

Rubber Fruit Shell (*Hevea brasiliensis*) as bio sorbent to remove FFA (Free Fatty Acid) content in CPO (Crude Palm Oil)

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Abstract. This study aimed to discover the effectiveness of the shell of rubber fruit as bio sorbent for removing FFA (Free Fatty Acid) content in CPO (Crude Palm Oil). Methods used in this study were pretreatment, activation (carbonating and chemically) and adsorption process at room temperature. In the beginning, the shell of rubber fruit was cleaned and dried under the sun. Then the shell was cut for about 0.5 cm of length and carbonated in a furnace for 1h at 600°C. After that, they were crushed to pass through 140 meshes and activated using three variations of chemical such as 6 of HNO₃, 6N of KOH and 6N of H₃PO₄ at certain ratio as 1:3, 1:4, and 1:5 (b/v). The adsorption process was carried out using bio sorbent with the highest iodine number in varying bio sorbent dosage and contact time. The highest iodine number was 913.680 mg/g and obtained at the ratio of bio sorbent to 6N of KOH as 1:5. The best removal of FFA content was 91.94% and at 1% bio sorbent dose and 30 min of contact time.

1. Introduction

Rubber plantation is one of a plantation which is well developing in agriculture in Indonesia. Physically the shell of rubber fruit (*Hevea brasiliensis*) is known as a plant with lignin contained. According are Zakaria *et al* (2015) [1], the shell of rubber fruit contains active compound which is lignin. The use of the shell of rubber fruit is not optimal yet although its content of lignin is relatively (35% - 54%) [1] Therefore it is potential to become an activated carbon product, namely bio sorbent. Several studies have been conduct that used part of a rubber tree, such as the powder of rubber wood sewed to diminish chromium (VI) content in a solution and the leaf of rubber plant to minimize cup rum ion using sodium hydroxide in solution [1].

The initial stage of CPO (Crude Palm Oil) rafi-nation is the removal of gum (degumming) followed by bleaching, deodorization and fractionation [2]. Conventionally, degumming is the flock's formation of substance that is colloidal in crude oil. Crude Palm Oil contains FFA (Free Fatty Acid) which has to be diminishing in a purification process. Free Fatty Acid is an acid which is liberate in fat hydrolysis by an enzyme. The disadvantage of the FFA presence in CPO is it will affect the oil stability so then the further process in CPO treatment. For example to produce biodiesel, if the FFA content more than 1% it will become soap instead of methyl ester [3]. Based on the preceding, the bio sorbent from the



shell of rubber fruit must be attempted to be applied as an alternative bio sorbent to diminish FFA content in CPO.

2. Material and Method

2.1 Material

The main materials were the shell of rubber fruit and crude palm oil that were obtain from the neighborhood around the University of Sumatera Utara. Potassium hydroxide, phosphate acid, and nitric acid were use in bio sorbent activation. Phenolphthalein, ethanol, and potassium hydroxide were used for analysis purpose.

2.2 Bio Sorbent Activation

The shell of rubber fruit was washed with water and dried in the sunlight. They were cutting in 0.5 cm long in average and then they were carbonated in a furnace for 1 hour at 600°C. After that, they were crushed to powder form and passed through 140 meshes. Bio sorbent was activateing with a solution of 6 N H₃PO₄. Other solutions for activating use were 6 N KOH and 6 N HNO₃. It was follow by washing several times with distilled water to remove the activating solution. The procedure was repeate for the ratio of bio sorbent: solution of 1:3, 1:4 and 1:5 (m/v).

2.3 Analysis of Iodine Number

Iodine number shows the unsaturated fatty acid composed of oil and fat. The unsaturated fatty acid can bind iodine and creates a saturated compound. Iodine number is stated as the number of iodin compound which is bound by 100 grams of oil or fat.

3. Results and Discussion

3.1 Effect of Type of Activating Solution and Ratio of Bio Sorbent to Iodine Number

Before and after activation, an iodine number of the bio sorbent was analyzed. The iodine number before activation was 545.799 mg/g, while the iodine numbers after activation were given in table 1 below:

Table 1. Iodine number of bio sorbent for any condition of activation at 600°C.

