The combination of activated natural zeolite-bentonite to reduce Fe and Cu in refined bleached palm oil (RBPO) by using atomic absorption spectrophotometer method

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Abstract. Indonesia is one of the crude palm oil (CPO) production country in the world. As many products are derivated from the CPO, the quality must be increased continuously. One of the things that influence the quality of palm oil is the Fe and Cu content. The objective of this research was to reduce Fe and Cu content in Refined Bleached Palm Oil (RBPO). In processing CPO or Refined Bleachead Palm Oil (RBPO) may be contaminated by Fe and Cu from metal tank and pipe in the factory. The zeolite and bentonite was activated by maceration method using hydrochloric acid (0,1 N). Four batch reactions consisting of refined palm oil (RPO), activated natural zeolite-bentonite (ANZB) was bleached by heating and stirring them at about $105^{\circ}C$ and 1200 rpm for 30 minutes. The results showed that all combinations of ANZB can reduce the Fe content. Thereafter, the optimal combination of ANZB was obtained in K1, K2 and K4 with Cu content 0.02 ppm. In the future, it is needed to study on the reduction of the Fe and Cu content in palm oil with the other adsorbent.

1. Introduction

Indonesia is one of crude palm oil (CPO) producer country in the world. The production reached 26 million tons in 2012 and 28 million tons in 2013, by which about 75% CPO is exported and only 25% for domestic requirement [1]. So, the prospect of palm oil industry will be potential by processing CPO to the high value products.

Crude Palm Oil (CPO) is the extracting product of the mesocarp of palm fruit. The derivated products of CPO, i.e. cooking oil and margarine, are obtained by further processing steps such as refining, bleaching and deodorizing. The CPO that has been refined and bleached is known as refined bleached palm oil (RBPO). The purpose of refining process is to produce a clean, attractive looking and palatable oil or fat, by removing the impurities content that cause the oil to have an unattractive colour and taste. After refining, the crude oil still contains other impurities, odour, pigment, Fe or Cu from the metal tank or pipe in the factory, that need to be lowered. They are reduced by using bleaching earth or activated clay, as the bleaching earth adsorbs the undesirable impurities such as trace metal, moisture, and insoluble matter [2]. Natural zeolite or bentonite is usually used and the adsorbent.

The reduction iron Fe by using natural bentonite has been studied. The adsorption of Fe increase sharply by elevating natural bentonite dosage [3]. The study of adsorption method using activated

zeolite as adsorbent to remove oil in water has been studied [4]. The heavy metals, Fe and Cu, still important to be researched, because they can contaminate to food product and make serious problems in healthy, as they can generate toxic derivatives in the body [5]. For instance, an excessive amounts of iron in specific tissues and cells (iron-loading) promote development of infection, neoplasia, cardiomyopathy and possibly neurodegenerative disorders [6-9].

Previous study used natural bentonite or activated zeolite as single adsorbent to reduce Fe and Cu in RBPO. This study, was aimed to study a combination of activated natural zeolite and bentonite as adsorbent for reducing Fe and Cu in refined bleached palm oil (RBPO).

2. Material and Methods
2.1 Materials and Equipment
Materials used in this study are crude palm oil (CPO), natural zeolite activated, natural bentonite activated, HCl 0.1 N (Merck), HNO_3 0.5 N (Merck), $HClO_4$ Pa (Merck), and aquades. While, the tools used are hammer mill (Van Aarsen), sieve 250 mesh (Patraproduk), hotplate-stirrer (Thermo Scientific), magnetic stirrer, oven (Jouan), vaccum (Value), desicator, whatmant 1, chemical equipment laboratory and atomic adsorption spectrophotometer (Hitachi Model Z-2000 Series Flame).

