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The Application of Pineapple Peel Derived-Adsorbent to Decrease FFA in Crude Palm Oil (CPO)

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Abstract:
Low FFA content in Crude Palm Oil (CPO) is preferred as it is one of some parameters for hydrolysis of oil has taken place. This research aims to produce decrease FFA content of CPO using adsorbent derived from pineapple peel waste. This research uses a research design with variations in heating time and temperature in the CPO adsorption process with the following variations: 30°C for 15 minutes; 40°C for 30 minutes, 50°C 45 minutes, 60°C for 60 minutes, and 70°C for 75 minutes. The result shows that activated carbon from pineapple peel with an activation time of 30 minutes has the characteristics of a water content of 3.21 %, ash content of 6.95%, iodine absorption capacity of 417.60 mg/g. the SEM-EDX images shows an open and even pore structure. The water content and ash content have met Indonesian National Standards, but not the iodine absorption capacity. During adsorption for 75 minutes at 70°C the FFA level drops to 4.60 %, which is an efficient time to reduce FFA levels. Meanwhile, the decrease in β -Carotene to 25.29 ppm.

Keywords: Pineapple Peel, Free Fatty Acid, Adsorbent, Crude Palm Oil (CPO)

1. Introduction

Pineapple waste is an organic material that contains lignocellulose, found in components such as leaves, stems, crowns, and peel. Lignocellulosic compounds are complex and consist of cellulose, hemicellulose, and lignin. Pineapple peel has good nutritional value, comprising 88.95% dry matter, 3.83% ash, 27.09% crude fiber, 8.78% crude protein, and 1.15% crude fat (Ibrahim, 2015). According to Joy (2010), pineapple peel contains calcium (16 mg), energy (52 calories), carbohydrates (13.7 g), fiber (1.4 g), iron (0.2 mg), magnesium (12 mg), protein (0.54 g), phosphorus (11 mg), potassium (150 mg), vitamin A, vitamin B1 (0.08 mg), vitamin B2 (0.03 mg), vitamin B3 (0.49 mg), vitamin B6 (0.11 mg), vitamin C (0.10 mg), and zinc (0.10 mg). Pineapple peel also contains calcium, potassium, fiber, and vitamin C. According to Mejia (2005), pineapple plants are classified under the kingdom Plantae, order Poales, family Bromeliaceae, genus Ananas, and species A. comosus.

According to Chaokaur et al. (2009), pineapple peel contains 23.39% cellulose, 42.72% hemicellulose, and 4.03% lignin. These components give pineapple peel the potential to act as a natural adsorbent. Activated carbon is carbon that has undergone an activation process, either physically or chemically, which opens the carbon pores and increases its surface area. This activation process depends on factors such as temperature, activator, and activation time.

Activated carbon is an amorphous solid with many pores and a large surface area. It is typically produced from carbon-containing materials by heating them to high temperatures. Various raw materials have been used to develop activated carbon, including coconut shells, various types of wood and bamboo, coal, and other materials with high carbon content (Miranti, 2012). The production of activated carbon involves two stages: carbonization and activation. Activated carbon is commonly used in households for water purification, color removal, and odor absorption. In industrial applications, it is used in wastewater treatment processes to reduce heavy metal levels, purify oil, and refine materials, among other uses.

Crude palm oil (CPO) contains by-products such as free fatty acids, phosphates, pigments, odors, and water. The quality of palm oil can be improved by removing these impurities. One key quality parameter for palm oil is its free fatty acid content (Widyanto, 2014). High levels of free fatty acids are undesirable in CPO and must be reduced before the oil is sold or processed into industrial products. One effective method for reducing free fatty acid levels in CPO is adsorption. NaOH is a chemical activator used in the production of activated charcoal and activated carbon, enhancing their porosity and adsorption capacity. Several studies have investigated the impact of NaOH concentration on the quality of activated charcoal and activated carbon. For instance, research indicates that a 1 N NaOH concentration yields optimal results in the production of activated charcoal (Zuliani et al., 2015). Another study found that a NaOH concentration of 0.3 M produces the best characteristics for peanut shell activated carbon as a phosphate adsorbent in laundry waste. The aim of this research was to process pineapple peel waste into adsorbent, to determine its characteristics and to assess the adsorption capacity of the adsorbents.

2. Research Methods

Material

The research was carried out using the fresh pineapple peel obtained from pineapple farm in Tangkit, Jambi Province. The other materials used include Crude Palm Oil (CPO), NaOH, distilled water, 5% wt HCl, 0.1N Iodine Solution, 0.1N Sodium Thiosulfate Solution, starch indicator, and 0.1N KOH. The equipment used includes furnace, magnetic stirrer, vertical reactor, funnel Buchner, horizontal reactor, autoclave, vacuum pump, and 100 mesh sieves.

