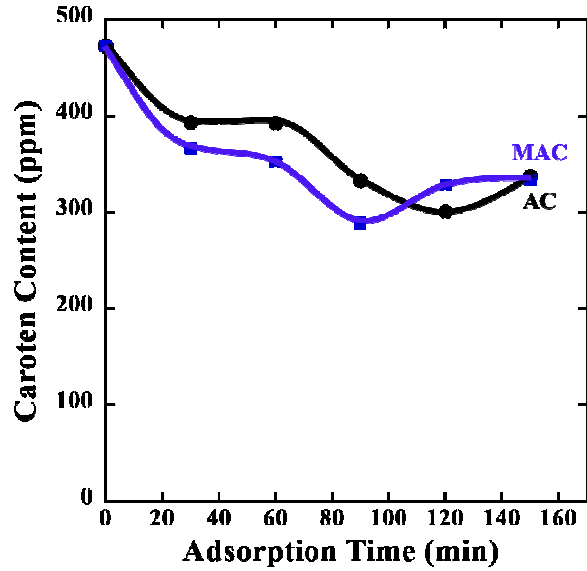


Figure 2. Time Variation of  $\beta$ -Carotene Adsorption

The concentration of  $\beta$ -carotene in CPO decreases with the length of the adsorption process. In other words, the concentration of  $\beta$ -carotene in the adsorbent will increase. The concentration of  $\beta$ -carotene in CPO which decreases with increasing time causes the concentration of  $\beta$ -carotene absorbed in the adsorbent to increase so that the adsorbent experiences a saturated absorption capacity.

After adsorption then need to see whether there is an effect of  $\beta$ -carotene adsorption using activated carbon and Fe-Cu activated carbon from EFB on free fatty acid levels in CPO. An analysis was carried out to calculate the free fatty acid content in CPO without adsorption treatment, and CPO as a result of adsorption resulting from variations in optimum contact time where the mass of the adsorbent was taken based on the optimum mass of activated carbon and Fe-Cu active carbon.

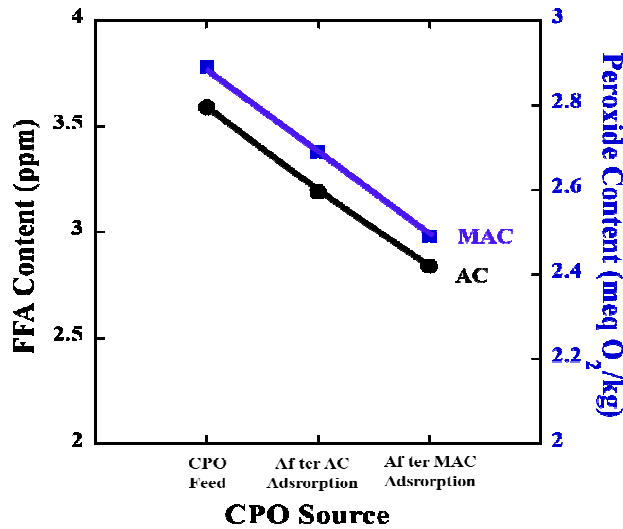


Figure 3. FFA and PV analysis upon after adsorption

In Figure 3 it can be seen that the levels of free fatty acids in CPO decreased as a result of the adsorption of  $\beta$ -carotene using activated carbon and Fe-Cu active carbon. The results of the analysis of free fatty acid levels in CPO were 3.59%, then decreased after adsorption with activated carbon with the results of free fatty acid levels of 3.19% and Fe-Cu activated carbon with free fatty acid levels of 2.84%. In this way, it can be stated that the  $\beta$ -carotene adsorption process using activated carbon and modified activated carbon from EFB has the effect of reducing the levels of free fatty acids in CPO. Activated carbon can reduce free fatty acid levels in CPO and Fe-Cu activated carbon is proven to be better at reducing free fatty acid levels in CPO. The CPO quality standard for free leak acid according to SNI 01-2901-2006 is 5%, therefore the CPO used in this research is still in accordance with existing quality standards.

During the adsorption process, free fatty acids can be formed from hydrolysis and oxidation reactions involving high temperatures. The adsorbent has increased absorption capacity at higher temperatures so that it is able to absorb the free fatty acid components produced during the adsorption process. CPO was predominantly was contain palmitic acid with a molecular weight of 256 and a composition of 41% of the total weight of the oil, thus producing quite a large amount of fatty acids. In the adsorption process, van der Waals forces are produced in the form of attraction between molecules of free fatty acid particles and the adsorbent, causing the free fatty acid to stick to the adsorbent.<sup>18,19</sup>

The results of the analysis of the peroxide value in CPO were 2.886 meq O<sub>2</sub>/kg then decreased after adsorption with activated carbon with the result of a peroxide value of 2.699 meq O<sub>2</sub>/kg and Fe-Cu activated carbon with a peroxide value of 2.497 meq O<sub>2</sub>/kg. In this way, it can be stated that the  $\beta$ -carotene adsorption process using activated carbon and Fe-Cu modified activated carbon from TKKS has the effect of decreasing the peroxide number in CPO. Activated carbon can reduce the peroxide value in CPO and Fe-Cu activated carbon is proven to be better in reducing the peroxide value in CPO.

#### 4. CONCLUSION

The optimum conditions for using activated carbon in the  $\beta$ -carotene adsorption process are a mass variation of 8 grams with the  $\beta$ -carotene remaining after adsorption being 432.4 ppm, whereas by using Magnetic Activated Carbon, CPO  $\beta$ -carotene after adsorption remains at 426.1 ppm. Meanwhile, increasing the adsorption time causes the absorption of  $\beta$ -carotene to become greater. By using Activated Carbon the remaining  $\beta$ -carotene is 300.1 ppm after 120 minutes, whereas by using Magnetic Activated Carbon the optimum absorption time is faster and the amount of  $\beta$ -carotene absorbed is greater. The remaining  $\beta$ -carotene after absorption with Magnetic Activated Carbon was 288.7 after 90 minutes of adsorption.

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