The model of adsorption kinetics on reduction of peroxide number in CPO (Crude Palm Oil) using rubber fruit shell (Hevea brasiliensis) as biosorbent

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Abstract. The object of this study was to discover the model of adsorption kinetics on reduction of peroxide number in CPO (Crude Palm Oil) using rubber fruit shell (Hevea brasiliensis) as biosorbent. The adsorption process was carried out using biosorbent with the highest iodine sorbent dosage and contact time. The best reduction of peroxide number was 83.86% at 0.5% biosorbent dose and 40 min of contact time. The adsorption kinetics model was conducted with difference of adsorption time (10, 20 and 30 min) and adsorption process was conducting at biosorbent concentration of 2%. Adsorption kinetics selected in this research was second order kinetics model after graph of t/qt (t is time and qt is adsorption capacity of time t) was made.

Keyword : Adsorption kinetics model, CPO (Crude Palm Oil), Peroxide number and Rubber Fruit Shell (Hevea brasiliensis)

1. Introduction
In Indonesia, the plantation which is developing well in agriculture is Rubber plantation. There are 3.4 millions acres of rubber plantation in Indonesia [1].Rubber plant is usually used as industry raw material provider. Almost all parts of rubber plant can be used to produce products which have economic value. Those parts are gum, wood, fruit and seed [2]. According to the information from directorate general of industry and chemical, industrial department [3] about the utilization of rubber plants, it is known that the rubber fruit shell has not been used optimally and even sometimes they are treated as a non-economic worth waste whereas this material actually has a potential to be processed to form a product that is useful and has economic value [4]. Rubber plant is known has lignin
contained. Lignin can also be found in the shell of rubber fruit (*Hevea brasiliensis*). According to Zakaria et al (2015) [5], the lignin contained in rubber fruit is quite high (35% - 45%) but the usage of the shell of the rubber fruit is not optimal [5]. As the high content of lignin in the shell of rubber fruit, biosorbent, an activated carbon product, can be made from it [4].

Biosorbent is a material with a lot of pores. Adsorption mainly happened at the walls of the pores or at the certain position of the particle. Component adsorbed is usually attached so hard so that it allows perfectly separation of certain component from a mixture happened [6]. An adsorbent must have a large specific surface area, pores with small diameter so that particle retention of adsorbate by adsorbent happened more effectively [7]. To increase the surface area and adsorption capacity, activation is needed in making biosorbent. Activation of biosorbent by using acid solution is the most often used method and has been proved to increase the adsorption capacity [8].

From the description above, this research is needed to be done to reduce the rubber fruit shell waste and to find out whether the activation by acid increase the adsorption capacity and reduce the peroxide number in CPO. The test of the equilibrium model depends on the value of determination coefficient (R²). When the R² is higher of approaching 1, then it can be claimed that the optimum equilibrium has been reached.

2. Materials and Methods

2.1 Materials

The materials used in this research were obtained around the University of Sumatera Utara. The shell of rubber fruit shell and crude palm oil were the main materials used. Some chemicals were used in biosorbent activation and analysis purposes. The chemicals used in biosorbent activation were potassium hydroxide, phosphate acid and nitric acid and the chemicals used in analysis purposes were acetic acid, chloroform, KI and Na$_2$S$_2$O$_3$.

2.2 Biosorbent Activation

The shell of rubber fruits were washed with water and dried under the sun. They were cut into 0.5 cm and carbonated at 500°C, 550°C, 600°C and 650°C for 1 hour using a furnace. Then, they were crushed until they become powder and were sieved using 140 mesh sieve. The biosorbent was activated by a solution of H$_3$PO$_4$ 6N. In activating the biosorbent, other solutions were used also. They were 6N KOH and 6N HNO$_3$. After the activating process, it was washed using distilled water to remove the activating solution. This procedure was repeated for the other ratio of biosorbent to solution (1:3, 1:4 and 1:5 m/v).

2.3 Condition of Adsorption Isotherm

The model of adsorption isotherm used was Langmuir and Freundlich with 30 min of time of equilibrium and the doses of biosorbent used was 1%, 1.5% and 2% of the amount of CPO used. First, the CPO was weighed for 100 g and poured into the beaker glass. It was heated on a hotplate at 90°C while being stirred by using magnetic stirrer. Then, biosorbent was added with the variable of doses as mentioned before. The CPO was then filtered by buncher funnel and filter paper at vacuum
condition. FTIR was done to the residue of filtration and peroxide number of the CPO after filtration was analyzed.

3. Results and Discussion

3.1 Characterization of Biosorbent Using FTIR Spectrophotometry

The biosorbent was characterized before and after the activation and after being used in the process of adsorption. By comparing the result on the graph with literature or IR correlation, the functional groups in biosorbent can be known [9].