Method

The research method used in this experiment is summarized in Table 1. The pineapples were sorted, only those that are ripe and yellow in color were used. The pineapple peel waste is chopped into small pieces, washed with running water, dried in the sun for ± 3 days and continued with the drying process using an oven for 30 minutes at a temperature of 105°C. The sample should be dry and easily brittle when handled.

Table 1. Research method

Raw material	Activation Time (Minute)	Reactor Temperature (°C)	Adsorption Time (Minute)	Adsorption Temperature (°C)
Pineapple Peel	30	300	15	30
			30	40
			45	50
			60	60
			75	70

Research Procedures

Carbonation

The pineapple peel sample (100 g) was placed in the reactor which was put down in the furnace for the carbonation process at a temperature of 300°C for 1 hour. The product of the carbonation process were cooled to room temperature, grinded using a chopper and then sifted using a 100 mesh sieves.

Carbon Activation

The activation carried out in this research was chemical activation using the NaOH. First, weigh 2 grams of pineapple peel carbon and soak it in 20 ml of NaOH solution with a concentration of 1M (1:10 ratio) for 30 minutes. Next, the sample was stirred using a magnetic stirrer on a hot plate for 1 hour to make it homogeneous. The activated carbon was further washed using distilled water until a neutral pH was obtained from the washing liquid. Finally the activated carbon was dried using an oven at 105°C for 12 hours.

Adsorption of Crude Palm Oil (CPO)

The adsorption process was carried out in a glass beaker with a weight ratio of activated carbon and CPO = 1:50. The mixture was heated using a hot plate for several adsorption times and temperatures: 30°C for 15 minutes; 40°C for 30 minutes, 50°C 45 minutes, 60°C for 60 minutes, and 70°C for 75 minutes. The mixture was homogenized using an electric motor at a speed of 120 rpm. After that, the mixture was filtered using filter paper and ready for analysis.

Water and Ash Content of Adsorbent

The water and ash content of adsorbent was analyzed using gravimetric analysis (AOAC, 2006).

Iodine Test (American Society for Testing and Materials, 2011)

1 gram of activated carbon was weighed, transferred into a 250 mL Erlenmeyer flask. 10 mL of 5% wt HCl solution was added to the erlenmeyer. The erlenmeyer flask was closed and heated on a hotplate until it boils for 30 seconds, then let it sit until it reached room temperature. 100 mL of 0.1N Iodine solution was pipetted into the flask. The flask was shaken for 30 seconds and filtered using filter paper. 50 mL of the filtrate was transferred to a 250 mL Erlenmeyer flask and titrated using 0.1N Sodium Thiosulfate solution until the filtrate color was pale yellow. 2 mL of starch indicator solution was added while the titration was continued until the color of the filtrate solution was colorless. The volume of Sodium Thiosulfate was recorded for calculation of Iodine absorption capacity.

SEM-EDX (Septiano et al., 2021)

Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) is a tool that can be used for quantitative and qualitative analysis of elements based on the spectral analysis of the characteristic SEM. SEM is a type of electron microscope that uses electron beams to image the surface profile of a sample. The work of the SEM itself is that the surface of the sample that is hit by the beam reflects the beam back or produces secondary electrons. Then the detector in the SEM will detect the reflected electrons. The sample surface area hit by the beam is scanned throughout the observation area. EDX is an analytical technique used to analyze and chemically characterize a sample. Measurement of chemical elements by EDX is carried out by analyzing X-ray light emissions from samples resulting from moving electrons.

Free Fatty Acid (ALB) (Kafiar et al., 2010)

Analysis of free fatty acids (FFA) in Crude Palm Oil (CPO) oil was carried out using the acid base titration method, namely first 3 grams of CPO was placed into an Erlenmeyer and then added 50 ml of 96% ethanol into the Erlenmeyer. The sample was heated on a hotplate for 10 minutes at 50°C while stirring until homogeneous. The sample is added with 2-3 drops of phenolphthalein indicator, titrated with 0.1 N KOH until it changes color. The volume of KOH solution used was recorded and then the free fatty acid content was calculated. Free fatty acid levels are calculated using the equation below.

$$FFA\ (\%) = \frac{volume\ titran\ x\ normality\ x\ MW\ CPO}{sample\ weight\ x\ 1000}\ x\ 100\%$$

Beta Carotene (Harahap et al., 2020)

One way to analyze beta carotene is by using the UV-Vis spectrophotometry method. UV-Vis spectrophotometry is an analysis method based on visible light using an ultraviolet electromagnetic radiation source using a spectrophotometer instrument.

