

Utilization of Adsorbent from Tamarind Seeds for Removing Red and Yellow Color in CPO (Crude Palm Oil)

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Abstract- This study is aimed to discover the effectiveness of tamarind seeds as adsorbent for removing red and yellow color in CPO (Crude Palm Oil). Methods used in this study were pre-treatment, activation of tamarind seeds, and adsorption process at 90 °C and 1000 rpm of mixing speed. The tamarind seeds were cleaned and crushed to pass through 140 mesh, and activated with 4 N nitric acid in certain ratio of adsorbent : nitric acid and heated at 80 °C for 2 hours, then dried in oven for 2 hours. The adsorption process was carried out using adsorbent with the highest iodine number in varying adsorbent dose and contact time. The highest iodine number was 511.773 mg/g and obtained at the ratio of adsorbent : nitric acid 1 : 2 and 130 °C of oven temperature. The best removals were 37.37% for red color and 10 % for yellow color, and was obtained at adsorbent 1.0% of dose and 35 minutes of contact time. This result was close to the Indonesian National Standard (SNI) for color in palm edible oil, which was 5,0/50 (red/yellow).

Index Terms- Tamarind seeds, adsorbent, CPO, color.

1. INTRODUCTION

The initial stage of CPO rafination is the removal of gum (degumming) followed by bleaching (bleaching), deodorization, crystallization, and fractionation [1].

Several ways for gum removal process include heating, addition of acid (H₃PO₄, H₂SO₄ and HCl) or base (NaOH), and gum hydrating by addition of salt such as sodium chloride and sodium phosphate [2]. Bleaching is the removal of color, oxidizing agent, remaining gums, soap, and trace metals by mixing the oil with a specific adsorbent or commonly known as bleaching earth [3]. Bleaching using bleaching earth effectively reduces colors in CPO and makes its appearance becomes clearer, but oftenly causes the carotenoid content of oil as a source of nutrients decreased dramatically [4].

Adsorbent can be made from many variety of biomass, including seeds of certain plants such as tamarind (*Tamarindus indica*). In many places, the widely used part of tamarind is the flesh as foodstuffs and additives, while the seeds are not used and disposed as waste [5].

Numerous studies have been conducted that used tamarind seeds as adsorbent, with and without activation. Ones with no activation are used for clarifying liquid waste of tofu [6], removing methylene blue dye [7], removing malachite green dye [8], and removing chromium [9, 10]. The acid activated ones was used for adsorption of heavy metal chromium (III) [11], adsorption of methylene blue and

malachite green dye [7, 12], and removing chromium (IV) [13]. The base-activated one was used in the preliminary study of removing acetone [5]. Moreover, there are many studies about oil purification using adsorbent, particularly at the stage of degumming and bleaching, where the results showed that acid - activated clays is more effective than neutral clay with clay suggested dose > 0.5% for a better removal of unwanted content in CPO [14]. A contact between used cooking oil with activated charcoal from coconut husk as an adsorbent proved to produce a better quality of used oil [13].

Based on the foregoing, the adsorbent from activated tamarind seeds may be attempted to be applied as an alternative adsorbent to remove gum as phosphatides content in CPO.

2. MATERIALS AND METHODS

2.1. Materials

The main materials were crude palm oil (CPO) and tamarind seeds that were obtained from the neighborhood around University of Sumatera Utara. Nitric acid was used in adsorbent activation. Iodine solution, starch solution, sodium thiosulfate, and distilled water were used for analysis purpose.

2.2. Methods

2.2.1. Adsorbent Activation

Tamarind seeds were washed with water and dried in the sunlight. They were crushed to powder form and

passed through 140 mesh. Adsorbent was activated with a solution of 4 N nitric acid [12] with a ratio of adsorbent : nitric acid was 1: 1 and heated for 2 h at 80 °C, then cooled. It was followed by washing several times with distilled water to remove residual acid. Adsorbent was placed in the oven for 2 h at 110 °C. The procedure was repeated for the ratio of adsorbent : nitric acid of 1: 2, 1: 3, and 1: 4 and the temperature of the oven 120, 130, and 140 °C.

