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EFFECT OF ACTIVATED ZEOLITE ON β-KAROTEN BLEACHED PALM OIL LEVELS

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Abstract

Palm oil is one of the Indonesian prima donna whose total national production is increasing every year. Palm oil can be used as a raw material for production of cooking oil products, industrial oil needs and energy sources. The base color of Crude Palm Oil (CPO) is due to the presence of a high β-carotene content in palm oil which can produce a red color in CPO. For this reason, it is necessary to bleach CPO. Most of the palm oil industry currently uses adsorbents as a pale material in the Bleaching process. This research does several things related to the process of making palm oil in general, the process is the production of adsorbents with activated adsorbents, removal of gum with H_2SO_4, bleaching process with adsorbents and analysis of bleaching oil (BPO). The experimental results show that zeolite can be used as an adsorbent for the bleaching process of palm oil. Zeolite has been activated by chemical methods using H_2SO_4 solution before being used as an adsorbent. From the experimental results, the best results for the application of β-carotene were obtained from 3% activated zeolite with 15% by weight zeolite.

***Keywords**: β-carotene; cpo; blanching; zeolite; adsorption; Activation*

INTRODUCTION

Palm oil is one of the most beloved Indonesian commodities that continues to grow in various regions in Indonesia. Until now the trend of domestic palm oil production continues to increase in line with the increasing demand for national and world palm oil. In Table 1 are the properties and contents of crude palm oil.

The main product of oil palm plantations is crude oil, Crude Palm Oil (CPO). Raw CPO from oil palm trees is not yet suitable for human use, so special processing is needed to improve its quality. The processes that are currently commonly used in processing CPO into ready-to-use palm oil are Degumming, Bleaching, and Deodorizing. Bleaching is a process to separate pigments in oil by using hydrogenation, solvent administration, exposure to heat and adsorption to obtain a brighter oil color (McClements, 2008; Bahri 2014). Baharain (1998) in his journal specifically revealed that the adsorption method is the most effective method for separating and removing pigments in the process of bleaching crude palm oil.

Table 1. Physiochemical Properties of Crude Palm Oil

Test Criteria	Quality requirements
Color	Reddish orange
Melting point	21-24 ^{0}C
Water content	0,5 %
Acid number	6,9 mg KOH/g oil
Lathering number	224-249 mg KOH/g oil
Free fatty acids	0,5 %
Refractive index	36,0 - 37,5
Iodic Number	50 – 55 g I/100 g oil

Source: (SNI, 2006; Hui, 1996)

There are two types of adsorption processes, namely physics and chemistry. Sarier, N. & Guler, C. (1998) explain that the adsorption process that occurs in β-carotene CPO by natural zeolite adsorbents is a chemical adsorption process (Chemisorption). This is known after zeolite which has absorbed β-carotene does not change color after being cleaned using benzene, carbon tetrachloride, and acetone (all three are solvents β-carotene).

The adsorbent used in this study is natural zeolite. Natural zeolites have variations in their structure, where variations in these structures have a role as a binding of impurities, especially in the porous portion. Therefore, zeolite must be activated before being used as an adsorbent. This is to improve the special nature as an adsorbent and eliminate impurities (Rosita, et al., 2004). Table 2 outlines the characteristics of zeolites:

Table 2. Characteristics of Zeolites

Density	1,1 gr / cc
Volume of porous structure	0,28-3 cc / gr
Macropore radius	30 - 100 nm
Micropore radius	0,5 nm
Surface area	1-20 m2/gr
Porousity	0,31

Source : Sutarti, 1994

Zeolites have Si / Al which has a function as the main framework for forming the structure of Zeolites in general. In three dimensions, the natural zeolite structure is tetrahedral with its main constituent TO_4 (T = Al, Si, ...). Each oxygen molecule shares the bond between the two T elements.

Shigemoto et al (1995) explain that T in TO_4 refers to Al and SI molecules which are present in natural zeolite structures, in the form of SiO_4 or AlO_4. This is a common form measured in IR spectrophotometer results with a wave number 471 nm-1.

This study aims to produce adsorbents as a bleaching agent from zeolites, observe the effect of zeolite activator levels on the adsorption power of dyes, and determine the levels of β-carotene from bleached palm oil.