3. Results and Discussion

The Characteristics of the Adsorbent

Determination of water content aims to determine the water content in the cavities or pores in the activated carbon of pineapple peel, indicated by the high and low levels of water content in the activated carbon. Low water content shows that there are many cavities and pores that can be occupied by adsorbate. Water content plays a very important role in the quality of the activated carbon produced, because the lower the water content obtained, the better the quality of the activated carbon produced (Deglas & Fransiska, 2020).

Table 2 shows that the water content of activated carbon with 1M NaOH activation is lower than carbon without activation. This is influenced by the higher concentration of the NaOH activator leading a more alkaline activated carbon which need more water was needed for the neutralization process. In other words, more water was trapped in the activated carbon pores as neutralization took a longer time. From the results obtained, activated carbon that has been activated by NaOH still has a lower water content compared to activated carbon without activation because one of the activator's functions is as a dehydrating agent. Likewise, if we refer to the active carbon quality standards set by SNI 06-3730-1995 (Table 2), the water content of the activated carbon produced from this research is in accordance with quality standard requirements based on the SNI standards obtained.

Table 2. The characteristics of pineapple peel derived-adsorbent

Parameter	Unit	Test results		Standard	
		carbon without activation	activated carbon	SNI 06-3730-1995	ASTM D4607-94
Water content	%	5.22	3.21	>15	-
Ash Content	%	15.13	6.95	<10	-
Iodine Adsorption Capacity	Mg/g	336,618	417.60	>750	600-1450

Determination of ash content aims to see the amount of metal oxide content consisting of minerals in a material or carbon that can evaporate during ashing. The quality of the ash content will affect the quality of the activated carbon, where if the ash content in an activated carbon is high, the quality of the active carbon will be lower.

Based on SNI 06-3730-1995 standards, the ash content of the activated carbon adsorbent produced from this research meets SNI standards, namely a maximum of 10%. However, the ash content contained in the carbon adsorbent without activation is still high. The minerals may block the pores of adsorbent leading it difficult to adsorb the adsorbate.

Determination of iodine adsorption capacity aims to determine the ability of activated carbon to adsorb adsorbate. Higher iodine adsorption value denotes a better adsorption capacity of the adsorbent. The iodine adsorption can be used as an approach to determine the surface area and pores of adsorbent with good precision (Turmuzi et al., 2015). Based on Table 2 above, it shows that the activation affects the iodine adsorption capacity. The iodine adsorption capacity of the adsorbent produced in current study is still do not meet SNI 06-3730-1995 implies a low quality of adsorbent (Rajagukguk, 2018).

SEM Image

The SEM image was used to observe the morphological form of adsorbent, while EDX was carried out to observe what elements are contained in the adsorbent. SEM -EDX characterization was carried out on 2 samples, namely pineapple peel carbon and pineapple peel activated carbon. The SEM images of the adsorbent at magnification of 10,000 times are presented in Figure 1.

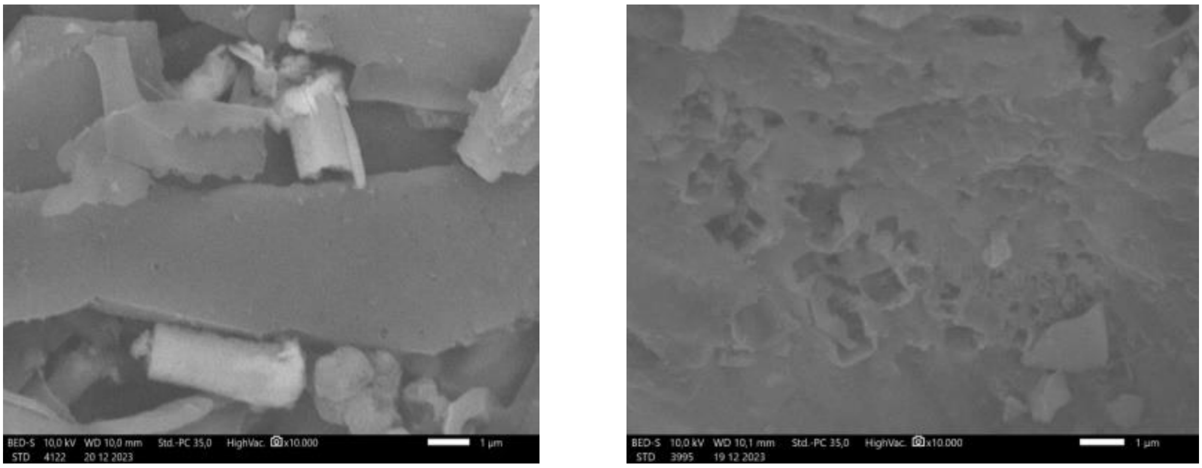

Figure 1 . SEM images of pineapple peel derived adsorbent: without activation (left) and with activation (right)

