Utilization of Cocoa Peel as Biosorbent for Oil and Color Removal in Palm Oil Mill Effluent (POME)

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Abstract. The aim of this study is to discover the effectiveness of cocoa peel as biosorbents for oil and color removal in POME. This study used biosorbent from cocoa peel with variation of particle size which passed through 70 mesh, 100 mesh, and 120 mesh and was activated with the ratio of biosorbent and 0.6 M HNO₃ of 1:2, 1:4, and 1:6 (m/v). The adsorption process was carried out using biosorbent with the highest iodine number in varying biosorbent mass and contact time. The highest iodine number was 596.684 mg/g and obtained at particle size 120 mesh and the ratio of biosorbent : HNO₃ as 1 : 4. The resulting biosorbents were analyzed for their characterization, such as vapor content, ash content, and volatile matter, including FT-IR and SEM-EDX. The POME were analyzed for their oil and color content, using gravimetric method and UV-Vis spectrophotometry. The best removal is were 80.88% for oil and 83.45% for color at 1.5 g biosorbent mass and 3 h contact time. The result for oil removal was close to the standard of Indonesian Environment Minister for oil in effluent. Also the adsorption of oil and color behaves as a pseudo-second-order kinetic models.

Keyword: Adsorption, cocoa peel, color, oil, POME (Palm Oil Mill Effluent)

1. Introduction

The needs for palm oil have increased, so it will be one of vegetable oils that has fastest growing every year. The capacity of the palm oil industry will increase too, including the waste, especially the Palm Oil Mill Effluent (POME). Generally, POME is not toxic, but it is a liquid waste which has high volume and an unpleasant odor. The organic content of POME will inhibit the transmission of light into the body of water, so that will be slowing down the process of photosynthesis and probably disrupt the food chain in the ecosystem. The oil content in POME can reach until 6000 mg/L [1]. The color of the POME is due to the presence of plant constituents, such as lignin and phenolic compounds and repolymerization of the color compound after anaerobic treatment [2]. Several ways have been done in POME treatment, such as aerated and facultative anaerobic biological processes, anaerobic biological processes and land applications system, biological processes of anaerobic tank-aeration advanced. However, this liquid waste treatment process takes about 120-140 days, require for large treatment area, high maintenance costs, and the generation of methane gas emissions into the air [3,4].

An alternative method that is quite effective and cheap has been much proposed by the use of biosorbents from agricultural waste and plantations that have high cellulose content. In Indonesia, cocoa fruit is one of the plantation commodities whose role is quite important. The only utilized parts are the seeds, but the skin was limited only for animal feed and raw materials fertilizer. Cocoa peel has a coarse texture, thick and hard. Cocoa peel weighs up to 75% of the total fruit weight. The content of cellulose in cocoa peel is about 23-54%, thus making it potentially biosorbent. Furthermore, the cocoa
peel also contains organic compounds such as protein 5.69-9.69%, fat 0.02-0.15%, glucose 1.16-3.92%, sucrose 0.02-0.18%, pectin 5.30-7.08%, crude fiber 33.19-39.45%. These compounds are polymers of carbon elements so that cocoa peel can be made as biosorbents that have high capasity [5]. Thus, the utilization of cocoa peel as a biosorbent can increase its economic value. Based on that description, the use of cocoa peel as a biosorbent is to be processed as an alternative treatment process.

2. Material and Method

2.1. Material
The main materials were the cocoa peel that were collected from the plantations in Medan and Palm Oil Mill Effluent (POME) from Palm Oil Mill in North Sumatera.

2.2. Preparation of the Biosorbent from cocoa peel
Cocoa peels were cutted in small pieces. They were washed with water and dried in oven at 80°C for 24 h. They were crushed to powder form and passed through 70 mesh. Biosorbent was acivated with a solution of 0.6 M HNO₃ at variation of ratio of biosorbent : HNO₃ of 1:2. It was followed by washing several times with distilled water to remove the activating solution. The procedure was repeat for the particle size which passed through 100 mesh and 120 mesh and the ratio of bio sorbent:nitric acid of 1:4 and 1:6 (m/v)

2.3 Batch Adsorption Process
Biosorbent (1 g, 1.5 g, 2 g) were poured into 50 mL of POME in a beaker glass and stirred at 200 rpm and pH 2 for 1, 2, 3, 4, and 5 h. Afterwards, POME was filtered with Whatman No. 1 filter paper.

2.4 Analysis of Oil and Color Residual
The oil residual was analyzed with gravimetric method. The color residual was analyzed with UV-Vis Spectrophotometer.

3. Results and Discussion

3.1 Effect of Particle Size and Ratio of Bio Sorbent : Nitric Acid to Iodine Number
Before and after activation, an iodine number of the bio sorbent was analyzed which were given in Figure 1 below.