Kind of Solution	Ratio Bio sorbent: Solution (m/v)	Iodine Number (mg/g)
6 N KOH	1: 3	744.887
	1: 4	736.134
	1: 5	913.680
6 N H ₃ PO ₄	1: 3	825.045
	1: 4	672.729
	1: 5	725.928
6 N HNO ₃	1: 3	431.562
	1: 4	431.562
	1: 5	482.334

From table 1, that irregularity occurred. It is maybe due to a water content of the after-water bio sorbent cannot be controlled. In general, it is shown that KOH as activating solution is more effective compared with H₃PO₄ and HNO₃. KOH is a strong base solution, therefore it is more affecting the active pore information. Furthermore the increase of the ratio of bio sorbent to activating solution fond increases the iodine number. A very *low* concentration of activator may cause the in complete formation of the active sites where as a very high ratio of activator may cause damage to the structure of the bio sorbent [4]. By comparing theory and result obtained from the research, it can be concluded

that the most favorable conditions to produce the bio sorbent from the shell of rubber fruit with the highest iodine number are the ratio of bio sorbent: potassium hydroxide of the 1:5 at 600°C.

According to SNI-06-3730-1995, the resulting bio sorbent is already qualified as activated carbon. It is seen from iodine number 913.68 mg / g, vapor content 2.64%, ash content 9.88% and water content 14.77%. Where the requirements given by SNI in the table below:

Table 2. Standard of activated carbon from SNI.

Requirements	Content
Iodine Number	> 750 mg/g
Vapor Content	< 25%
Ash Content	<10%
Water Content	<15%

Bio sorbent characterization using FTIR Spectrophotometry the characterization was conducted fix bio sorbent before and after the activation, and after used in the adsorption process. Functional groups on bio sorbent can be inferred by comparing result on the graph with literature or IR correlation [6]. The graphs are in figure 1, 2 and 3.

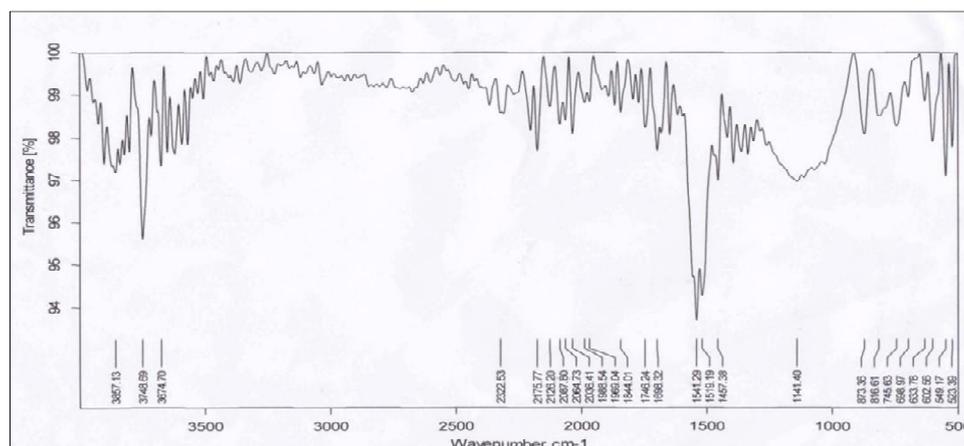


Figure 1. FTIR spectrophotometry result for bio sorbent before activation.

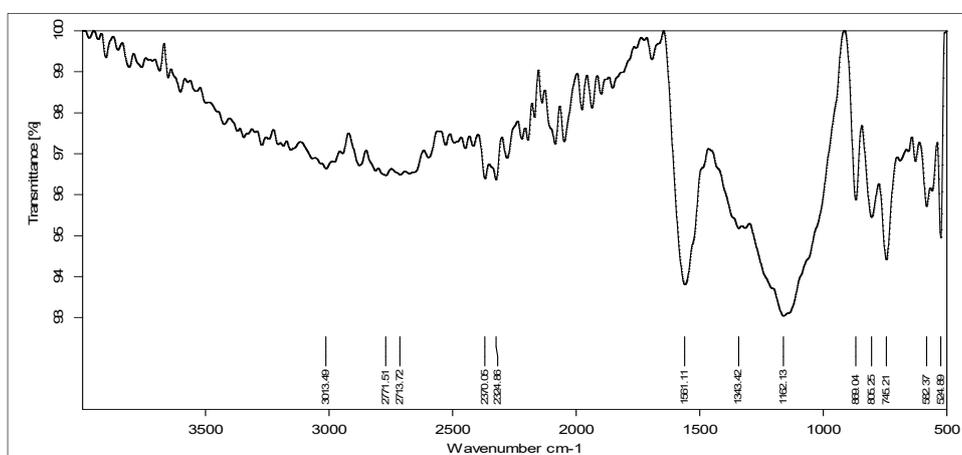


Figure 2. FTIR spectrophotometry result for bio sorbent after activation.