The graphs can be seen in figure 1, 2 and 3 below:

![Figure 1. FTIR spectrophotometry result for biosorbent before activation](image)

![Figure 2.](image)

![Figure 3. FTIR spectrophotometry result for used biosorbent](image)
Figure 1 shows the functional groups of biosorbent before activation, figure 2 shows the functional groups of biosorbent after activation and figure 3 shows the functional groups of biosorbent after being used to adsorbed CPO impurities. Biosorbent before activation consists of alcohol, amine, carboxylic acid, alkane, halide acid, nitro component, alkyl aril eter and alkene functional groups. After activation there is no carboxylic acid in the biosorbent because the boiling point of carboxylic acid is near the boiling point of water [10] so the carboxylic acid is probably evaporated while the biosorbent was dried. Activation by using acid solution resulted cation exchange from mineral with ion H- of acid which caused adsorbent is negatively charged so that the adsorption capacity increased. Besides, this ion exchange will cause the adsorbent surface area wider [11]. Biosorbent which has been contacted with CPO shows it has adsorbed carboxylic acid functional groups at 2919.05 cm$^{-1}$ which indicates that there is free fatty acid being adsorbed and it also shows ketone and aldehyde functional groups in which these are the cause of rancidity in oil [12]. It also shows that it adsorbed ester at 1146.65 cm$^{-1}$.

3.2 Characterization of Biosorbent Using SEM (Scanning Electron Microscope)

In order to determine the changes of shape on the surface of the biosorbent, SEM characterization of the biosorbent before and after activation is done with 1000x magnification.

The graphs can be seen in figure 4 and 5 below.

**Figure 4.** Scanning Electron Microscope result for biosorbent before activation

**Figure 5.** Scanning Electron Microscope result for biosorbent after activation
From the figures above, we can see that the biosorbent after activation shows more pores than before activation. Carbonation and activation affects the pores structures of a material. After activation, the pores formed were wider and dispersed all over the surface of the biosorbent. The more pores at the surface of biosorbent causes higher adsorption capacity [13]. Besides, the more activator used in activating the biosorbent will also cause more pores formed in the biosorbent [14].

3.3 The Test of Equilibrium Model Used

The value of determination coefficient ($R^2$) determine the equilibrium model. If the $R^2$ is higher or approaching 1, then the model can be used [15].

The graph of Langmuir isotherm can be seen in figure 6 below.

![Figure 6. Peroxide number Langmuir isotherm model](image1.png)

It shows that if the active sides of the biosorbent’s surface has not been saturated with the adsorbats then it will cause the higher peroxide number being absorbed as the higher decreasing percentage of the peroxide number. It shows that the $y = -2.319x + 8.753$ and the correlation of $R^2$ was 0.9995.

The model of Langmuir isotherm assumes that the value of the energy absorbed is equivalent for every sides of adsorption and the surface of adsorbent is homogen. The interaction of active sides of adsorbent with adsorbate cause the chemi-adsorption happens and the interaction is only happened on the surface of adsorbent cell’s single layer adsorption (monolayer adsorption) [16].

The model of isotherm Freundlich is shown below.

![Figure 7. Peroxide number Freundlich isotherm model](image2.png)
The curve on the graph shown is almost linear. The correlation coefficient $R^2$ was 0.995 and formed the linear equation $y=0.145x - 2.839$.

The test of equilibrium model was done to find out the fit model for the research. It depends on coefficient of determination ($R^2$) [18].

The graph of kinetics model for second order is shown below.

![Figure 8. Peroxide number second order kinetics curve](image)

Then the data was evaluated to find the fit kinetics. The value of correlation coefficient $R^2$ was 0.767 with the equation $y=1293x+3210$. It could be accepted that the second order kinetics model was fit to be used for adsorption system of peroxide number in CPO by biosorbent of rubber fruit shell. The results were adsorption capacity at equilibrium ($q_e$) was 0.164 and coefficient of second order adsorption rate ($k_2$) was 0.008.

3.4 Effect of Biosorbent Dose and Contact Time on Peroxide Number in CPO
The initial peroxide number in CPO used was 0.0153 meq/kg. Peroxide number were formed from unsaturated fatty acid. According to the experiment data, desorption process cause the capability of adsorbent does not increase as the contact time gets longer. Desorption happened because of the surface of adsorbent become saturated. After the adsorption process, the standard peroxide number in CPO is zero meq/kg. The removal of the peroxide number in this research was 83.86% with 40 min of contact time using 0.5% dose of biosorbent.

4. Conclusion
There are some conclusions can be concluded from this research:
1. FTIR results shows that the biosorbent has adsorbed the component which can cause rancidity in oil.
2. SEM results shows that biosorbent after activation has more pores.
3. The peroxide number of the CPO was reduced after the CPO was adsorbed by the biosorbent at the condition of 40 minutes of contact time and using 0.5% dose of biosorbent.
4. The model of Langmuir and Freundlich isotherm matched the adsorption process with the constant of parameter.
5. The model of adsorption kinetics used on reduction of peroxide number in CPO using rubber fruit shell as biosorbent is the second order kinetics model.

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