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Adsorption of Free Fatty Acids from Crude Palm Oil Using Calcium Silicate ($CaSiO_3$) Adsorbent Glycerol Template

Ananda Putra Siahaan, Seri Bima Sembiring*
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan, 20155, Indonesia
*Corresponding Author: seribima@usu.ac.id

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ABSTRACT

The adsorption of free fatty acids (FFA) in crude palm oil (CPO) using two types of adsorbents, namely Calcium Silicate ($CaSiO_3$) template 5% glycerol (CTG5) and Calcium Silicate ($CaSiO_3$) template 10% glycerol (CTG10). The experimental results showed that the titration method determined the decrease in FFA levels in CPO. This study used mass variations of adsorbent as much as 0.5 g, 1 g, and 1.5 g and agitation time (stirring) for 1, 3, 5, and 7 minutes. Based on the adsorption process, the most significant FFA adsorption results were obtained by using a CTG5 adsorbent with an adsorbent mass of 1.5 g and stirring time for 7 minutes at 80% with the weight of FFA adsorbed as much as 0.203 g FFA of 0.254 g FFA in 2 g of CPO.

Keywords: Calcium Silicate, Crude Palm Oil, Free Fatty Acid, Glycerol Template

ABSTRAK

Adsorpsi asam lemak bebas (FFA) pada minyak sawit mentah (CPO) menggunakan 2 jenis adsorben yaitu template kalsium silikat ($CaSiO_3$) 5% gliserol (CTG5) dan template kalsium silika ($CaSiO_3$) 10% gliserol (CTG10). Hasil percobaan menunjukkan bahwa penurunan kadar FFA pada CPO ditentukan dengan metode titrasi. Pada penelitian ini dilakukan variasi massa adsorben sebanyak 0,5 g, 1 g dan 1,5 g dan waktu pengadukan (stirring) selama 1, 3, 5 dan 7 menit. Berdasarkan proses adsorpsi, hasil adsorpsi FFA terbesar diperoleh dengan menggunakan adsorben CTG5 dengan massa adsorben 1,5 g dan waktu pengadukan selama 7 menit sebesar 80% dengan berat FFA teradsorpsi sebanyak 0,203 g FFA dari 0,254 g FFA dalam 2 g CPO.

Keyword: Asam Lemak Bebas, Kalsium Silikat, Minyak Sawit Mentah, Template Gliserol

1. Introduction

The oil palm (*Elaeis guineensis Jacq*) is one of Indonesia's main productive palm trees. This plant is the world's largest producer of vegetable oil, mainly because oil can be produced from fruit fibers and kernels. This oil can be used for cooking, industrial, or as a raw material for making biodiesel. Its properties resist oxidation under high pressure, and its ability to dissolve chemicals not soluble in other solvents. Its high coating ability makes it suitable for various purposes. Oil palm plantations in Indonesia are the largest in the world. This places Indonesia as the leading country exporting crude palm oil (CPO) and various processed products [1].

According to data from the Association of Indonesian Palm Oil Producers (GAPKI), Indonesia's contribution to the global CPO market is very high. CPO production in 2017 was recorded to have contributed up to 58.72% or 38.17 million tonnes of global output of 65 million tonnes. Meanwhile, CPO exports reached 31.5 million tons or contributed 81.34% of total production [2].

In trade, the quality of CPO has an essential meaning. One of the quality standards for CPO is that the content of free fatty acids (FFA) must be lower than 5% [3]. FFA can be formed due to the hydrolysis of oil by lipase enzymes and water in fresh fruit bunches (FFB) before processing in palm oil mills (PKS) [4]. The higher the FFA content, the lower the quality of CPO. The influence of low or high FFA and CPO yields also lies in the quality of the fruit harvested. The most formation of FFA is when in the field or before being processed at the palm oil factory (POF). The longer FFB is processed at the POF, the more FFA content in the CPO is produced. Besides that, rough handling can also increase the FFA rate. [5]

In general, several ways have been carried out to reduce FFA content in CPO. The first step is to mix poor quality CPO (FFA content > 5%) and combine with good quality CPO (FFA content <3%) so that a mixture of CPO is obtained. With FFA levels that meet the quality standards of palm oil [6]. FFA on CPO can also be adsorbed using adsorbents from tamarind seeds that have been dried and mashed, then activated with HNO_3. The adsorbed FFA level was 3.92 %, with a reduction percentage of 20.52% [7].