2.2 Zeolit and Bentonite Adsorbent Preparation
Natural zeolite, originated from Sarulla area of North Tapanuli, was crused and sieved to obtain the appropriate size of 250 Mesh. Zeolite was dried in an oven at temperature of 200^0C for 2 hours, cooled to room temperature and stored in a desicator. Then, zeolite was activated with 0.5 N hydrochloric acid for two hours, 1200 rpm at temperature 75^oC using hotplate stirrer (Thermoscientific Cimarec), washed with distilled water until the pH was neutral. Zeolite was dried in an oven at temperature of 105^0C for two hours, so that it can be used as an adsorbent.

Similarly, natural bentonite, originated from Bener Meriah area of Aceh Singkil, was crused and sieved to obtain the appropriate size of 250 Mesh. Bentonite was dried in an oven at temperature 200^0C for 2 hours, cooled to room temperature and stored in a desicator. Then, bentonite was activated with 0.5 N hydrochloric acid for two hours, 1200 rpm at temperature 75^oC using hotplate stirrer (Thermoscientific Cimarec), washed with distilled water until the pH was neutral. Bentonite was dried in an oven at temperature 105^0C for two hours and ready to be used as an adsorbent.

2.3 Experimental Procedure
The combination of activated natural zeolite:bentonite are K1 (30%:70%), K2 (40%:60%), K (60%:40%) and K4 (70%:30%) each one was mixed to CPO. It was stirred using 1200 rpm at temperature 105^oC for 30 minute using hotplate stirrer (Thermoscientific Cimarec) and vacummed. CPO was filtrated with whatman 1. Then, it was dried in oven at temperature 105^oC for 24 hours, cooled to room temperature and stored in a desicator. Two grams of sample was mixed with 1.5 ml of $HClO_4$ and 3.5 mL HNO_3, then the container was closed and left for 24 hours.

Furthermore, the obtained solution was heated over a water bath at $60-70^oC$ for 2-3 hours (until the solution is clear). If the sample is not soluble, 5 mL $HClO_4$, 5 mL HNO_3, and 3 mL of aquades were added, then the mixture was reheated until the solution is almost dry. RBPO was cooled at room temperature and added 1 mL of HNO_3 and stirred slowly, then added 9 ml of aquadest. The samples are ready to be measured with AAS by using triplo replication. Further, the data will be analyzed by analysis of variance method that is run by using software microsoft office excel 2007.

3. Result and Discussion
3.1. The characteristic of crude palm oil (CPO)
Based on the study conducted in the Laboratory of Mutu dan Kimia STIPAP, the characteristic of CPO of CPO is shown in Table 1.

Table 1. Characteristic of crude palm oil (before processing)

Parameter	Unit	Value	Spesification	Standard
FFA content	%	1.13	Max. 5	
Moisture content	%	0.09	Max. 0.25	SNI 01-2901-2006
Impurities content	%	0.01	Max. 0.25	

According to Table1, the characteristic of raw material (CPO) like free fatty acid (FFA), moisture and impurities, were still within standard range. Moisture could affect FFA content, because the higher moisture enhance hydrolysis reaction that effect (more than 5%) breaking and increase FFA in oil. It means that the quality of raw material in this research was good and beyond the maximum limit of the standard quality of CPO.

3.2. The Fe and Cu content in RBPO with ANZB

The results of Fe and Cu analysis in refined bleached palm oil (RBPO) with activated natural zeolite-bentonite (ANZB) are shown in Table 2.

Table 2. The Fe and Cu analysis in RBPO with ANZB

	Activated natural zeolite (%)	Activated natural bentonite (%)	Replication (ppm)			Mean (ppm)	Stdev
			I	II	III		
Fe							
CPO	0	0	5.39	4.81	4.59	4.93	0.41
K1	30	70	0.21	0.23	0.20	0.21	0.02
K2	40	60	0.13	0.12	0.10	0.12	0.02
K3	60	40	0.13	0.12	0.14	0.13	0.01
K4	70	30	0.14	0.15	0.14	0.14	0.01
Cu							
CPO	0	0	0.03	0.02	0.03	0.03	0.01
K1	30	70	0.02	0.02	0.03	0.02	0.01
K2	40	60	0.02	0.03	0.02	0.02	0.01
K3	60	40	0.02	0.03	0.03	0.03	0.01
K4	70	30	0.02	0.03	0.02	0.02	0.01