![Figure 1](image-url)

**Figure 1.** Effect of Particle Size on Iodine Number for Certain Ratio of Biosorbent : Nitric Acid (b/v)

From the Figure 1, it can be seen that iodine number tend to increase by decreasing of the particle size for the same ratio of biosorbent : nitric acid (b/v) and by increasing the ratio of biosorbent : nitric acid (b/v) for the same particle size. However, the iodine number was decrease at the ratio 1:6 of
biosorbent : nitric acid (b/v). The surface of biosorbent increase by decreasing of the particle size, hence more percentage removal in the adsorption process. The active site formation depends by the concentration of the activator used. At the higher activator concentration, the larger amount of porous structure was produced by the stronger dehydration or condensation. But perhaps too much activator had blocked a part of macroporous, so the adsorption capacity decreased [6]. A very high volume of activator may eliminate active biosorbent properties due to the damage caused by dissolution and breakup of pores on the biosorbent [7]. The increasing of the iodine number until the ratio of biosorbent : HNO$_3$ of 1:4, showed that a very low volume of the activator may cause the active sites formation was incomplete. However, the iodine number deceased at the ratio of biosorbent : HNO$_3$ of 1:6. These can be happened because the volume of the activator was very high. It can be concluded that the particle size 120 mesh and the ratio of biosorbent : nitric acid (b/v) of 1:4 were the the most favorable conditions to produce the biosorbent from cocoa peel with the highest iodine number. According to SNI-06-3730-1995, the resulting bio sorbent is close to qualified as activated carbon. It is seen from iodine number 596,684 mg/g, 9.89% water content, 0.52% ash content, and 84% volatile matter content, Where the requirements given by SNI in the table below:

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

### 3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Bio sorbent characterization using FTIR Spectrophotometry 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 [8]. The graphs are in figure 2 below:

![Figure 2(a) FTIR Spectrophotometry Result for Biosorbent Before Activation](image1)

![Figure 2(b) FTIR Spectrophotometry Result for Activated Biosorbent](image2)
Based on Fig 2., the biosorbent before activation generated several peaks of wave numbers in each range of the region, such as -OH group (alcohol), C-H group (alkane), C=C group (alkenes), C-N group (amine), and C-O group (ester). However, after activation there is some wavelength and intensity of the functional groups changes. It may indicate a \( \text{HNO}_3 \) solution used as an activator that has been decomposed of the mineral salts present in the sample. Thus, the functional groups increasingly formed on the biosorbent, so that can increase the biosorbent capacity in adsorption process by forming the complex compound [9]. In Figure 2c. showed the biosorbent that has been contacted with POME there are several functional groups attached by the biosorbent after the adsorption. The presence of C=O group in the absorption of 1716.65 cm\(^{-1}\) is the cause of the cloudy appearance [7], and indicates the amount of oil which is the triglyceride. By comparing the result from the \( \text{HNO}_3 \) activated biosorbent and the used biosorbent, it shows the interaction between the biosorbent functional groups and the molecules present in POME. From the results of IR spectrophotometry, it can be concluded that the functional groups that play a role in oil and color removal in POME are hydroxyl, carbonyl, amine, nitro and alkoxy groups.

3.3 Results of Analysis Morphological Characteristics Biosorbent

![Figure 3(a) Morphology Analysis Report for Biosorbent Before Activation (Magnification 1000 times)](image1)

![Figure 3(b) Morphology Analysis Report for Activated Biosorbent (Magnification 1000 times)](image2)
Figure 3(c) Morphology Analysis Report for Used Biosorbent (Magnification 1000 times)

The figure 3., showed that the micropores of activated biosorbent are wider and clearer. The figure 3a and 3b showed that the activation process give a significant change of the surface morphology of the biosorbent. This is correspond with the purpose of activation that the activator can eliminated the impurity metals. Thus, the activated cocoa peel biosorbent with HNO₃ has higher capacity adsorption than the biosorbent without activation. Based on the result of SEM analysis on cocoa peel biosorbent before activation there are metal and mineral elements. The presence of these metals and minerals indicates that ash content is usually present in the biosorbent [10]. The SEM micrograph in fig 7. shows that the micropore structures of the biosorbent after being contacted with POME has been covered with muddy-line substances. These muddy-line substances perhaps are the components of adsorbate which is indicated by the decreasing color and oil content of POME. The presence of muddy-line substances proves that the components present in POME were adsorbed by the active group on the biosorbent.