2.2.2. Analysis of Iodine Number

1 g of adsorbent was dried at 110 ° C for 3 h and then cooled. 50 ml of 0.1 N iodine solution was added and stirred with a magnetic stirrer for 15 minutes. The mixture was filtered and the filtrate was taken as 10 ml, and then titrated with 0.1 N sodium thiosulfate solution until the yellow color was fading. After 1% starch indicator was added, titrated back until the solution was colorless. Titration was also performed for the blank solution.

$$\text{Iodine Number } \left(\frac{\text{mg}}{\text{g}} \right) = \frac{10 \cdot \frac{V \times N_1}{N_2}}{W_2} \times W_1 \times \text{Df}$$

where,

V = volume of used sodium thiosulfate (ml)

N₁ = normality of sodium thiosulfate (N)

N₂ = normality of iodine (0.1 N)

W₁ = amount of iodine for every ml of 0.1 sodium thiosulfate (12.69 mg/ml)

W₂ = mass of sample (g)

Df = dilution factor (5)

[15]

2.2.3. Adsorption of Color in CPO

100 g of CPO was poured into the glass beaker and heated on a hot plate to a temperature of 90 ° C while being stirred at 1000 rpm using a magnetic stirrer. Adsorbent was added at a dose of 0.5% (w: w) of CPO used and the temperature was maintained at 100-110 °C for 25 minutes. Afterwards, oil was filtered with a Buchner funnel and Whatman No. 1 filter paper immediately under vacuum conditions. The procedure was repeated for a contact time of 35 and

45 minutes and adsorbent dosage of 1% and 1.5% (b: b) of CPO used [16].

2.2.4. Characterization of Functional Groups on Adsorbent

Analysis of the functional groups on the adsorbent was performed before and after activated, and after contacted with CPO. About 1 mg of sample was pulverized with a mortar with potassium bromide, and pellet was made from a mixture of these materials. Pellet was pressed with a hydraulic pump at 80 KN pressure for 5 minutes. Afterwards, pellet was placed in the sample holder in the beam path of FTIR instrument. The measurement with FTIR instrument was done and the graph formed was observed [17].

2.2.5. Analysis of Color in CPO

Oil was diluted if necessary, and filtered to remove water and impurities. Oil was placed into the Lovibond proper cell size. The light source was turned on and viewed with eye lens. The colors on the rack was set to match the color of the sample with standard color.

3. RESULTS AND DISCUSSION

3.1. Effect of Oven Temperature and Ratio of Adsorbent : Nitric Acid on Iodine Numbers of Adsorbent

Before and after activation, iodine number analysis (mg I²/g adsorbent) of the adsorbent was done. The iodine number before activation is 379.812 mg/g, while the iodine numbers after activation were given in Table 1 below. The results can also be graphed in Figure 1.

Table 1. Iodine Numbers of Adsorbent for Any Condition of Activation (mg/g)

Temp. (°C)	Ratio of Adsorbent:Nitric Acid (w:v)			
	1:1	1:2	1:3	1:4
110	372.364	405.217	408.870	404.055
120	387.563	448.565	448.565	444.595
130	417.920	511.773	475.029	471.622
140	456.028	506.839	504.220	501.493

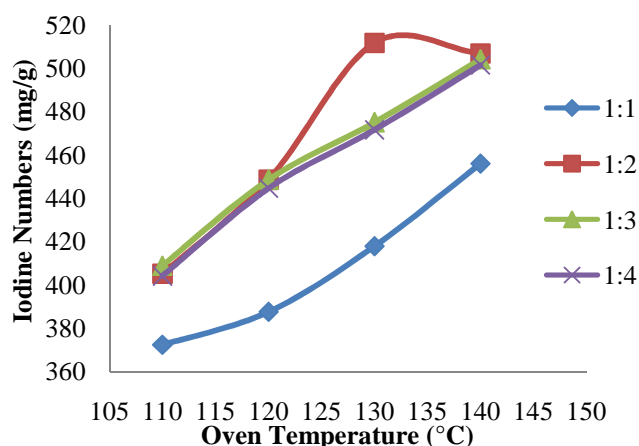


Fig. 1. Effect of Oven Temperature on Iodine Numbers of Adsorbent for Certain Ratio of Adsorbent : Nitric Acid

From Table 1. And Fig. 1, it can be seen that iodine numbers tend to increase by the increasing of oven temperature for the same ratio of adsorbent : nitric acid, and by the decreasing of the ratio for the same oven temperature. The highest iodine number was obtained at 130 °C and ratio of 1:2, it was 511.773 mg/g.

