

## ACTIVATION AND PURIFICATION OF BENTONITE FOR THE TREATMENT OF CRUDE PALM OIL AS VEGETABLE OIL

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### ABSTRACT

**ACTIVATION AND PURIFICATION OF BENTONITE FOR THE TREATMENT OF CRUDE PALM OIL AS VEGETABLE OIL.** Crude Palm Oil (CPO) to be used for cooking oil requires processing that includes bleaching step which is typically done using bleaching earth made from activated bentonite. Bentonite is a type of mineral that is very rich in montmorillonite. Currently, substantial amount of activated bentonite used by vegetable oil industries are imported. In this research, the bentonite was obtained locally from the region of Leuwiliang (Bogor, West Java). The bentonite was purified using solution of sodium-hexa-metaphosphate ( $\text{NaPO}_3$ ), and was activated using acid reflux methods ( $\text{H}_2\text{SO}_4$ , 100°C). The bentonite activation was done at two different reflux times (1 and 3 hour), and three different acid concentrations (1 M, 2.5 M and 5 M). To assist the interpretation of results, the bentonite samples were also studied using XRF and XRD. Bleaching power of active bentonite was initially studied using adsorption of methylene blue for optimization, which was followed by bleaching of CPO. The results showed that, the purified bentonite and activated at 1 molar  $\text{H}_2\text{SO}_4$  for 1 hour duration, had the highest bleaching capacity. In addition, the treated oil also showed substantial reduction of peroxide number, and also some reduction of free fatty acid content (FFA) which further improve the quality treated palm oil.

**Key words :** Bentonite, Bleaching earth, XRD, XRF, Crude palm oil, CPO

### ABSTRAK

**AKTIFASI DAN PURIFIKASI BENTONIT UNTUK DIGUNAKAN DALAM PEMROSESAN MINYAK SAWIT MENTAH SEBAGAI MINYAK GORENG.** Minyak sawit mentah (CPO) yang akan dipergunakan untuk minyak goreng memerlukan pemrosesan, termasuk adanya *bleaching* yang dilakukan dengan menggunakan bahan *bleaching earth* yang berasal dari bentonit yang telah diaktifasi. Bentonit merupakan salah satu mineral hasil tambang yang kaya dengan *montmorillonite*. Saat ini, jumlah bentonit aktif yang dipergunakan oleh industri minyak goreng merupakan hasil impor. Dalam penelitian ini, bentonit yang dipergunakan ditambang dari daerah Leuwiliang (Bogor, Jawa Barat). Bentonit ini dipurifikasi menggunakan sodium hexa meta phosphate ( $\text{NaPO}_3$ ) dan diaktifasi menggunakan proses refluks asam ( $\text{H}_2\text{SO}_4$ , 100 °C). Proses pengaktifan bentonit dilakukan variasi waktu refluks yang berbeda yaitu 1 jam dan 3 jam dengan konsentrasi asam yang berbeda yaitu 1 M, 2,5 M dan 5 M. Untuk membantu interpretasi dari data yang dihasilkan, sampel bentonit juga dipelajari menggunakan *X-Ray Fluoresence Spectroscopy (XRF)* dan *X-Ray Diffractometer (XRD)*. Kekuatan *bleaching* dari bentonit aktif pada tahap awal diukur menggunakan proses adsorpsi dari *methylene blue* untuk proses optimasi, diikuti dengan *bleaching* langsung terhadap CPO. Hasil menunjukkan bahwa bentonit yang telah dimurnikan dan diaktifkan dengan 1 M  $\text{H}_2\text{SO}_4$  selama 1 jam memiliki kapasitas *bleaching* yang paling tinggi. Selain itu, minyak yang telah memperoleh perlakuan dengan bentonit juga memperlihatkan penurunan bilangan peroksida dan kandungan asam lemak bebas (FFA) yang berarti meningkatkan kualitas dari minyak sawit.

**Kata kunci :** Bentonit, *Bleaching earth*, XRD, XRF, Minyak sawit mentah, CPO

### INTRODUCTION

Crude Palm Oil (CPO) is one of the agricultural commodities that are considered important for Indonesia.

Indonesia is the world major producer of Crude Palm Oil with a production, in 2008, of about 18.5 million tons [1].