The initial Fe content in CPO was 4.93 ppm, which is almost reached the maximum standard level of Fe content in CPO (5.0 ppm) [10]. The increase in Fe content migt be resulted by contamination of the corrosion equipment to CPO that by the suboptimal maintenance of metal tank or pipe in the factory. In addition, Cu content in CPO was 0.03 ppm, which was lower than the standard of allowed Cu content (0.4 ppm) [10]. According to the analysis of variance method was known that in probability $\alpha=0,01$ F-count > F-table values (Fe : 668,93 > 6,93 and Cu : 41,20 > 6,93). It means that all combinations of ANZB have siginiffican effect to Fe and Cu content.

The analysis indicated that the initial Fe in CPO was very high, so that the process to decrease the Fe content by refining and bleaching is necessary. The reduction of Fe content could be reached by mixing the CPO with the activated natural zeolite-bentonite (ANZB), by which the zeolite and bentonite was acting as adsorbents.The chemical formula of natural zeolite and bentonite has negatively charged Al^- and $(Si\text{-}O)^-$. These negative entities might bind metal ions especially at lower pH. Therefore, the HCl solution may achieve the optimum adsorption. The binding of metal ions might be influenced on the surface of natural zeolite and bentonite [3].

The aim of the activation with chemical method by using hydrochloric acid is to exchange Ca^{2+} that exist in zeolite and bentonite to become H^+ and release ion Fe, Al and Mg and other impurities in the zeolite and bentonite structures, so that the zeolite and bentonite become more active. Hydrochloric acid (HCl) are used as the chemical compound and HCl are also used as catalyst in zeolit and bentonite activation. By dissolving in acid solution, the surface area of zeolite and bentonite become larger. So, the absorption was more effectively [12].

This research has two steps of treatment for zeolite and bentonite, there are the activated physically through the heating process in 75^oC and chemically by using hydrochloric acid as activator, to give better results. The heating process on hot plate was conducted to keep the form of bentonite stable during the adsorption process. In thermal activation, high temperature can omit water molecule and other impurities. The change of structure and composition during the heating process can vary based on the chemical composition of natural zeolite and bentonite and time of heating.

In this current study, the reseachers do not use too high temperature because the over heating can make the short space in structure and interlayer of zeolite and bentonite, the small interlayer space can cause the particle diffusion closer to another atom that can affect the space surface. Moreover, the high temperature can make degradation the natural component of palm oil.

3.3. The trending of ANZB to the Fe and Cu content in RBPO
The trending of the combination activated natural zeolite-bentonite to Fe and Cu contents are shown in the Figure 1 and 2.
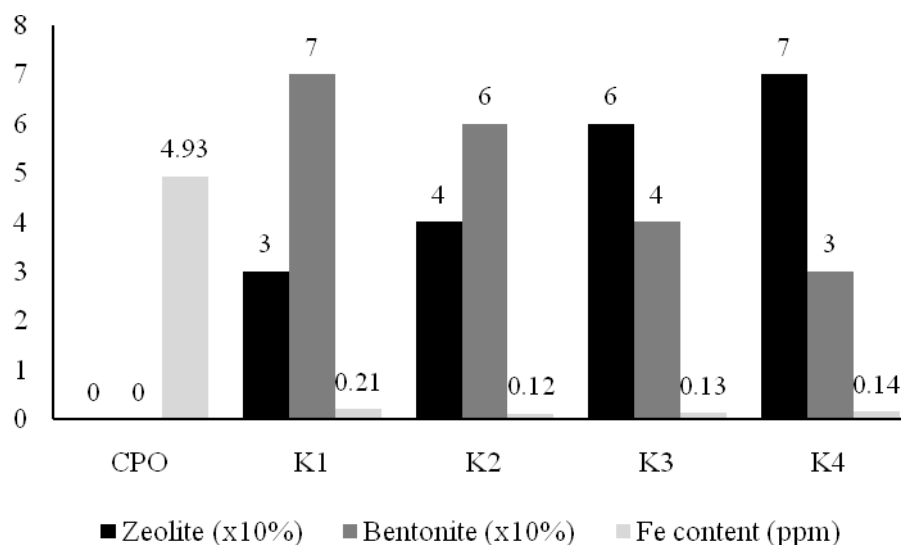