Irregularity was occurred on some datas as shown in the Fig. 1. These can be happened for some probabilities. Firstly, water content of the after-washed adsorbent can not be controlled, thus affecting the heating process inside the oven which was aimed to evaporate water content and volatile compounds. Secondly, at ratio pf 1:2 and oven temperature of 140 °C, cracking has occured and it caused the reduction of mesopores and micropores on the adsorbent. Thirdly, at higher volumes of activator (more than 1:2), adsorbent has been damaged due to the dissolution of its structure.

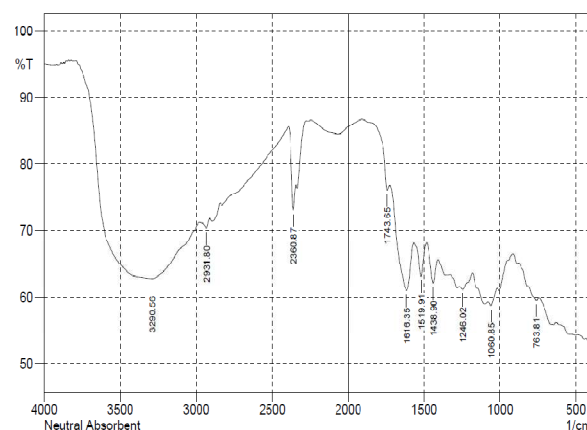
Chemical modification is usually carried out at a lower temperature than the physical method [18]. Higher temperature will increase the reaction rate for the reduction of impurities and volatile compounds that filled the pores of the adsorbent thereby optimizing the active pores formation. However, overheating may impact on the reduction of mesopores and micropores [19]. A very low concentration of activator may cause the incomplete formation of the active sites, whereas a very high ratio of activator may cause a damage to the structure of the adsorbent [20]. A very high volume of activator may eliminate active adsorbent properties due to the damage caused by dissolution and breakup of pores on the adsorbent.

By comparing theory and results obtained from the research, it can be concluded that the most favorable conditions to produce the adsorbent from tamarind

seeds with the highest iodine number is the ratio of adsorbent: nitric acid of 1:2 and at oven temperature of 130 °C.

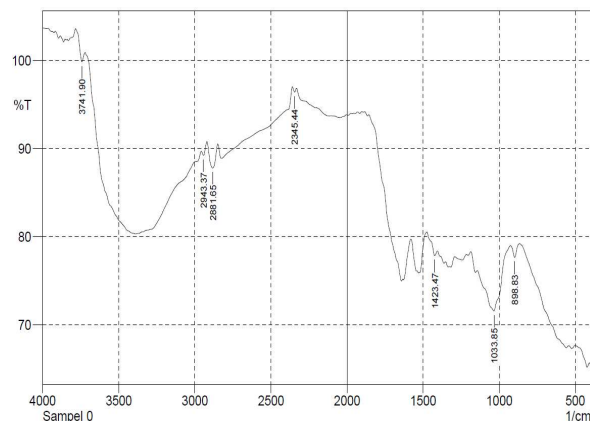
3.2. Effect of Oven Temperature and Ratio of Adsorbent : Nitric Acid on Iodine Numbers of Adsorbent

The characterization was conducted of adsorbent before and after the activation, and after it was used in the adsorption process (used adsorbent). Functional groups on the adsorbent can be inferred by comparing the results on the graph with the literature or IR correlation table [21, 22]. The graphs are given in Figure 2, 3, and 4 below.