In cooking palm oil industries, Crude Palm Oil undergoes some processing to become what is known as commercial frying oil. One of these processes is the bleaching stage. One of the examples of bleaching agent applied is bentonite. To be useful as bleaching earth in the palm oil industries, the bentonite needs to be activated such as through acid reflux treatment. Furthermore, bentonite coming from different places can have different properties, and may or may not be the most appropriate for use as bleaching earth. Because the demand of bentonite for industries is increasing, substantial amount of activated bentonite are currently imported from Malaysia and China. However, bentonite deposits in Indonesia are still quite massive, predicted to be approximately more than 380 million tons. These deposits are found in the Island of Java, Sumatera, Kalimantan and Sulawesi [2].

## EXPERIMENTAL METHODS

The raw bentonite from Leuwiliang (Bogor-West Java) was provided in the form of rock pieces by PT. Sumber Alam Makmur (Serang-Banten). Clarified Crude Palm Oil (CPO) used was obtained from PT. Memorintama Perkasa (Cikupa-Banten). In the pretreatment stage of the raw bentonite, all bentonite samples were crushed into small pieces, dried at 105 °C for about 4 hours in the oven, and were finally ground to pass through a mesh size 120 (0.125 mm). The bentonite samples prior to purification, after purification and after acid treatment, were analyzed for their elemental compositions using X-Ray Fluorescence (XRF) and Atomic Absorption Spectrophotometer (AAS). Characterization of the crystalline nature bentonite samples were performed by X-Ray Diffraction (XRD). The bentonite samples were purified using 0.5 % ( $\text{NaPO}_3$ )<sub>6</sub> solution, and was activated using acid reflux method ( $\text{H}_2\text{SO}_4$ , 100 °C). The ratio of bentonite to  $\text{H}_2\text{SO}_4$  solution was 1:10 (w/v). Different acid concentrations (1 M, 2.5 M and 5 M) and reflux time (1 hour and 3 hours) were used in the activation.

Adsorption of methylene blue (380 ppm) from solution was done by mixing and shaking each of the treated bentonite at 25 °C, 1 hour, 150 rpm. The amount of methylene blue adsorbed onto bentonite was then calculated. Degumming of the CPO, using a solution of 85 %  $\text{H}_3\text{PO}_4$  at 100 °C for 20 minutes, was carried out prior to the bleaching. In the bleaching, a mixture of 0.5 g of dry bentonite and 50 mL of CPO was heated under continuous stirring (100 °C, 30 minutes). Following the treatment, the bentonite was removed by centrifugation. Color changes in the treated oils were measured by UV-Vis Spectrophotometer. The bleaching capacities were then calculated. As part of quality control, following treatment with bentonite, free fatty acid (FFA) content and peroxide number of the palm oil were also measured. Measurement of FFA was based on

titration with NaOH solution, using phenolphthalein as indicator. Peroxide number measurement was based on titration with  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Prior to measurement, the oil sample was diluted with acetic acid-isooctane mixture, and then treated with KI. The result was expressed in milliequivalent per kilogram of oil.

## RESULTS AND DISCUSSION

### Methylene Blue Adsorption Capacity

After purification and acid treatment, the raw bentonite was initially studied for its bleaching capacities using adsorption of methylene blue. Bentonite was found to be able to absorb methylene blue dye from the aqueous solution. Figure 1 showed that there were no substantial performance differences between the purified and non-purified bentonite samples. Treating the bentonite using higher acid concentration, however (i.e. at 2.5 M and 5 M), appeared to reduce the bleaching capacities. Moreover, 1 hour acid reflux time for the

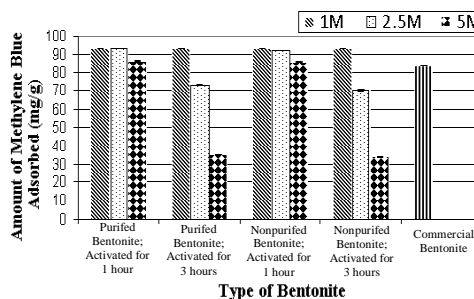


Figure 1. Graph of Methylene Blue Adsorption onto Various Treated Bentonites with a Ratio of Bentonite to Methylene Blue Solution equal to 1:250 (g/mL)