Another way that can be done to reduce FFA levels is by using an adsorbent such as calcium silicate. Calcium silicate ($CaSiO_3$) is an inorganic compound formed from sodium silicate (Na_2SiO_3) and calcium chloride. $CaSiO_3$ generally contains hydrate during the crystallization process. $CaSiO_3$ is white in color with low density, high absorption power, and a specific surface area. This compound is insoluble in ethanol and water but forms a gel with mineral acids [8]. The use of $CaSiO_3$ as an adsorbent has been widely reported, including to remove aflatoxin B1 from aqueous solutions [9], remove endotoxin from water [10], remove color in organic waste [11], and adsorb carotenoids from low-quality palm oil [12,13] used four adsorbents namely M-PSS (M = Mg, Ca, Sr, and Ba; PSS = polystyrene sulfonate) to adsorb carotenoids from CPO and they reported that the d orbitals were empty of alkaline earth metals (Mg, Ca, Sr, and Ba) can interact with olefin carotenoid bonds through polar-polar interactions.

The $CaSiO_3$, which is made from sodium silicate and calcium chloride which is calcined at 800°C for 3 hours, produces a pore size of 2.0089 nm and can be used as an adsorbent to adsorb FFA from CPO with a decrease of 69.86% - 94.78%. Because the adsorbent is nanoporous or has a small pore size, FFA molecules cannot enter the pores of the adsorbent. Therefore, there is a possibility of polar-polar interactions between the adsorbent and FFA, as shown in Figure 1.

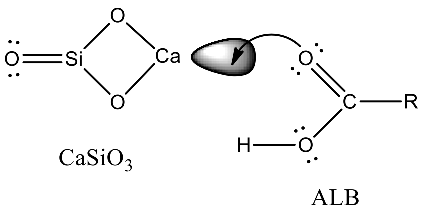

Figure 1. Interaction between adsorbents and FFA [14]

On the other hand, adsorption can also occur through the pores of an adsorbent. The larger pore size is required to adsorb larger molecules. Therefore, to increase the adsorption capacity of $CaSiO_3$, researchers are interested in increasing the pore size of the adsorbent so that the substance to be adsorbed can enter the pores of the adsorbent, as shown in Figure 2.

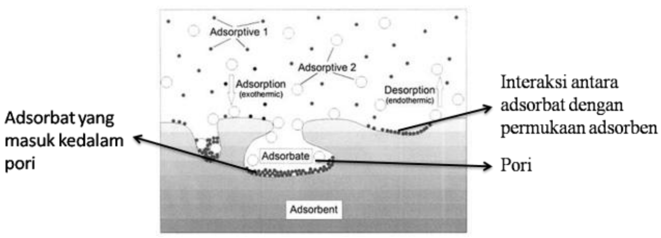

Figure 2 Adsorbent mechanism with the pores [15]

One effort that can be made to increase the pore size is by using a template molecule. A molecule that can be said to be a guiding molecule or a template can be a ligand, emulsifier, surfactant, or organic molecule. The pore size of an adsorbent is determined by the template added to the hydrothermal process according to the size of the template used [15].

In this study, researchers are interested in using glycerol as a template. This is because glycerol as a template meets the requirements as a template, namely having the properties of being liquid, soluble in water, and flammable. To make the adsorbent with glycerol template by mixing sodium silicate plus calcium chloride, mixing it with glycerol, then calcining at 800ºC. The organic matter (template) will burn during calcination and leave empty, porous spaces. This adsorbent is then used to adsorb FFA from CPO.

2. Materials and Methods

2.1. Equipment

The tools used in this study included a beaker glass, measuring cup, Erlenmeyer, burette, volume pipette, analytical balance, funnel, statives and clamps, rubber balls, dropping pipettes, shaker tools, boiling stones, spatulas, and stirring rods.