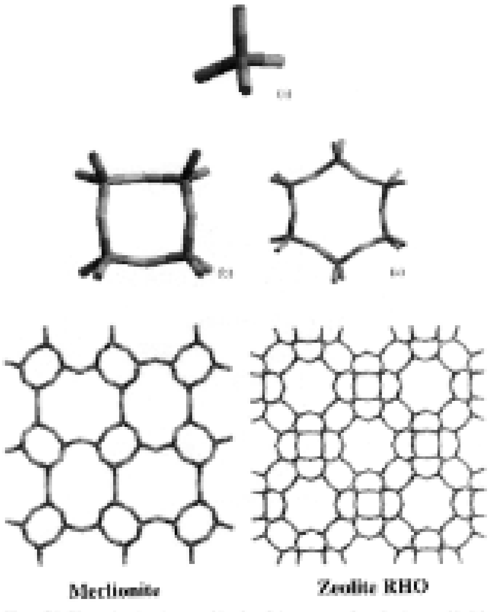

Figure 1. (a) Tetrahedral TO_4 bond, (b) four membered ring bond, (c) six membered ring bond TO_4 ties.

METHODOLOGY

Tools and Materials

The tools that will be used in this study include: glassware (beaker, erlenmeyer), porcelain cups, filter paper, magnetic stirrers, analytical scales, ovens, and pH meters. The devices used are UV-Vis and FT-IR spectrophotometers. The materials used are aquades (H_2O), crude palm oil (CPO), H_2SO_4 solution, H_3PO_4 solution, and natural zeolite.

Adsorbent Production

Zeolite is crushed to powder using a porcelain cup. Zeolite which has been refined through the grinding process is sieved using an automatic sieve to obtain 100 mesh granules. Then the zeolite is washed using distilled water to remove impurities and is heated to 105 oC for 2 hours or until a constant weight is obtained.

The activation process begins by weighing 40 grams of zeolite using a digital scale. Then zeolite is poured into 500 ml beaker and mixed with H_2SO_4 with a concentration variation of 3%, 4%, and 5% v / v. Temperature is maintained at 30^{o}C for 1 hour with constant stirring of 500 rpm. The mixture is then filtered with whatman 42 filter paper installed in a vacuum pump. The filtered filtrate is the main product, as a liquid coagulant, while the paste on filter paper is used as an adsorbent sample in this study. This paste is then washed until pH 6-7 is reached. This paste is heated to dry using an oven at 105 ° C until it reaches a constant weight.

Palm Oil Preparation
Preparing palm oil is done through degumming. This process has the goal of eliminating the content of phosphatides, proteins and resins in the form of gum. This process was carried out at a temperature of 90°C, CPO and H_3PO_4 85% as much as 0.1% (v / v) cooked into a three neck flask. The mixture will also be stirred at a speed of 500 rpm for approximately 30 minutes. Next, the solution is put into a centrifugation tube and the gum is separated. The centrifuge is then set at 4000 rpm with a processing time of approximately 15 minutes.

Bleaching Palm Oil
Furthermore, the degumming palm oil is given another treatment in the form of a bleaching process using activated adsorbents. In this bleaching process, the weight of the adsorbent is varied by 5%, 10%, and 15% (w / w) with the temperature of palm oil constantly maintained at 100°C for 30 minutes.

ANALYSIS

Adsorbent Analysis done by testing infrared spectroscopy, which is useful for identification of organic compounds because of its very complex spectrum which consists of many peaks. (Chusnul.2011).
Palm Oil Analysis done by doing beta-carotene analysis. Carotene, also known as orange pigment, causes palm oil to turn orange yellow. (Tim Penulis PS,1992).

RESULTS AND DISCUSSION

Methylene Blue Absorption Test
The results of the analysis of the color of the MB solution (originally colored blue), experienced a color change to clear with a very thin blue color after adding activated adsorbents. From these observations prove that the adsorbent from zeolite is very efficient for adsorbing pigments.

