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Research paper

Utilization of Cocoa Shell As Adsorbent Purification For Used Cooking Oil

Pemanfaatan Kulit Buah Kakao Sebagai Adsorben Dalam Pemurnian Minyak Goreng Bekas

Rini Marlina*, Ade Oktasari, and Rohmatullaili*****

Departement Of Chemistry, Universitas Of UIN Raden Fatah Palembang
Universitas Islam Negeri Raden Fatah Palembang, Palembang 30126
Corresponding author :
*rini17marlina@gmail.com, ** adeoktasari@radenfatah.ac.id ***rohmatullaili.th@gmail.com

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ABSTRACT

Obtained cellulose from the cocoa shell is expected to reduce the free fatty acid content, water content, and peroxide value in used cooking oil. The highest contaminants from used cooking oil will harm health and the environment. The effectiveness of the adsorbent on the content of free fatty acids and peroxide value from used cooking oil was carried out by a titration process. Further information, the moisture content was carried out by drying from the oven to a constant weight. Based on the results obtained adsorption process on a 100 mesh reduction of free fatty acids 0.327%, 0.010% moisture content, and peroxide value of 3.25 meq O_2/kg. At 120 mesh the free fatty acids were 0.278%, the water content was 0.009% and the peroxide value was 1.25 meq O_2/kg. The decrease occurred caused the interaction between the hydroxyl group (OH^-) of cellulose with –COOH in the free fatty acids, the interaction of hydroxyl group (OH^-) with active peroxide, and the interaction hydroxyl group (OH^-) with oxygen atoms at water content. The particle size of the adsorbent has the optimum adsorption ability of 120 mesh. This happens because the surface area is greater than 100 mesh.

***Keywords**: Cocoa shell, cellulose, adsorbent, used cooking oil, free fatty acid, peroxide value*

INTRODUCTION

Cooking oil is a triglyceride in liquid form at room temperature which can provide 9 kcal/g of energy to the body. Cooking oil consists of two types, namely vegetable oil and animal oil. Cooking oil that is often consumed by the community is a vegetable oil made from palm oil. The most abundant chemical compound in palm cooking oil is a palmitic fatty acid ($CH_3(CH_2)_{14}COOH$). Cooking oil functions as a heat conductor, a savory taste enhancer, an increase in caloric value, and a solvent for vitamins A, D, E, and K in foodstuffs. (Ubaidah & Nuryanti, 2018).

Along with the development of the food business in Indonesia, many business people use cooking oil repeatedly in the frying process. This happens to save the capital spent. Cooking oil that is used repeatedly can cause a decrease in the quality of cooking oil, which can be seen from the physical changes in the oil and harms health. Fitriani, et al. (2018) revealed that the deterioration of cooking oil can be characterized by a change in color to brown, a change in taste, foaming, and odor.

Damage to cooking oil occurs due to a heating process that causes an increase in water content, free fatty acids, and peroxide values in cooking oil. Yustinah, *et. al*, 2015 reported that during heating, cooking oil degraded, namely a decrease in quality caused by oxidation, hydrolysis, and polymerization reactions. Oxidation reactions also occur during the storage process. Oxidation events that occur in oil can trigger peroxide and aldehyde reactions.

The number of peroxides and free fatty acids can increase due to heating at a temperature of 300-350oC which can cause poisoning, cancer, and accumulation of fat in the blood vessels (arthero sclerosis) (Octarya & Fernando, 2016). The high free fatty acids in cooking oil indicate that the quality of the cooking oil has been poor so that if it is discharged into the environment, it can disturb the environment and clog the sewers. (Waluyo et al, 2020).

Reduction of peroxide number, free fatty acid, and water content contained in cooking oil can be done by the purification process. The purification of cooking oil can be carried out by an adsorption process using an adsorbent so that the purified oil can be reapplied and suppress the community's economy (Yustinah et al, 2017).