Figure 1 shows the differences in pore structure between carbon without activation and carbon activated by 1M NaOH. It can be seen that the carbon has a rod shape, while activated carbon has open pores or an expanded surface. This shows that the activator can open pores and expand the pore surface. The surface area of activated carbon is determined by the size of its pores. The smaller pore size of activated carbon will result in a larger surface area, so that the speed and capacity of the adsorption process will increase. The effect of concentration on pore surface area depends on the carbonation temperature, the ratio between the activator and the carbon to be activated and the length of time the carbon is soaked in the activator. Pore formation occurs due to erosion due to the reaction of the carbon surface with the activating agent.

Free Fatty Acid Levels (FFA)

The quality of palm oil as a food ingredient has quality aspects related to free fatty acid content parameters. High levels of free fatty acids will cause a decrease in the quality of CPO, for example causing rancidity in the oil, causing an unpleasant taste, changes in color and also a decrease in oil yield.
A good free fatty acid content based on SNI standards is <5%. Analysis of free fatty acid levels in this study used the acid-base titration method. Determination of Free Fatty Acid levels is based on the color change that occurs in the sample, known as the end point of the titration. Free fatty acid content is the percentage of free fatty acids contained in CPO that are neutralized by NaOH. The results of FFA levels obtained after CPO was adsorbed using pineapple peel activated carbon can be seen in Table 3.

Table 3. FFA levels in CPO after treatment with pineapple peel derived adsorbent

Time (minutes)	Temperature (°C)	FFA Level (%)
15	30	5.90 ± 0.00
30	40	5.50 ± 0.14
45	50	4.90 ± 0.00
60	60	4.78 ± 0.00
75	70	4.60 ± 0.04

Based on Table 3, it can be seen that samples treated using condition 50°C 45 minutes, 60°C for 60 minutes, and 70°C for 75 minutes were effective in reducing FFA levels in CPO which meet the free fatty acid standard, namely below 5%. Basically, the longer the adsorption and stirring time, the lower the FFA content after the adsorption process. Sufficient contact time is required to reach adsorption equilibrium. If the liquid phase containing the adsorbent is in a stationary state, the adsorbate diffusion through the adsorbent surface will be slow, so stirring is needed to speed up adsorption (Sulistyo et al., 2016).

β-Carotene

Beta carotene is one of the ingredients found in CPO. One of the ingredients contained in CPO is Beta carotene. Beta carotene is included in one of the carotenoid product. It is provitamin A which can be converted in the body into active vitamin A after undergoing metabolism (Stutz et al., 2015).

The principle of the UV Vis spectrophotometer is one of absorption of visible light for ultraviolet light with a molecular temperature which can result in the excitation of molecules from a low energy level to a higher energy level. A UV Vis spectrophotometer can be used to measure light absorption in the UV region with wavelengths in the range 100-200 nm and visible light in the 200-700 nm region. β-Carotene content in CPO before and after adsorption using pineapple peel derived adsorbent as shown in Table 4 shows that the adsorbent significantly reduced β-Carotene in CPO. The decrease in β-Carotene should be a concern despite its ability to decrease FFA. This information is important for designing the experiment to optimize the time and temperature for the adsorption using pineapple peel derived -adsorbent to obtain the highest possible β-Carotene content and lowest possible FFA content in CPO.

Table 4 . β-Carotene content in CPO before (sample A) and after adsorption (sample B to F)

Sample	Adsorption Time (minutes)	Adsorption Temperature (°C)	Absorbance Value (300nm)	β-Carotene concentration (ppm)
A	0	0	0.480	64.13
B	15	30	0.381	49.78
C	30	40	0.344	44.42
D	45	50	0.307	39.06
E	60	60	0.293	37.03
F	75	70	0.212	25.29

Conclusion

Based on research on pineapple peel, it can be concluded that pineapple peel has the potential to be an adsorbent with good results. Activated carbon from pineapple peel with an activation time of 30 minutes has the characteristics of a water content of 3.21 %, ash content of 6.95%, iodine absorption capacity of 417.60 mg/g, and SEM-EDX analysis has an open and even pore structure. The water content and ash content meet Indonesian National Standards, while the iodine absorption capacity does not meet SNI quality standards. At a contact time of 75 minutes with a temperature of 75℃ the FFA level drops to 4.60 %, which is an efficient time to reduce FFA levels. Meanwhile, the decrease in β-Carotene which occurred in 75 minutes at a temperature of 70℃ resulted in an absorbance of 25.29 ppm.

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