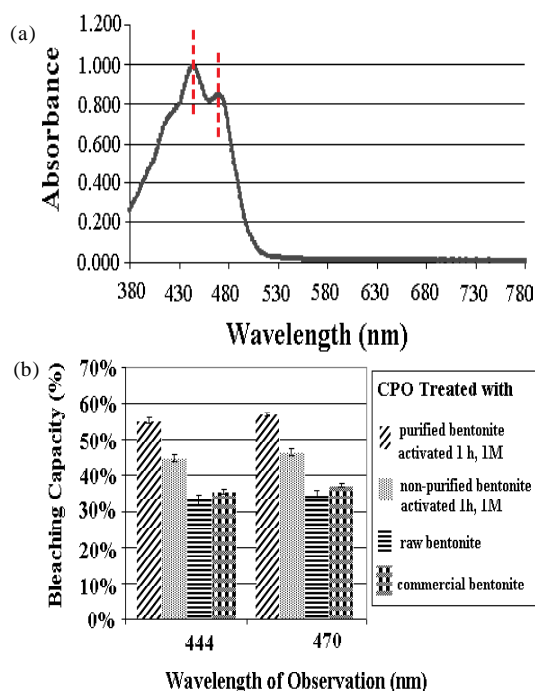


Figure 2. (a) Graph of CPO Absorption Spectra and (b) Bleaching Capacity of Various Treated Bentonites with a Ratio of Bentonite to CPO equal to 1:100 (g/mL)

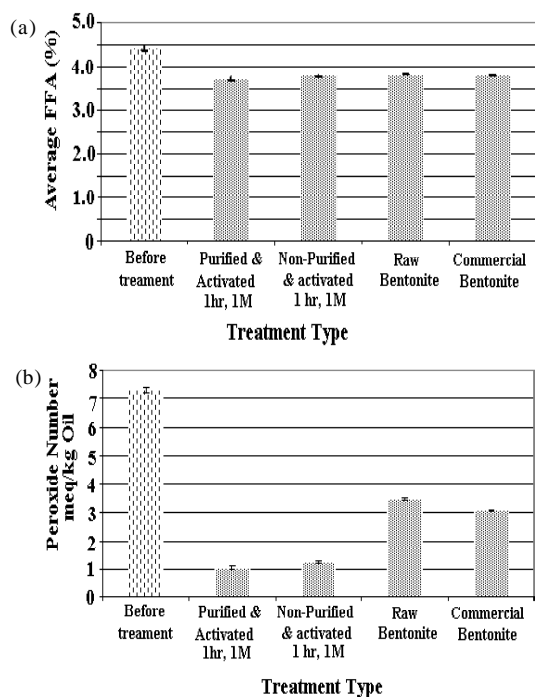


Figure 3. (a) Graph of Free Fatty Acid and (b) Peroxide Number in Crude Palm Oil Samples before and after Bleaching

bentonite appeared to yield better results than the 3 hours reflux time.

### Bleaching Capacity

Based on these results, some samples of bentonite that yielded the best results were selected for further studies for their bleaching performance of CPO (1 hour treatment with 1 M  $H_2SO_4$ ). The results are shown in Figure 2(b). Figure 2(a) showed the maximum absorption spectra of unbleached CPO with peaks that were located at 444 nm and 470 nm. These peaks showed the presence of 13 cis  $\beta$ -carotene that gives the reddish orange color of the natural unbleached CPO.

Figure 2(b) indicated that the purified bentonite; activated with 1 molar  $H_2SO_4$  for 1 hour, had the highest bleaching capacity. Following this, the nonpurified bentonite, treated with the same parameters, had the second highest bleaching capacity. Meanwhile, the commercial and raw bentonites were in the third and fourth place, respectively. It could be concluded that acid activated bentonite was more adsorptive towards the target compounds, and more chemically active than the raw bentonite. The optimum acid concentration needed as found in this study was 1 M  $H_2SO_4$ . This finding however does not exclude the possibility of better bleaching performance at acid concentrations lower than 1 M. This is noted for further studies.

Bleaching capacity was related to the adsorption process, which in turn correlated with the surface phenomena. Natural bentonite is rich in surface hydroxyl groups which are responsible for the adsorption

process. The presence of these hydroxyl groups could be increased through the acid treatment process. The additional surface hydroxyls were obtained when the octahedral layers of the montmorillonite, which is the principle component of bentonite, were disrupted due to acid attack, leaving behind the hydroxylated segments or silica tails derived from the remaining tetrahedral layer. Surface hydroxyls, acting as the active sites, played important roles in the adsorption of  $\beta$ -carotene.  $\beta$ -carotene was chemisorbed either via electrostatic, or via coordination bonding to the active sites of bentonite structure [3]. These adsorptions of  $\beta$ -carotene resulted in CPO that has lighter color, missing its reddish orange color.