In this study, the adsorbent used was derived from cocoa pods. Cocoa pods contain the main components that can be used as adsorbents, namely, cellulose 36.23%, hemicellulose 1.12%, and lignin 20-27.95% (Purnamawati et al., 2014). However, the cocoa pod skin has not been used further. Patria (Sukmawati et al., 2014) reported that 75% of the waste generated was cocoa pods. This causes environmental pollution if left unchecked and the benefits are not transferred (Sukmawati et al., 2014). Therefore, cocoa pod peels are used as adsorbents by utilizing the cellulose contained in them, following Patria's research (Sukmawati et al., 2014) that cocoa pod peels can be used as bio adsorbents because they contain 23-54% cellulose.

One of the factors that affect the adsorption capacity of the adsorbent is particle size. The smaller the particle size, the larger the surface area of the adsorbent so that the absorption of the adsorbate is more effective. Suryadi et al, (2019) reported in his research that the adsorbent of kepok banana peel which was effective in reducing free fatty acids was an adsorbent with a particle size of 230 mesh of 73.38%, and a particle size of 35 mesh of 8.57%.

The adsorption capacity of the adsorbent can be increased through an activation process using either an acid or a base solution. According to Oktasari, 2018, the peanut shell adsorbent activated with NaOH had a higher adsorption ability to decrease Pb metal content than acid activation and without activation which were 100%, 95.36%, and 97.561%, respectively. Meanwhile, according to Neni 2014, the 1 N NaOH solution used as an activator gave a 39.97% reduction in peroxide value and 52.73% free fatty acids in used cooking oil.

Dewi et al, (2019) reported in his research Teak leaves can be made into natural adsorbents with NaOH activator. The greater the concentration of NaOH, the greater the adsorbed FFA. The adsorption process was carried out with different concentrations of 5%, 10%, and 20%. The best FFA adsorption results were shown by activated carbon activated with 20% NaOH, where the remaining FFA content in used cooking oil was 0.2976%. In addition, Yustinah's research (Yustinah, 2015) reported that the adsorbent activated with 1 N NaOH solution had optimum results in reducing the free fatty acid content by 55% and peroxide number by 47%. Thus, alkaline-activated adsorbents have a more effective adsorption capacity than acid-activated and non-activated adsorbents. Therefore, a study was conducted on Purification of Used Cooking Oil Using Cocoa Fruit Peel Adsorbent (*Theobroma Cacao L*), with 1 N NaOH activator, which has a variation of adsorbent particle size of 100 mesh and 120 mesh, with test parameters of free fatty acid content, number peroxide, and water content in cooking oil.

METHODOLOGY

Materials

The following materials were used in this study, cocoa pods from Karang Waru Village, Musi Banyuasin Regency. Used cooking oil from the canteen of UIN Raden Fatah Palembang, GR stretch indicator, filter paper, NaOH ensure 0.1 N and 1 N, ethanol 96%, *aquadest*, KI *emsure*, chloroform, $Na_2S_2O_3$ *emsure* 0,01 N, *phenolphthalein* (pp) indicator *ACS*.

Tools

The following tools were used in this study, 250 mL Iwaki beaker, Philips blender, Ohaus analytical balance, vaporizer cup, cimarec+ digital Thermo scientific hot plate, Memmert UN55 oven, 50 mL pyrex measuring cup, pyrex volume pipette, dropper pipette, desiccator, Erlenmeyer *Iwaki 250* mL, buret Iwaki 25 mL, *magnetic stirrer*, sieve 100 *mesh* dan 120 *mesh*, FTIR *Bruker Alpha*.