2.2. Materials

The materials used in this study were calcium silicate ($CaSiO_3$) template glycerol 5% (CTG5), calcium silicate ($CaSiO_3$) template glycerol 10% (CTG10), Crude Palm Oil (CPO), sodium hydroxide (NaOH), aquadest, *n*-hexane, isopropyl alcohol, phenolphthalein indicator.

2.3. Solvent Preparation

Before conducting the research, n-hexane, and isopropyl alcohol were distilled to purify the solvent.

2.4. Initial Free Fatty Acid Determination in Crude Palm Oil

As much as 75 g of coconut coir powder was weighed into a beaker glass, then add 1000 mL of HNO_3 3.5% (v/v) and 10 mg of CPO were placed into the Erlenmeyer (250 ml), and n-hexane (20 ml), then stir until homogeneous, then pipette (5 ml) into three Erlenmeyer pieces (250 ml), then add isopropyl alcohol (5 ml each), then stirred until homogeneous. The phenolphthalein indicator (3 drops) was added to this mixture, then titrated with NaOH (0.0993 N), and the percentage of free fatty acids was calculated. In this study, 12.70% of free fatty acids were obtained. In this study, FFA adsorption was carried out by varying (i) the amount of adsorbent and (ii) the agitation time (stirring) during the adsorption process using two types of adsorbents, namely CTG5 and CTG10.

2.5. Adsorption of FFA from CPO Using Adsorbent CTG5 and CTG10 with Variation of Adsorbent Mass

As much as 2 g of CPO and 20 ml of n-hexane were placed in 250 ml of Erlenmeyer and stirred until homogeneous. Into the mixture, added 0.5 g of CTG5, stirred allowed to stand for 30 minutes, filtered, and rinsed with n-hexane. The filtrate obtained was then put into a measuring flask (20 ml) and pipetted (5 ml) each into three Erlenmeyer pieces (250 ml), then added isopropyl alcohol (5 ml), then stirred until homogeneous. The phenolphthalein indicator (3 drops) was added to this mixture, then titrated with NaOH (0.0993 N), and the percentage of free fatty acids was calculated. The same was done for the CTG5 adsorbent weighing 1 g and 1.5 g, respectively. Furthermore, the same thing was done as above for the CTG10 adsorbent.

2.6. Adsorption of FFA with Shaker Assistance with Variation of Adsorbent Mass and Agitation Time Using Adsorbents CTG5 and CTG10

As much as 2 g of CPO and 20 ml of n-hexane were placed in 250 ml of Erlenmeyer and stirred until homogeneous. The adsorbent CTG5 (0.5 g) and boiling stones were added to the mixture, stirred with a shaker for 1 minute, and filtered and rinsed with n-hexane. The filtrate obtained was then put into a measuring flask (20 ml) and pipetted (5 ml) each into three Erlenmeyer pieces (250 ml), then added isopropyl alcohol (5 ml), then stirred until homogeneous. The phenolphthalein indicator (3 drops) was added to this mixture, then titrated with NaOH (0.0993 N), and the percentage of free fatty acids was calculated. The same was done for adsorption times of 3, 5, and 7 minutes. The effect of FFA was determined with adsorption on mixing time and adsorbent mass; the same procedure was done for the CTG5 adsorbent weighing 1 g and 1.5 g, respectively. Then the same thing was done as above for the CTG10 adsorbent.

3. Results and Discussion

Before adsorbing free fatty acids from CPO, the CTG5 and CTG10 adsorbents were characterized using X-Ray Diffraction (XRD) to determine the CaSiO3 content.