Effect of Activator Levels with FT-IR Analysis
From the results of FT-IR testing at the Integrated Laboratory of the Islamic University of Indonesia, the results for activator 3%, 4%, and 5% are as follows:

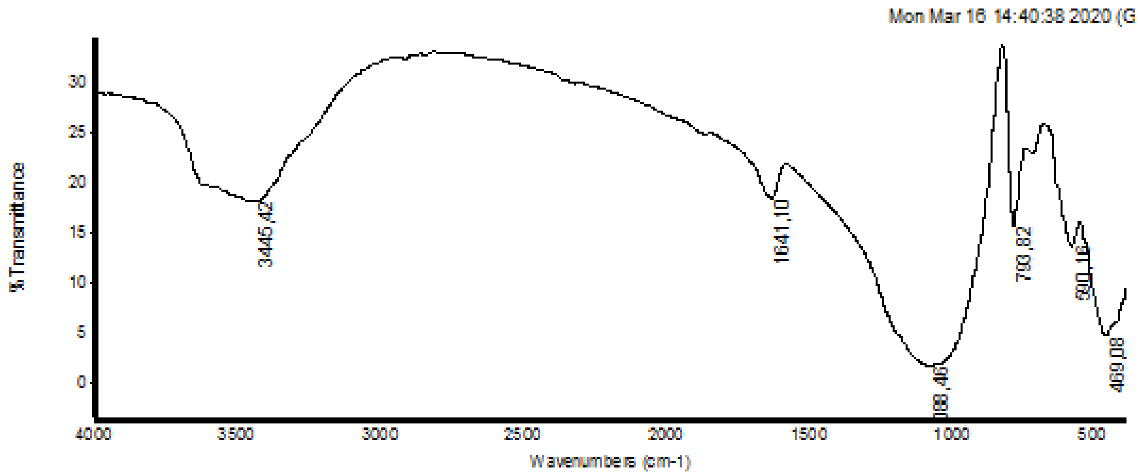

Figure 2. Testing Zeolite 3% FT-IR

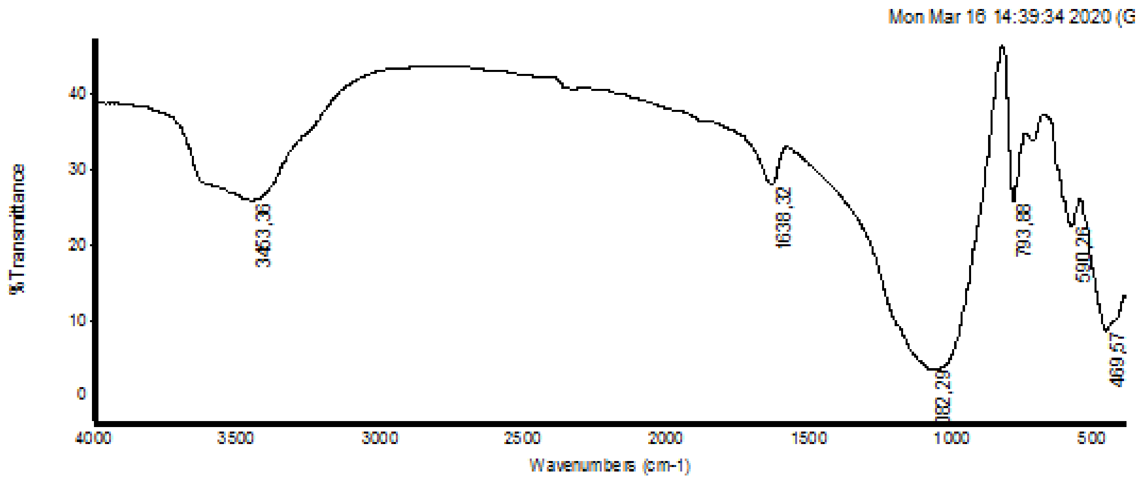

Figure 3. Testing Zeolite 4% FT-IR

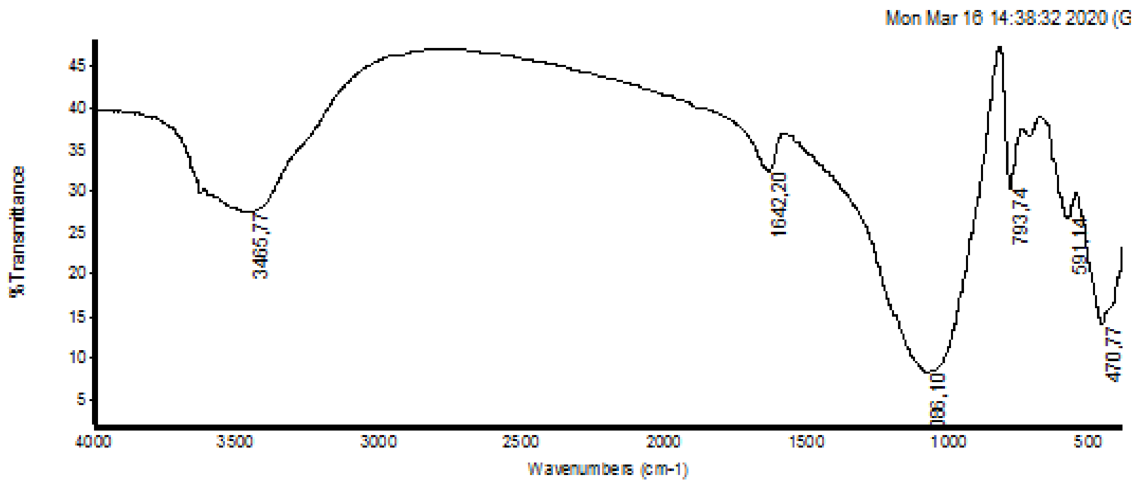

Figure 4. Testing Zeolite 5% FT-IR

The FT-IR results are then compared with the FT-IR results in the previous journal (Heraldy, 2003), the following are presented in tabular form in Table 3:

Table 3. FT-IR of Zeolites

Vibration type	Wave Number (cm-1) (Reference)
O-H stretching vibration	3442,7 and 3448,5
TO_4 Vibration Stretching	1043,3 and 1052,3
T-O Bend Vibration on external braid (Zeolite Framework)	794,6
T-O Bend Vibration	447,2 and 470,6

The first peak at Zeolites 3%, 4%, and 5% is at wave number 3465.77; 3453,36; and 3445.42 cm-1. At this peak, the wave number shows the O-H group stretching vibration of the absorbed water molecule, this band has medium intensity. The second peak in Zeolites 3%, 4%, and 5% has the number 1642.20; 1638,32; and 1641.10 cm-1. The range of these Wave Numbers indicates the bending vibrations of the O-H group of the absorbed water molecules.

In the 3% and 4% H2SO4 treatment there was a decrease from 3465.77 cm-1 to 3453.36 cm-1 then in the 5% H2SO4 treatment it decreased again to 3445.42 cm-1. This downward trend is expected due to the release of water molecules in zeolites that are physically bound. So that the acidic activator levels show loss of absorption because zeolite solids are cleaner than impurities so zeolite pores will be more open.