Procedures

a. Cocoa Fruit Peel Preparation

Cocoa pods are cleaned and then cut into small pieces. Cocoa pods that have been cut are dried in the sun until the moisture content is reduced, crushed, and sieved using 100 mesh and 120 mesh sieves. Furthermore, the adsorbent powder was characterized using FTIR.

b. Activation

Cocoa pods that have been sifted weighing 25 grams are put in a 250 mL Erlenmeyer, 100 mL of 1 N NaOH solution is added, and the mixture is shaken using a shaker for 2 hours and filtered. Then rinsed using distilled water until the pH is neutral and dried in an oven at 105ºC. The activated cocoa powder is cooled in a desiccator, then weighed repeatedly until the weight is constant. The activated adsorbent powder was characterized using FTIR.

c. Preparation and Refining of Used Cooking Oil

Used oil is filtered to separate the rest of the frying pan. Next, the oil was put in a 72 mL beaker glass, then 6 g of activated cocoa powder was added, stirred for 8 hours, filtered and the filtrate separated. Furthermore, the samples obtained were taken and analyzed.

d. Cooking oil test parameter

The following are the test parameters carried out in this study::

1. Free fatty acids (FAA)

Cooking oil weighed 5 grams, then put in an Erlenmeyer and added 30 mL of 96% ethanol that had been mixed with phenolphthalein (pp) indicator. Then the sample was titrated using 0.1 N NaOH solution until it changed to a pink color and did not disappear for 30 seconds.

$$\% FFA = \frac{V.NaOH \times N.NaOH \times 25{,}6}{Sample} \times 100\%$$

Description :

% FFA : Free fatty acids

V NaOH: Volume titration NaOH

2. Water content

The empty evaporating dish was weighed and the weight was recorded. Furthermore, the cooking oil weighed 5 grams, heated in an oven at 105ºC for 1 hour, removed and cooled in a desiccator and the water content was calculated.

$$Water\ content = \frac{m_1 - m_2}{m_1} \times 100\%$$

Description :

m_1: sample weight before heating (gram)

m_2: sample weight after heating (gram)

3. Peroxide number

Used cooking oil weighed 5 grams, put into a 250 mL Erlenmeyer then added 30 mL of acetic acid-chloroform solution (3: 2), shaken until homogeneous, then add 0.5 mL of homogenized saturated KI solution, add 30 mL of distilled water. The mixture is titrated with 0.01 N Na2S2O3 until the yellow color decreases, add starch indicator and titrate again until a color change occurs and the peroxide value is calculated.

$$Peroxide\ number: \frac{ml\ Na_2S_2O_3 \times N.\ Na_2S_2O_3 \times 1000}{Sample}$$

Description :

$Na_2S_2O_3$ (mL): The volume of sodium thiosulfate solution required for the titration.

N $Na_2S_2O_3$ (0,01 N): Normality of sodium thiosulfate standard solution (eq/V).

Sample mass (gr): Cooking oil weight

RESULT AND DISCUSSION

a. Cocoa Fruit Peel Preparation

Cocoa pod preparation begins with cleaning the cocoa pod skin from impurities such as soil and sap. Cleaning is carried out to maintain the quality of the adsorbent. Then, the cocoa rind is cleaned and dried. Furthermore, it is mashed and sieved to obtain cocoa rind powder with particle sizes of 100 mesh and 120 mesh.

b. Cocoa Fruit Peel Adsorbent Activation Process

The activation process of NaOH causes the breaking of bonds from the basic structure of lignin (Kusumawardani, Zaharah, & Destiarti, *et. al*, 2018). The bonds that are broken during activation are hydrogen bonds (OH-) which are the link between cellulose and lignin or hemicellulose with lignin. Meanwhile, Na+ will bind to lignin to form sodium phenolate. This phenolic salt has properties that are easily soluble (Rudy, 2015). Moreover, according to Fui (Liew et al., 2015), NaOH solution used in the activation process causes severance between lignocellulosic which then with an excess amount of NaOH solution causes the reaction to continue so that the ester bond in hemicellulose is broken according to the FTIR spectra in Figure 3.