### Determination of Free Fatty Acid and Peroxide Number

According to Figure 3, after bleaching, some reduction in the percentage of FFA and substantial reduction of peroxide number were also observed. It should be noted that the percentage of FFA should be checked properly. Acid activated bentonite that was not subjected to proper washing could cause the hydrolysis of triacylglycerol in CPO, resulting in the generation of additional FFA which is not desired. However, the opposite phenomenon was observed, indicated by a slightly decrease in the percentage of FFA.

During bleaching, FFA in the form of palmitic acid interacted through its carbonyl group with the surface hydroxyls present in the montmorillonite via hydrogen bonding. Meanwhile, both acid activated and raw bentonite substantially reduced the peroxide number (Figure 3(b)). The peroxide number was an indicator of the primary oxidation of oil, and hence, it is not desired.

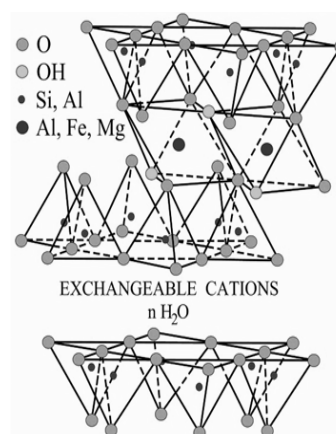


Figure 4. Montmorillonite Structure [5]

Table 1. The Elemental Composition of the Raw Bentonite (the Balance being Oxygen and Hydrogen Atoms)

Component	Fe	Ca	K	Si	Al	Mg	Na
Content %	1.783	0.502	0.115	70.469	9.019	6.815	0.0071

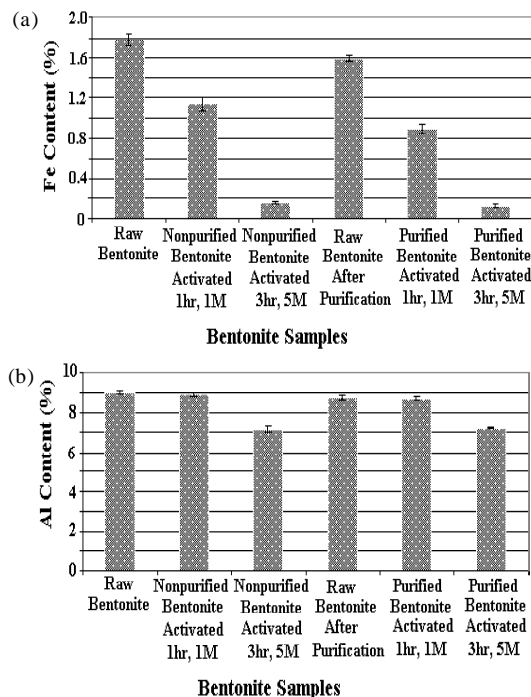


Figure 5. Graph of Iron (a) and Aluminum (b) Analysis in Six Different Bentonite Samples

It was observed that the bleaching using the purified bentonite; activated with 1 molar  $H_2SO_4$  for 1 hour, was the most effective in removing the primary oxidation products. Hence, it can be seen that the bleaching process using acid activated bentonite was a combination of actions, in which the peroxides and FFA were reduced, and accompanied with adsorption of pigments from the oil.

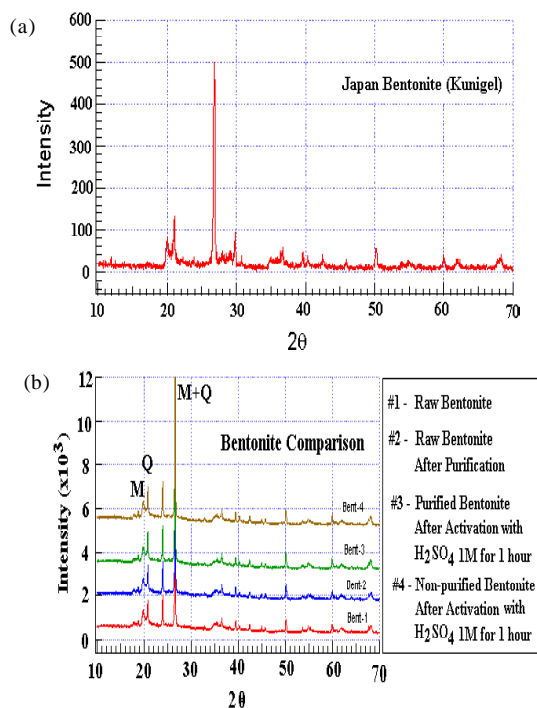


Figure 6. Graph of XRD of Japan Bentonite/Standard (a) and XRD Comparison between Bentonites Produced in this Study. M: Montmorillonite, Q: Quartz (b)