Figure 1. The histogram chart of combination ANZB to Fe content

The Figure 1 showed the histogram of the activated natural zeolite-bentonite (ANZB) combination to the Fe content in the CPO after refining and bleaching. It was found that the highest Fe content was noted at CPO that without mixing with ANZB and the lowest Fe content was found at K2 (activated natural zeolite : activated natural bentonite = 40 : 60). The Fe content of palm oil decreased slightly with the combination of ANZB (Table 2). The lower Fe content was achieved after mixing with combination ANZB because natural zeolite and bentonite as the adsorbents have negative ions that might bind the Fe in palm oil [3].
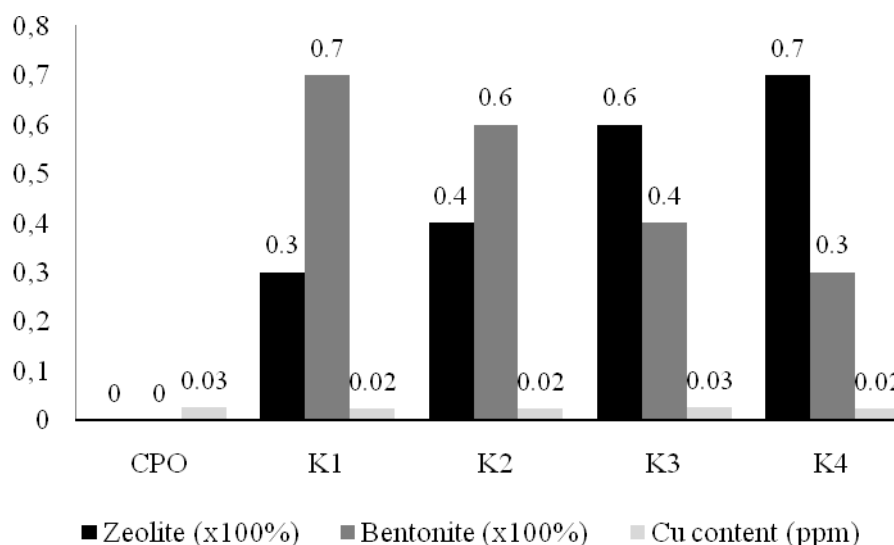
Figure 2. The histogram chart of combination ANZB to Cu content.

The Figure 2 showed the histogram of combination activated natural zeolite-bentonite (ANZB) to Cu content in RBPO. The highest activated zeolite and bentonite in K4 and K1 was 70%. Therefore, the lowest activated zeolite and bentonite in CPO was 0%. The Cu content in CPO, K1 and K4 was 0.03 ppm, 0.02 and 0.02 ppm, respectively. It means that the highest activated zeolite and bentonite is able to decrease the Cu content in RBPO. Because activated zeolite and bentonite as the adsorbents that might bind the Cu in palm oil [3].

4. Conclusion

The activated natural zeolite and bentonite was used as bleaching earth to reduce Fe and Cu contents in refined bleached palm oil. The Fe content in RBPO with combination ANZB K1; K2; K3 and K4 (ppm) was 0.21; 0.12; 0.13 and 0.14 respectively. The Cu content in RBPO with combination ANZB K1; K2; K3 and K4 (ppm) was 0.02; 0.02; 0.03 and 0.02. The result showed that the combination of ANZB can reduce the Fe content more effectively than the Cu content.

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