Following is the reaction for breaking the bonds between lignin and cellulose:

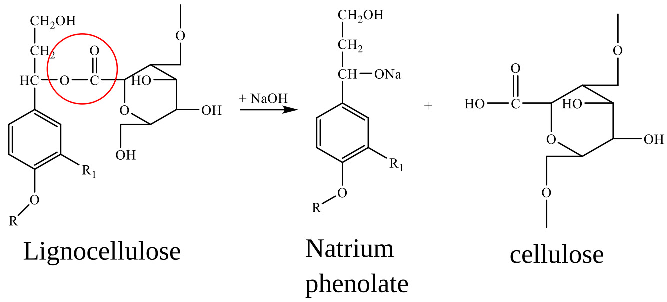


Figure 1. The reaction of breaking the bonds of lignin and cellulose

The decrease in lignin content was indicated by the formation of a black solution, and a change in sample weight, where the activated sample had a lighter weight than the weight before activation, which was originally 25 g to 15 g for a particle size of 100 mesh and 12 g with a particle size of 120 mesh. . This indicates that the lignin has dissolved in the activation process.

The following is a picture of the absorbent before and after the activation process.

(a) (b)

Figure 2. (a) before activation (b) after activation.

Cocoa rind adsorbents were further characterized using FTIR which aims to determine the functional groups contained in Cocoa rind powder, before and after activation. The FTIR spectra of the cocoa rind changed properties due to absorption shifts. FTIR spectra of Cocoa rind before and after activation can be seen in Figure 3.

Based on the FTIR spectra above, shows a shift in the absorption of the hydroxyl group (OH) from the wave number 3308 cm-1 to 3306 cm-1. The IR spectra also show that stretching vibrations –C-H sp3 occur at wavenumbers 2914 cm-1 and 2907 cm-1. At a wavenumber of 1608 cm-1, the absorption shift of the aromatic -C=C group becomes 1604 cm-1. In addition, at a wavenumber of 1738 cm-1, there is a significant difference in absorption between the cocoa pod skin before and after activation which indicates the -C=O group is lost after the activation process. This happens because of the addition of NaOH solution in the activation process which causes the breaking of the ester bond between cellulose and lignin. The loss of the -C=O group indicates that the activation process has been carried out optimally and the lignin contained in the cocoa pod skin has also been dissolved in the NaOH solution.

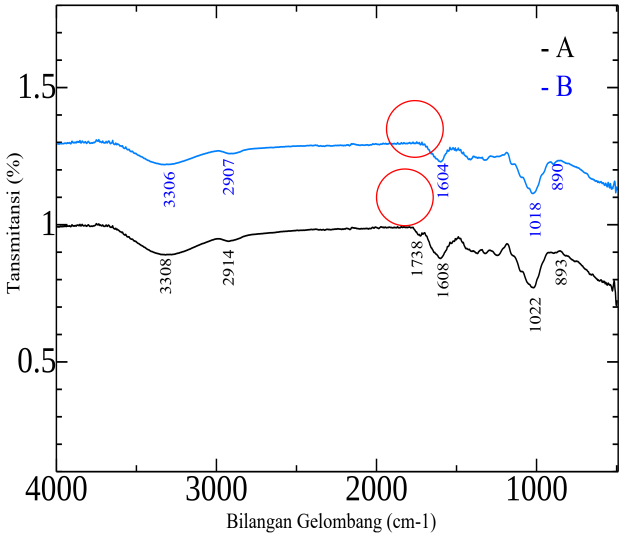


Figure 3. (A) Spektra FTIR kulit buah kakao sebelum aktivasi (B) kulit buah kakao setelah aktivasi.

Table 1. Differences in FTIR absorption characterization of Cocoa rind adsorbents.

Wavenumber cm^{-1}		
Cocoa Fruit Peel	Cocoa Fruit Peel After Activation	Functional Group
3308	3306	Stretching vibration OH
2914	2907	C-H sp^3
1738	-	Stretching vibration -C=O
1608	1604	Stretching vibration -C=C
1022	1018	Vibration C-O
893	890	Asymmetrical ring out of the field

The activation process serves to increase the absorption of the adsorbent. In addition, activation aims to separate substances or compounds that can interfere with the adsorption process, namely lignin from cellulose. According (Yogi, 2019), the alkaline solution used as an activator can dissolve lignin so that the adsorption power of the adsorbent increases. Characterized by the maximum adsorption capacity of peanut shells for Cd ions 80 mmol g following the Langmuir isotherm pattern with an adsorption energy of 27671.19 kJ mol^{-1}. In addition, the alkaline activator will dissolve hemicellulose which has the same properties so that its levels are reduced. A study (Rambat et al, 2015) reported that activated cocoa pods with NaOH solution were able to reduce lignin and hemicellulose content by 32.11% and 42.87%, respectively.