Note :

- Bent-1 : raw bentonite before purification
- Bent-2 : raw bentonite after purification
- Bent-3 : purified bentonite, activated with  $H_2SO_4$  1 molar for 1 hour
- Bent-4 : nonpurified bentonite, activated with  $H_2SO_4$  1 molar for 1 hour

## Analysis of Bentonite

The results of elemental analysis of the raw bentonite were presented in Table 1. The raw bentonite showed a higher content of calcium compared to sodium, and thus it indicated the presence of calcium bentonite. Montmorillonite was a three-layered sheet of aluminosilicate mineral (Figure 4). Hence, silicon and aluminum comprised higher than 50 % of the bentonite elemental composition. This bentonite also contained iron as one of the main compositions, located in either octahedral or interlayer region of montmorillonite. Iron was present in the interlayer region and might represent impurities that needed to be removed. Note that not all of the data of the elemental analysis were presented here. The complete set of data can be found at Yuliantina (2010) [4].

Any ions present in the interlayer region, for instance Fe, were easier to be removed, and were replaced by sodium due to ion exchange phenomena such as during purification with  $(NaPO_3)_6$  solution. Figure 5 confirmed that, after purification, Fe content decreased substantially. Moreover, during acid activation, hydronium ions from the strong acid solution dissolved the octahedral cations (Mg, Fe, and Al). Figure 5 showed that iron and aluminum, decreased after acid treatment. The decrease was more severe when the bentonite was activated with 5 molar  $H_2SO_4$  for 3 hours. This was possible considering that an increase in acid concentrations caused an increase in the damages into the octahedral structure due to acid attack. This finding agreed with previously discussed data and is supported further by the XRD results. When the bentonite was activated with 5 molar  $H_2SO_4$  for 3 hours, it exhibited the lowest methylene blue adsorption capacity.

## Characterization of Bentonite with XRD

The main purpose of using XRD in this study was to determine if there were detectable changes of diffraction pattern of the bentonite due to purification and acid activation. The XRD pattern of the raw bentonite before purification indicated that the sample consisted of montmorillonite along with substantial amounts of impurities, namely quartz (Figure 6).

Figure 7 described the example of diffraction pattern of the purified bentonite activated with 5 molar  $H_2SO_4$ . It was observed that there were some missing peaks, one of them located in the  $2\theta$  of  $20^\circ$  which was the signature of montmorillonite [5]. This phenomenon

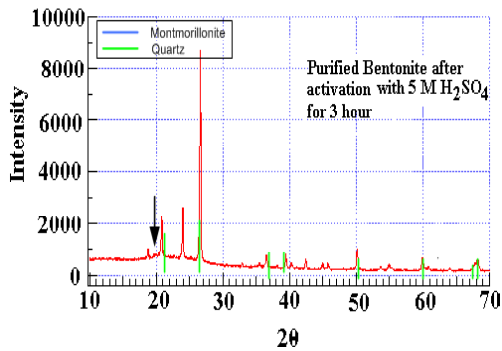


Figure 7. Graph of XRD of Purified Bentonite, Activated with 5 molar  $H_2SO_4$  for 3 hours.

occurred due to the use of high acid concentrations, probably causing some damages in the crystal geometry of the bentonite structure [4,6].

## CONCLUSION

The results showed that the optimum activation condition was at constant temperature of 100s °C, using 1 molar of  $H_2SO_4$  and 1 hour acid reflux. The highest bleaching capacity was found to be almost 60s % under optimum condition, which was higher than the adsorption capacity of the available bentonite in the market. If the concentration of acid was too high, the acid would cause damages to the crystal structure of bentonite hindering the bentonite adsorption capacity as shown by the chemical and XRD spectra analysis.

## ACKNOWLEDGMENT

The author would like to thank PT. Sumber Alam Makmur as well as PT. Memorintama Perkasa for providing the bentonite samples and the CPO, respectively.

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