3.1 *Characterization of X-Ray Diffraction (XRD)*

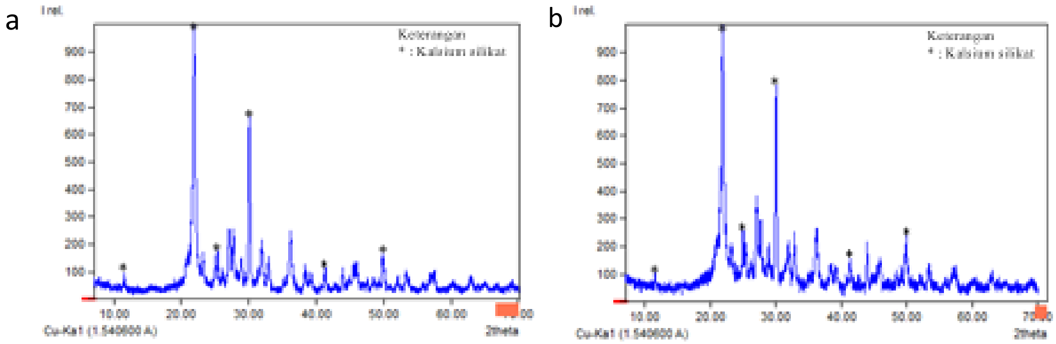

Figure 3. (a) CTG5 diffractogram; (b) CTG10 diffractogram

Figure 3 shows the XRD data diffractogram of the two adsorbents. There is the highest peak at an angle of 2 θ 20 º -25 º, which indicates the presence of a calcium silicate compound in the form of a bound mineral, namely $CaSiO_3$ wollastonite, so it can be said that the two adsorbents are the same or identical, namely calcium silicates ($CaSiO_3$).

3.2. *Adsorption of FFA from CPO (12.70%) Using Adsorbent CTG5 and CTG10 with Variation of Adsorbent Mass*

In this study, two types of adsorbents were used, namely CTG5 and CTG10, by varying the mass of each adsorbent by 0.5 g, 1 g, and 1.5 g. The results of FFA adsorption with CTG5 (red) and CTG10 (blue) adsorbents can be seen in the graphs in Figure 4.

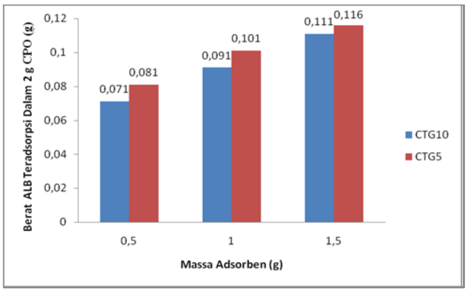

Figure 4. Graph of FFA adsorption from *CPO* (12.70 %) with CTG5 and CTG10

From this study, it can be seen that the decrease in FFA content in *CPO* from various *template concentrations* and adsorbent mass. For both adsorbents, the more adsorbent used, the more ALB absorbed, but not directly proportional.

Based on Figure 4 shows that the most excellent absorption rate of ALB was obtained by using the CTG5 adsorbent with a mass of 1.5 g of adsorbent, which was 45.669% with the weight of FFA adsorbed as much as 0.116 g of FFA from 0.254 g of FFA in 2 g of CPO. While the lowest absorption rate of FFA was obtained by using the CTG10 adsorbent with a mass of 0.5 g of adsorbent, which was 27.952%, with the weight of FFA adsorbed as much as 0.071 g of FFA from 0.254 g of FFA in 2 g of CPO. This also shows that adding two times the glycerol concentration in the adsorbent preparation does not cause a significant increase in FFA adsorption.

3.3. Adsorption of FFA from CPO (12.70%) with the help of a shaker with variations in adsorbent mass and agitation time using CTG5 and CTG10

In this study, two types of adsorbents were used, namely CTG5 and CTG10, by varying the mass of each adsorbent by 0.5 g, 1 g, and 1.5 g with agitation time (stirring) for 1, 3, 5, and 7 minutes. The graph of FFA adsorption from CPO (12.70 %) with CTG5 adsorbent with variations in adsorbent mass and agitation time (stirring) can be seen in Figure 5.