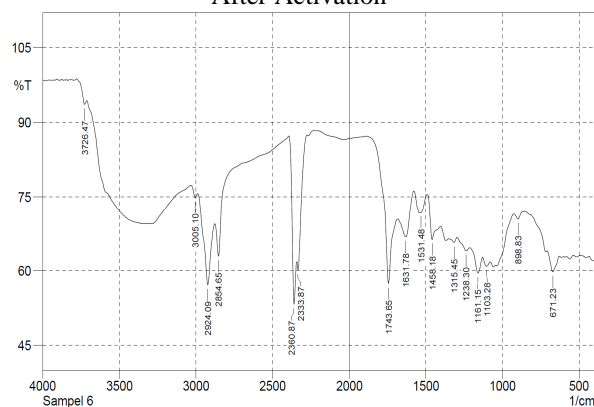
- 763.81 cm⁻¹: C-H group (aromatic alkenes)
- 1060.85 cm⁻¹: C-O group(carboxylic acid)
- 1246.02 cm⁻¹: C-N group (amine)
- 1519.91 cm⁻¹: NO₂ (nitro compounds)
- 1743.65 cm⁻¹: C=O group (ester)
- 2360.87 cm⁻¹: CO₂ (carbondioxide)
- 3290.56 cm⁻¹: O-H group (alcohol)

Fig.2. FTIR Spectrophotometry Results for Adsorbent Before Activation



898.83 cm^{-1} : C-H group (aromatic alkenes)
1033.85 cm^{-1} : C-N (amine)
1423.47 cm^{-1} : Si-O group (silicate compounds)
2345.44 cm^{-1} : C=O group (carbonyl oxide)
2881.65 cm^{-1} : C-H group (methyl)
3741.90 cm^{-1} : Si-OH group (silanol)
2943.37 cm^{-1} : O-H group (alcohol)

Fig.3. FTIR Spectrophotometry Results for Adsorbent After Activation



671.23 cm^{-1} : C-H group (aromatic alkenes)
1103.28 cm^{-1} : C-O group (ester)
1161.15 cm^{-1} : C-O group (carboxylic acid)
1315.45 cm^{-1} : NO₂ group (nitro)
1631.78 cm^{-1} : C=N group (amide compounds)
1743.65 cm^{-1} : C=O group (ketone carbonyl)
2333.87 cm^{-1} : -CO- group (aldehyde)
3005.10 cm^{-1} : N-H group (amine)

Fig.4. FTIR Spectrophotometry Results for Used Adsorbent

From the both graphs in Fig 2. and 3, it can be seen that the activation process did not change the frame structure of the adsorbent, which is characterized by the absence of change in the fraction angle of the both graphs. Moreover, it can be seen that the nitric on the neutral adsorbent was replaced by silica compounds. Si-O group and silanol acts to adsorb colors, free fatty acids, organic substances, and other polar compounds such as peroxide [23].

For the difference in activated adsorbent and used adsorbent, it can be seen that there are several functional groups bound by the adsorbent after contacting. In the wavelength of 1103.28 cm^{-1} there is C-O bond which is esters. In the wavelength of 1161.15 cm^{-1} there is C-O bond carboxylic acid compound. Wavelength 1631.78 and 1743.65 cm^{-1}

correspond to C = C and C = O bonds which respectively were ketone carbonyl and ketones. In the wavelength of 2333.87 cm^{-1} there is a -CO- bond that is aldehydes. In the wavelength of 3726.47 cm^{-1} there is O-H bond which is alcohol compounds.

Orange pigment in palm oil is caused by carotene, unsaturated hydrocarbon compounds [24]. From the results obtained, adsorbent adsorbed ester, aldehydes, and ketones groups, which are the main cause of the turbidity of oil.

Therefore it can be concluded that the adsorbent from activated tamarind seeds can adsorb color in CPO.

3.3. Effect of Adsorbent Dose and Contact Time on Color in CPO

The initial color value in CPO is 9.9/20 (red/yellow), after being contacted with adsorbent is given in Table 2. and can also be graphed in Figure 5 and 6 below.

Table 2. Color in CPO after Adsorption (Red/Yellow)

Adsorbent Dose (%)	Time (minutes)		
	25	35	45
0.5	7.9/18	6.8/18	6.5/18
1.0	7.0/18	6.2/18	6.5/18
1.5	6.9/18	5.9/18	6.3/18