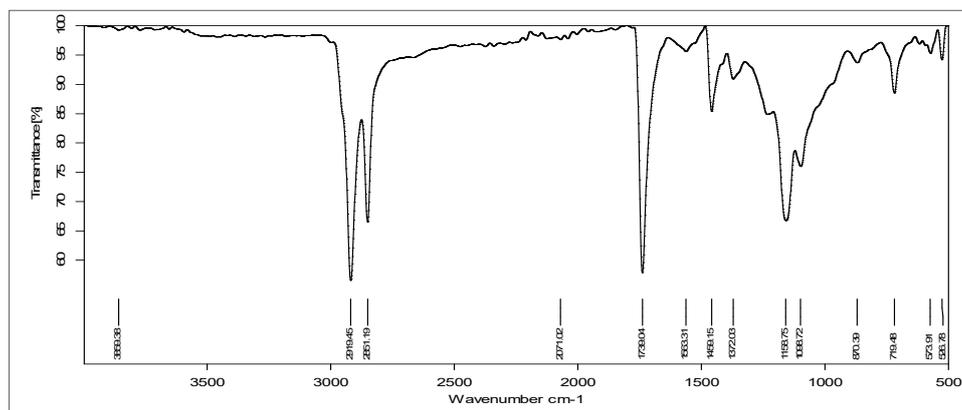


Figure 3. FTIR spectrophotometry result for used bio sorbent.

3.2 Effect of Bio Sorbent Dose and Contact Time on FFA Content in CPO

The initial FFA content in CPO used was 2.48%, while the FFA content in CPO after being contacted with bio sorbent is given in table 3 and can also in figure 4.

Table 3. FFA content in CPO after adsorption (%).

Dose of Bio sorbent (%)	Time (minutes)		
	30	40	50
0.5	1.037	0.259	0.332
1.0	0.200	0.360	0.460
1.5	0.590	0.920	0.860

3.3 Characteristics of Functional Group on Bio Sorbent from the Shell of a Rubber Fruit with FTIR Spectrophotometry

Bio sorbent before and after activation and bio sorbent that has been used for adsorption of impurity contents on CPO subsequently characterized its functional groups by FTIR spectrophotometry. The groups present in the bio sorbent can be summarized by comparing the wave peaks formed with the literature, which is from the IR correlation table [5]. From figures 1 and two can be compared to the functional groups present in the bio sorbent, before and after activation. The bio sorbent before to activation contains an alkene group, an aromatic carbon ring compound, a carbon dioxide, an -OH group of alcohols, a nitro compound, an alkyne and an alkane. After activation, there is no more alkyne in the bio sorbent. Activating agent (KOH) will oxidize carbon and damage the inner surface of the carbon. Then there may be the possibility of loosening of the carbon double bond in the bio sorbent after it is activated. The content of the hydroxyl -OH group in the rubber shell tends to interact with adsorbate [6].

Alkanol or alcohol groups affect the bio sorbent, free fatty acids, peroxides, and polar organic substances. KOH will react with carbon so that it will form new pores and produce carbon dioxide that diffuses to the carbon surface, where the activating agent (KOH) will oxidize the carbon and damage the inner surface of the carbon so that pore will be formed and increase adsorption [7]. In bio sorbents that have been contact with CPO, there are several functional groups bound by bio sorbents after contacting. At the wave number 2919.45 cm^{-1} , there is a C-O group of carboxylic acid which is an indication of free fatty acid compound. In the wave number 3859.38 cm^{-1} there is -OH group which is an indication of the attached polar peroxide compound HOOH. Aldehydes are compounds that cause turbidity and rancid odor or rancid in oil. In the wave number 1739.04 cm^{-1} , there is an ester group. The amine and nitro compounds present in the bio sorbent, both before and after activation, and after contact with CPO, are most likely to be obtained from rubber shells from soil and crop fertilizers.

The major fat or oil damage is due to oxidation and hydrolytic events, both enzymatic and non enzymatic. Damage to palm oil causes rancid or rancid odors mainly caused by aldehydes and ketones [3]. From the results of IR spectrophotometry, it can be concluded that the bio sorbent from the shell of the rubber fruit can adsorb the carboxylic acid content in the form of free fatty acids, peroxide compounds, and aldehydes from palm oil.

3.4 Adsorption of Free Fatty Acid Content (FFA) in CPO

From this study can be seen the decrease in free fatty acid (FFA) in the optimum CPO of various variations of contact time and a dose of bio sorbent. At 40 minutes with the addition of 1%, bio sorbent dose resulted in the greatest decrease in FFA levels. The results in the graph in the following figure.