The third peak of Zeolite 3%, 4%, and 5% was at 1086.1; 1082.29; and 1088.46 cm-1. These results approach the natural zeolite characters of Ponorogo (1043.3 cm-1) and Wonosari (1052.3 cm-1) (Heraldy, 2003). Heraldy said the values of 1043.3 and 1052.3 cm-1 indicate the existence of Si-O-Si or Al-O-Al asymmetric stretching vibrations in zeolites originating from Ponorogo and Wonosari. Fourth peaks in Zeolites 3%, 4%, and 5% are at 793.74; 793.88; and 793.82 cm-1. The three peaks are the image of zeolite main structure unit absorption that is aligned structure, vibration of bending of Si - O on the outer fabric (Zeolite frame).

The fifth peak of Zeolite is 3%; 4%; and 5% are at 591.14; 590.26; and 590.16 cm-1. At peak 562.2 cm-1, TO4 forms a Double Four-Membered Ring (D4R) bond (Shigemoto et al 1995). The numbers continue to decrease inversely with higher levels of activator.

T-O buckling vibration absorption was in the range of 420-500, while Peak 6 values were 3% zeolites; 4%; and 5% are at the value of 470.77; 469,57; 469.08 cm-1, therefore the three values fall into the T-O buckling vibration range. In this vibration absorption, the number also continues to decrease. From these figures it can be concluded that the zeolite framework that was built was larger than the TO_4 frame. Thus, the greater the level of absorption ratio obtained, the greater the absorption that occurs in the wave number region of 500-650 cm-1, which states that many double ring formed from tetrahedral TO_4.