After activation of the cocoa rind adsorbent, the pH was measured using a universal indicator to indicate the presence of an activating agent in the adsorbent. The initial pH of the activated adsorbent was 12, then the cocoa rind adsorbent was rinsed using distilled water until the pH was neutral. The function of rinsing the adsorbent after activation is to balance the value of OH^- with H^+ so that it does not interfere with the work of the adsorbent in the adsorption of the adsorbate. The high and low pH of the activated adsorbent is avoided because at low pH it has H+ ions which will affect the OH- ions of the adsorbent. Meanwhile, a high pH can cause the formation of hydroxide with adsorbate (Kusumawardani et al, 2018).

The rinsed cocoa rind adsorbent was then dried at 105ºC. This is done to reduce the water content. When the adsorbent has high water content, it will be hygroscopic, meaning it can absorb water vapor in the surrounding environment. The high water content can clog the pores of the adsorbent, and interfere with the absorption between the adsorbent and the adsorbate. (Ayu et al, 2016) reported that the high water content of the adsorbent can be a barrier for free fatty acids to interact with the adsorbent surface.

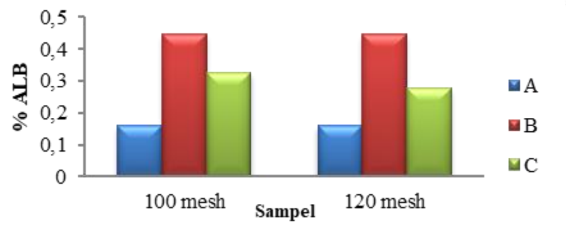
c. Refining Used Cooking Oil

Before use, used cooking oil is filtered to separate the oil from the rest of the frying pan. The filtered cooking oil was put into an Erlenmeyer, then the activated cocoa rind powder was added, and shaken using a shaker. The stirring process serves to speed up the reaction so that the entire surface of the adsorbent is in contact with the oil.

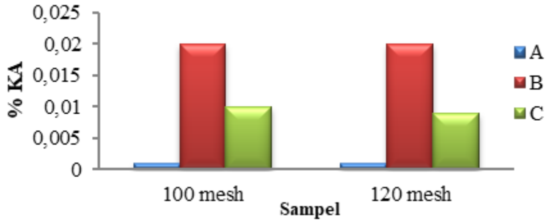
d. Test Parameters

The results of this study can be seen as follows:

a.



b.



c.

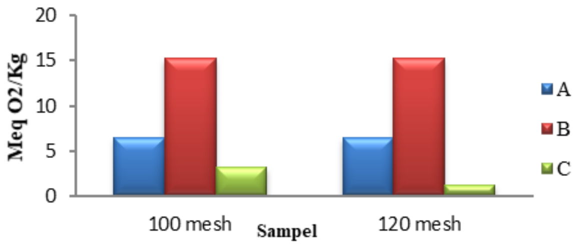


Figure 4. Graph (a). Free fatty acids, (b). Water content, (c). peroxide number. (A) new oil, (B) used oil, (C) 100 and 120 mesh adsorption

Figure 4 above shows a decrease in the free fatty acid content, water content, and peroxide value in the cooking oil adsorbed by the cocoa rind adsorbent with particle sizes of 100 and 120 mesh. The results of the decrease were free fatty acids which were originally 0.448% to 0.327% for 100 mesh and 0.278% for 120 mesh. Moisture content from 0.020% to 0.010% for 100 mesh and 0.009% for 120 mesh. Peroxide numbers from 15.3 meq O2/kg to 3.25 meq O2/kg for 100 mesh and 1.25 meq O2/kg for 120 mesh.