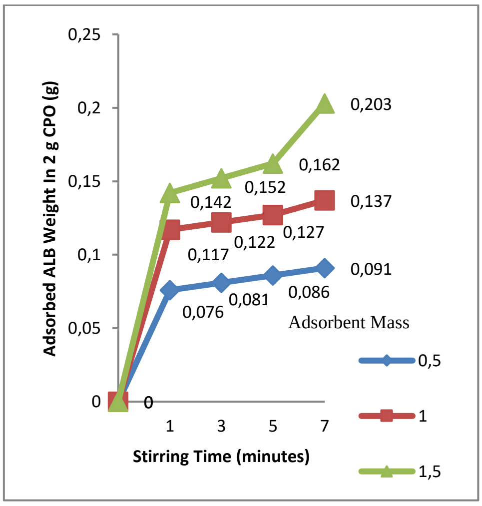

Figure 5. Graph of FFA adsorption from CPO *(*12.70 %) using CTG5 with a variation of agitation time and adsorbent mass

Figure 5 shows that the most excellent absorption rate of FFA was obtained by using the CTG5 adsorbent with an adsorbent mass of 1.5 g and an agitation time of 7 minutes, which was 80% with a weight of FFA adsorbed of 0.203 g FFA from 0.254 g FFA in 2 g CP*O*. While the lowest absorption rate of FFA was obtained using the CTG5 adsorbent with an adsorbent mass of 0.5 g and an agitation time of 1 minute, which was 29.921 % with a weight of FFA adsorbed of 0.076 g FFA from 0.254 g FFA in 2 g CPO.

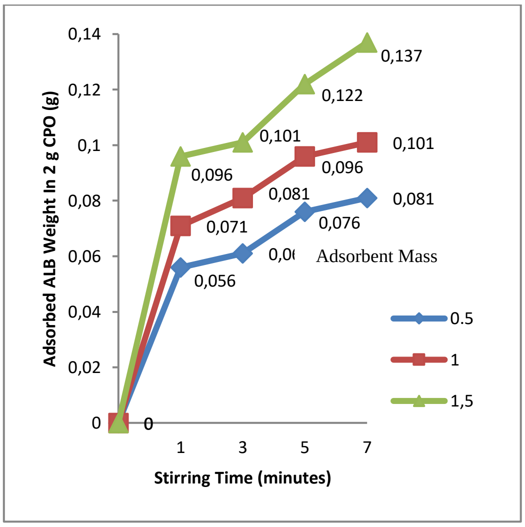

Figure 6. Graph of FFA adsorption from CPO (12.70 %) using CTG10 with a variation of agitation time and adsorbent mass

Figure 6 shows that the most remarkable absorption rate of FFA was obtained by using the CTG10 adsorbent with an adsorbent mass of 1.5 g and an agitation time of 7 minutes, which was 53.937% with a weight of ALB adsorbed of 0.137 g FFA from 0.254 g FFA in 2 g of CPO. While the lowest absorption rate of FFA was obtained by using the CTG10 adsorbent with a mass of 0.5 g of adsorbent and an agitation time of 1 minute, which was 22.047 % with a weight of FFA adsorbed of 0.056 g of FFA from 0.254 g of FFA in 2 g of CPO.

Based on the description above, it can be seen that the adsorption process is determined based on the capacity and percentage of adsorption efficiency over a specific time range. The more adsorbent used and the longer the agitation (stirring) time, the more FFA will be absorbed, but not directly proportional. Longer contact times allow for better diffusion and attachment of adsorbate molecules

FFA is the most excellent absorption rate using the CTG5 adsorbent, which was 80%. This is inversely proportional to using the $CaSiO_3$ adsorbent without *a template*, which has a pore size of 2.0089 nm and can adsorb FFA from CPO with an absorption rate of 69.86% - 94.78% [14]. At the same time, the adsorbent $CaSiO_3$ *template* glycerol can only adsorb FFA from CPO with an absorption rate of 80%. This may be due to the not high temperature during the calcination process, so there is a possibility that the adsorbent still contains glycerol which causes no maximum pore formation. Therefore, the possible interaction is polar-polar interaction through the empty d-orbital of calcium metal with the oxygen atom of FFA.

4. Conclusion

Based on the adsorption process carried out from the two adsorbents, namely CTG5 and CTG10, it can be seen that CTG5, with a weight of 1.5 g and an agitation time of 7 minutes, can adsorb FFA from CPO by 80%, while CTG10 with the same conditions can only adsorb FFA from CPO by 54%.

5. Acknowledgements

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6. Conflict of Interest

Authors declare no conflicts of interest

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