Adsorbent Application

Figure 4. CPO color comparison before bleaching (left), with BPO (Left: 5% adsorbent weight; Middle: 10% adsorbent weight; Right: 15% adsorbent weight)

If you see it with your eyes, you can see the difference in the color of the bleaching or Bleached Palm Oil (BPO). CPO which has the brightest color is CPO which is adsorbed using 3% activated zeolite with 5%, 10%, and 15% adsorbent weight. Proof using β-carotene content testing conducted at the UGM Center for Food and Nutrition Study Laboratory on the three samples gave the following results:

Table 4 β-carotene levels

No	Sample Code	Analysis Results
		B Carotene µg/g (ppm)
1.	Zeolite weight 5%	47,56320 46,70711
2.	Zeolite weight 10%	44,60916 44,87311
3.	Zeolite weight 15%	38,37246 38,62821

From the beta carotene test results it can be concluded that CPO 3% with 15% adsorbent weight has lower beta-carotene levels. So that the color is brighter compared to 3% CPO activator with 5% and 10% adsorbent weight. This is in accordance with the amount of weight of the adsorborbent in CPO, so the adsorbent will absorb more color in CPO. However, when seen more clearly, CPO with higher levels of activator shows that the CPO is clearer even though the color is still orange.

CPO that has not experienced Degumming and Bleaching The process in this study has beta carotene levels of 467 ppm. In the test results after bleaching, the content of beta carotene remaining in 5% zeolite weight samples was 47.56320 ppm; the weight sample of 10% zeolite was 44,60916; and the weight sample of 15% zeolite was 38.37246. The binding efficiency of beta carotene by zeolites in this experiment is as follows:

$$\text{Efficiency} = \frac{(\beta-carotene\ levels\ before\ testing)-(\beta-carotene\ levels\ after\ bleaching)}{\beta-carotene\ levels\ before\ testing} x100\%$$

Then the absorption efficiency of β-carotene for each weight percent is:

Zeolite weight 5% $= \frac{467-47{,}56320}{467} x100\%$
$= 89{,}815161\ \%$
Zeolite weight 10% $= \frac{467-44{,}60916}{467} x100\%$
$= 90{,}447717\ \%$
Zeolite weight 15% $= \frac{467-38{,}37246}{467} x100\%$
$= 91{,}783199\ \%$

The efficiency of increasing adsorption of zeolites with 5%, 10% and 15% weight content can be seen in the following Figure 4 scheme:

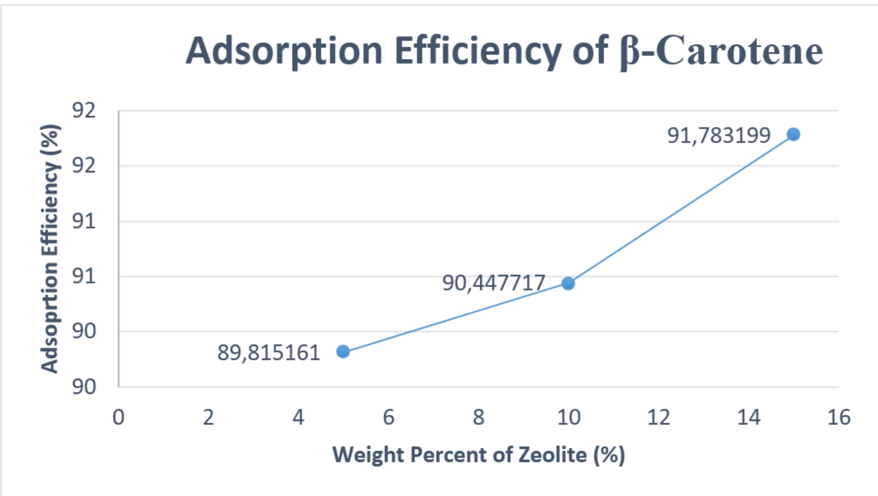

Figure 5 Efficiency of absorption of β-carotene with adsorbent variations

CONCLUSIONS

From the results of the research that has been done, the Zeolite FTIR results show that there are 6 Peak Vibration Bands of zeolite structure constituent groups, with 4 main peaks (1,3,4, and 6) added with 2 (2 and 5) peaks arising from Vibration main peak group. Visually, the best results from the Degumming and Bleaching process series are samples with a variation of activated zeolite 3% H_2SO_4. The resulting color is brighter compared to 4% and 5% H_2SO_4 activated zeolite samples. The results of testing the levels of β-carotene in 3 Bleached Palm Oil samples showed a very high level of efficiency, namely the level of β-carotene absorbed was higher than 85% of its initial value. Zeolite 5% has an efficiency of 89.81%; zeolite 10% by 90.44%; and zeolite 15% by 91.78%. The best efficiency level of the three β-carotene absorption test samples is owned by the activated Zeolite Sample 3% H_2SO_4 with 15% zeolite weight, which is 91.78%

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