The decrease in free fatty acid content occurs because the active hydroxyl group (OH-) of the adsorbent cellulose can interact with the -COOH group of free fatty acids (Setyawan & Dwi, 2009). The decrease in water content occurs due to the interaction between the active group of cellulose adsorbent with oxygen atoms from the water forming hydrogen bonds, while the peroxide number decreases due to the interaction between the hydroxyl group (OH-)

of cellulose with free radical atoms in the active peroxide (Setyawan & Dwi, 2009).

A significant decrease occurred in the peroxide value, where the value obtained was lower than the new oil (6.46 meq O_2/kg), namely 3.25 meq O2/kg and 1.25 meq O_2/kg. This happens because the new oil used in the study has changed the storage process. Following Yulia's research that the peroxide number can increase during the storage process and the peroxide number content of the new oil is 0.203 meq O_2/kg. In addition, the peroxide number contained in cooking oil can decrease because it contains a polar peroxide group. While the adsorbent has a hydroxyl group that is polar so the similarity in these properties causes the peroxide number to be absorbed by the adsorbent and the peroxide number decreases.

In this study, the adsorbent that has optimum absorption is the adsorbent with a particle size of 120 mesh. Following Sirrajudin's research (Sirrajuddin, 2018), the smaller the particle size, the larger the surface area of the adsorbent. In addition, according to Dian et al, (2006) the larger the surface area, the more substances will be adsorbed and the adsorption process will be more effective. With the characteristics of the 120 mesh adsorbent, which is a larger surface area than 100 mesh, it causes a better reduction in free fatty acids, water content, and peroxide number.

The proposed reaction mechanism for the adsorption process of the cocoa pod rind adsorbent on the free fatty acid content, water content, and peroxide number is shown in Figure 5.

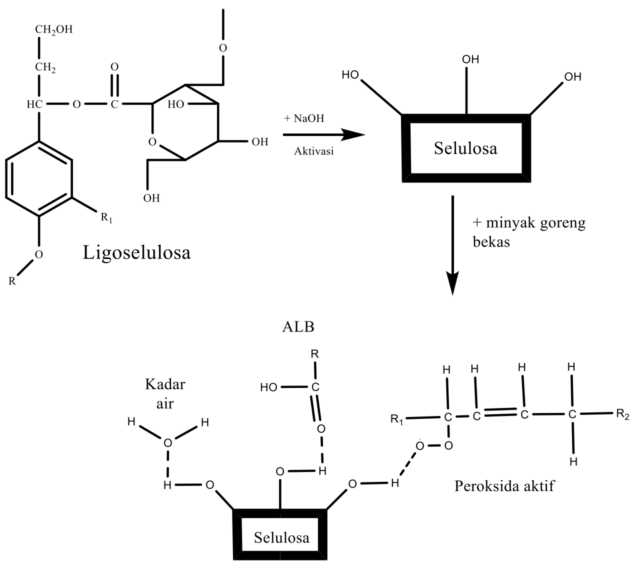


Figure 5. Proposed mechanism of the adsorbate adsorption reaction by the adsorbent

Based on Figure 5, it can be seen that the possible bond between the adsorbent and the adsorbate is hydrogen bonding. Following Donatus' research (Setyawan & Dwi, 2009) that the water content in used cooking oil can decrease due to the bond formed between the active group of the adsorbent and the O atom in the water content. While the free fatty acids bond between –COOH and the adsorbent, and hydrogen bond interactions between the active peroxide and the active group of the adsorbent.

CONCLUSION

Based on the research that has been done, cocoa rind adsorbent affects reducing free fatty acid levels, peroxide numbers, and water content. The decrease occurred due to the interaction between the hydroxyl group (OH-) of cellulose with –COOH in free fatty acids, the interaction of the hydroxyl group (OH-) with active peroxide, and the interaction of the hydroxyl group (OH-) with oxygen atoms at water content. The particle size of the adsorbent which has the optimum adsorption ability is 120 mesh. This happens because the surface area that is owned is greater than 100 mesh.

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