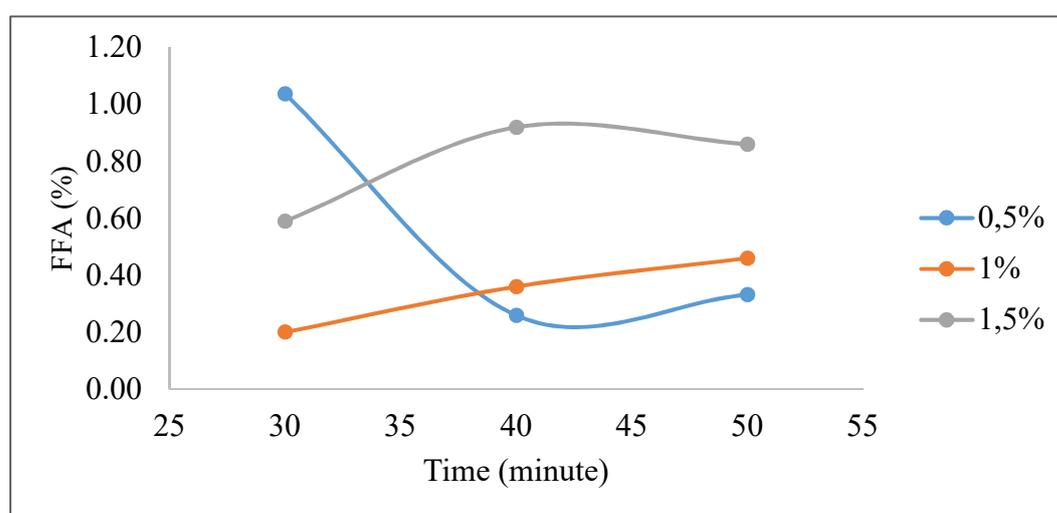


Figure 4. Graph of decreasing fatty acid content (FFA) of oil palm at a specific time.

The initial free fatty acid content in palm oil was 2.48%. For the addition of a dose of 0.5 mg of rubber shell bio sorbent in the oil at 30 minutes, the fatty acid content in the oil decreased to 1.037%. At 40 minutes the free fatty acid content in the oil drops to 0.259%. And at 50 minutes the levels of free fatty acids in the oil increased to 0.332%. Furthermore, for the addition of the dosage of the bio sorbent of the rubber shell of 1.0% in the oil at 30 minutes, the free fatty acid content in the oil decreased to 0.20%. At 40 minutes the free fatty acids content in the oil increased to 0.36%. And at 50 minutes the levels of free fatty acids in the oil increased to 0.46%. Then for the addition of dosage of the bio sorbent of the shell of the rubber fruits by 1.5% in the oil at 30 minutes, the fatty acid content in the oil decreased to 0.59%. At 40 minutes the free fatty acid content in the oil increased to 0.92%. And at 50 minutes the levels of free fatty acids in the oil decreased again to 0.86%. According to Puah *et al.* [3], the best-activated dose of the bio sorbent to remove the undesirable content of CPO is > 0.5%. The standard fatty acid content of CPO adsorption using degumming agent and bleaching earth is 3 - 5% [8]. In the palm oil refining industry using conventional degumming agent (85% phosphoric acid) with a dose of 1% by weight of oil, free fatty acid content increased from 5% to 5.05%. The FFA concentration at the 0.5% bio sorbent dose decreased by 40 minutes and increased at 50. Also, at 1% and 1.5% of the free fatty acid doses increased by 30 to 50 minutes.

This may be due to the longer contact time of palm oil with bio sorbents resulting in longer oil interacting with the heat that triggers the formation of free fatty acids. From the results of the research, the utilization of the activated rubber shell activator with potassium hydroxide with a ratio of (b: v) 1: 5 with a dose of addition of bio sorbent to oil of 1.0% of the weight of the oil with contact time for 30 minutes yielded decrease in free fatty acid content is greatest from 2.48% to 0.20. Therefore, given the

economic consideration of the amount of bio sorbent used, a dosage of 1.0% was selected as the best dose for the adsorption of free fatty acid content in palm oil and has met the standard free fatty acid content in palm oil after adsorption. The percentage decrease of FFA content is 91.93%.

4. Conclusion

The iodine number of the rubber shell of 913.680 mg/ g is obtained from activation at 600°C using 6N KOH with bio sorbent ratio: KOH is 1: 5. The minimum Free Fatty Acid content obtained was 0.20% with a decreasing percentage of 91.94%, at a dosage of 1% bio sorbent and a contact time of 30 minutes.

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