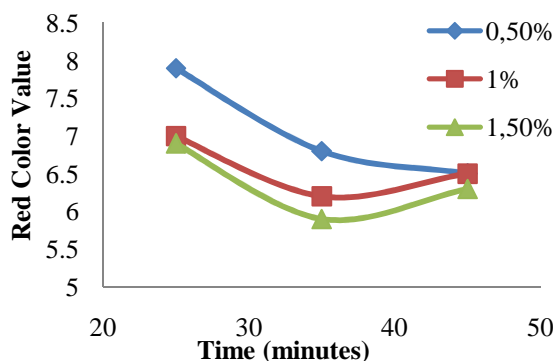


Fig.5. Effect of Contact Time on Red Color in CPO for Certain Dose of Adsorbent

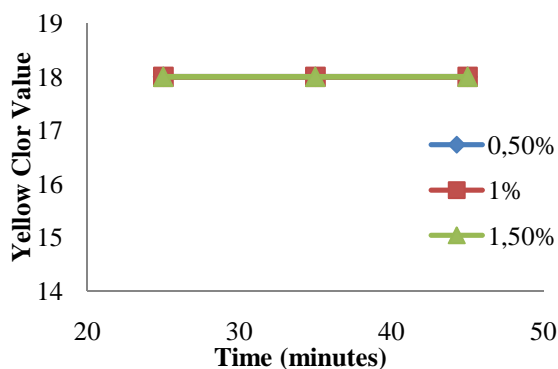


Fig.6. Effect of Contact Time on Yellow Color in CPO for Certain Dose of Adsorbent

From Fig. 5. it can be seen that at the same contact time, either 25 and 35 minutes, it decreased red color value along with the increasing of adsorbent dose. While at 45 minutes, red color value was similar along with the increasing adsorbent dose from 0.5 to 1.0%, and decreased at 1.5% adsorbent dose. These may be happened due to several possibilities. Firstly, the adsorbent could not adsorb more of the red color because the entire pore surface has been covered by impurities and color-causing compounds. Secondly, the difficulty of controlling the reaction temperature so that the adsorption process occurred was not optimal.

From Fig. 6, the graph gave a straight line for each variable, which indicates that for every variation of contact time and adsorbent dosage, yellow color did not happen to degrade. Yellow color experienced a similar degradation from 20 to 18 for each condition and could not be downgraded again. These may happened due to several possibilities. Firstly, the adsorbent could not adsorb more of the yellow color because the entire pore surface has been covered by impurities and color-causing compounds. Secondly, adsorbent was less specific to adsorb yellow color in palm oil.

Acid-activated adsorbent removes colors more efficiently compared to neutral adsorbent [25]. Color of the CPO will continue to decrease with the increasing of adsorbent dose. At high dose of adsorbent, color tends to decrease due to the adsorption of carotene content that will happen more effectively on the deodorization stage with vacuum distillation process [26].

There is no specific standard for color of CPO after bleaching, but the color standard for CPO is reddish orange, and the color standard for RBDP (Refined Bleached Deodorized Palm) Olein or CPO that has been through rafination and fractionation stages is 5.0/50 (red/yellow) [27]. In palm oil rafination industry, the red color of CPO has declined by 2 Lovibond units using 1.74% of bleaching earth dose and 0.05% of phosphoric acid dose and 30 minutes of contact time.

Based on the results, adsorbent gave more effect to the removal of red color in CPO than to yellow color. The best removal was 5.9/18 (red/yellow) and obtained at 35 minutes of contact time and 1.5% of adsorbent dose, while the second best result was 6.2/18 (red/yellow) and obtained at 35 minutes of contact time and 1.0% of adsorbent dose which did not provide a significant difference. By the economic considerations, dose of 1.0% at 35 minutes of contact time is selected as the best condition for the color

adsorption of CPO. The removal was 3.7 unit (red) or 37.37% and 2 unit (yellow) or 10%.

4. CONCLUSIONS

The conclusions drawn from this study are :

- The highest iodine number of the adsorbent is 511.17 mg/g and was obtained at the ratio of adsorbent : nitric acid of 1:2 (w:v) and at the oven temperature of 130 °C.
- From the characterization of adsorbent using FTIR spectrophotometry, it can be concluded that the activated adsorbent contained Si-O and Si-OH bond that would act to adsorb color-causing compounds in CPO, while the used adsorbent contained ester, aldehydes, and ketones groups.
- The best removals are 3.7 unit (red) or 37.37% and 2 unit (yellow), and was obtained at 1.0% of adsorbent dose and 35 minutes of contact time. The result is close to the Indonesian National Standard (SNI) for color in palm edible oil, which is 5,0/50 (red/yellow).

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