3.4 Adsorption of Oil and Color in POME

![Graph showing effect of biosorbent mass on removal of oil percentage](image)

**Figure 4.** Effect of Biosorbent mass on Removal Oil Percentage for Certain Contact Time
Fig 4. shows the removal oil percentage in POME of initial concentration (2411 mg/L) after adsorption onto biosorbent at different biosorbent mass (1.0 g, 1.5 g, 2.0 g) and at different contact time (1, 2, 3, 4, and 5 h). The results showed that the removal oil percentage increases by increasing the contact time at the same mass of biosorbents. Likewise, the percentage removal of oil tended to increase by increasing the biosorbent mass at the same contact time. This is correspond with study which has been done by Ahmad, et al. [11], the adsorption of oil will increase since the biosorbent mass increases. However, the percentage removal of oil fluctuates at the contact time of 3 h and 5 h. The adsorption of oil on the condition of strong acid or low pH, can disrupt the oil layer to become unstable. Biosorbents may provoke the physicochemical properties of the oil layer, so that demulsification may occur, which will result in increasing small oil sizes which will increase the adsorption of the oil in solution [12]. At longer mixing times, the demulsification process is increasing. Damage to the oil layer (demulsification) will cause the contact surface area between the biosorbent and the oil to increase, thus increasing the adsorption of residual oil [11]. The discrepancy may be due to the uncontrollable oil content of POME at any initial adsorption condition.

![Figure 5. Effect of Biosorbent mass on Removal Color Percentage for Certain Contact Time](image)

Figure 5. Effect of Biosorbent mass on Removal Color Percentage for Certain Contact Time

Fig 5. shows the removal color percentage in POME of initial concentration (7340 mg/L) after adsorption onto biosorbent at different biosorbent mass (1.0 g, 1.5 g, 2.0 g) and at different contact time (1, 2, 3, 4, and 5 h). From Fig 4, it can be seen that there is an optimum time of each biosorbent mass used. It can prove that the active site contained in the biosorbent takes time to absorb adsorbate. According to Faisol, et al. [13], that the contact time can be as a test of the performance and endurance of the biosorbent before it reaches a condition where the biosorbent can not absorb adsorbate or called saturation point. At contact time of less than 3 hours the adsorption process is not optimum. This can be due to the active site contained in the biosorbent has not reached its saturation point, so the adsorption process can continue to increase. However, at contact time of 4 hours to 5 hours the adsorption power of biosorbent continues to decrease, means that the biosorbent has reached saturation point. According to Hening Purnamawati and Budi Utami [14], this is because the biosorbent has desorbed which is release of ions or molecules that have binded to the active group on the biosorbent, so that a number of dye molecules are released back into the solution. The highest removal percentage for oil and color was obtained at the biosorbent mass of 1.5 g with 3 hours contact time, that is 80, 88 % and 83.45%.
3.5 Adsorption Kinetic Studies

The adsorption kinetics shows the adsorption rate closely related to the absorbency between the active site and the adsorbate molecule. The adsorption kinetics can be obtained empirically by using the pseudo model of first order and second order \[15\] as in eq. (1) and (2).

\[
\frac{1}{q_t} = \frac{k_1}{q_e} t + \frac{1}{q_e} \tag{1}
\]

\[
\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{2}
\]

Where \(q_t\) and \(q_e\) are the amount of adsorbate at equilibrium and at any time \((t)\), \(k_1\) and \(k_2\) are the adsorption rate constant at first order and second order. The linear plot as shown in Figure 6.

![Figure 6 (a). Kinetic model for Pseudo first order](image1)

![Figure 6 (b). Kinetic model for Pseudo Second order](image2)

The graphs obtained in Fig 6a. show that the kinetic model for pseudo first order has a poor correlation coefficient. The graphs obtained in Fig 6b. show that the kinetic model for pseudo second order has a very high correlation coefficient (> 0.99). Second-order equation on oil adsorption obtained value \(r^2 = 0.997\) and the first-order equation on the color adsorption obtained value \(r^2 = 0.997\). Thus, it can be concluded that the adsorption of oil and color follow the pseudo kinetics mechanism of second order. According to Ho and McKay [16], the pseudo second order kinetic allows chemical reactions to the adsorption process involving the power of valence through division or electron exchange between adsorbent and adsorbate.

3. Conclusion

The highest iodin number of biosorbent from cocoa peel was 596,684 mg/g at particle size which passed through 120 mesh and ratio biosorbent : HNO\(_3\) (b/v) is 1:4. Characteristic of biosorbent of cocoa peel is 9.89% moisture content, 0.52% ash content, and 84% volatile content. The HNO\(_3\) solution used as an activator that has been decomposed of the mineral salts present in the sample which is proved through the FTIR Spectrophotometry and SEM results. The highest removal percentage for oil and color in POME was obtained at the biosorbent mass of 1.5 gram with 3 hours contact time, that is 80.88% and 83.45%. Adsorption kinetic of oil and color in POME follows the pseudo-second order kinetic model. Therefore the cocoa peel could be useful as a biosorbent for removing oil and color.
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