The Model of Adsorption Isotherm 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 research was to determine the model of adsorption isotherm on reduction of peroxide number in CPO (Crude Palm Oil) using rubber fruit shell (*Hevea brasiliensis*) as biosorbent. The pretreatment of activation (carbonating and chemically) was started by washing and drying the rubber fruit shell under the sun. The adsorption process was done by using biosorbent with the highest iodine sorbent dosage and contact time. The highest iodine number was 913.680 mg/g and was obtained at 1:5 biosorbent to KOH 6 N solution ratio. The best reduction of peroxide number was 83.86% at 0.5% biosorbent dose and 40 min of contact time. The model of adsorption isotherm on reduction of peroxide number was realized with dosis of biosorbent 1%, 1.5% and 2% at time of equilibrium 30 min. The model used was Freundlich and Langmuir isotherm. The result was the constant of Langmuir parameter was maximum adsorption capacity ($q_m$) = 0.0009 and adsorption constant ($k_l$) = -130.488. On the other side, the constant parameter of Freundlich was adsorption constant ($n$) = -0.579 and capacity of adsorption ($k_f$) = $1.169 \times 10^{-6}$.

1. Introduction

Indonesia has a lot of plantations. Indonesia has 3.4 millions acres of rubber plantation since it is one of the most developing plantations in Indonesia. [1]. Several product manufacturers use rubber plant as raw material in their manufacturing process. Gum, wood, fruit and seed of rubber plant can be used and converted to products with economic value [2]. However, the rubber fruit shells are often treated as waste as if it has no economic value though it is potential enough to be processed to be useful product. The utilization of rubber plants is not optimal yet [3]. Lignin can be found in rubber plant. Rubber fruit shells also contains lignin [4]. According to Zakaria, et al (2015), lignin is an active compound which can be found in rubber fruit shell. The lignin content in the rubber fruit shell is relatively high. It is about 35%-45%. It can be used to be made biosorbent or other useful materials [5].

Biosorbent is a material which has a lot of pores. Adsorption occurred at the walls of the pores or at the certain position of the particle. Perfect separation of certain component from a mixture occurred because the component absorbed is usually attached hard [6]. An adsorbent must have pores with small diameter and large surface area so that more effective particle retention of adsorbate by adsorbent can occur [7]. Activation is done to biosorbent to increase the surface area and adsorption capacity. The most used method to activate biosorbent is by using acid solution and it has been proved to increase the adsorption capacity [8]. Therefore, the rubber fruit shell has a potential to be made become an activated carbon product named biosorbent. The test of the equilibrium model depends on the value of...
determination coefficient ($R^2$). The optimum equilibrium is achieved if the $R^2$ is higher or approaching 1.

2. Material and Method

2.1 Material
Rubber fruit shell and crude palm oil were the main raw material used in this research. They were obtained from the neighbourhood around University of Sumatera Utara. Nitric acid, phosphoric acid and potassium hydroxide were used in activating the biosorbent and for analysis purposes, acetic acid, chloroform, KI and Na$_2$S$_2$O$_3$ were used.

2.2 Biosorbent Activation
The biosorbent activation was begun by washing and drying the rubber fruit shells under the sun. The rubber fruit shells were cut into 0.5 cm and were carbonated for 1 hour at 500°C, 550°C, 600°C and 650°C by a furnace. They were crushed to form powder and sifted by 140 mesh sieve. The biosorbent was activated by H$_3$PO$_4$ 6N solution. Other solutions used to activate the biosorbent were 6N KOH and 6N HNO$_3$. Then, it was washed by distilled water several times to eliminate the activating solution. The procedure was repeated for 1:3, 1:4, 1:5 (m/v) biosorbent to solution ratio.

2.3 Condition of Adsorption Isotherm
The doses of biosorbent used was 1%, 1.5% and 2% while the time of equilibrium was 30 min. The model of adsorption isotherm used was Langmuir and Freundlich.

3. Results and Discussion

3.1 Biosorbent Characterization Using FTIR Spectrophotometry
The characterization using FTIR spectrophotometry was done to before activation, after activation biosorbent and biosorbent after being used to adsorbed crude palm oil. The spectrum obtained from the characterization was compared with literature or IR correlation to define the functional groups of biosorbent [9].

The FTIR spectrophotometry results are shown below:

![Figure 1. Non-activated biosorbent FTIR spectrophotometry result](image-url)
3.2 Biosorbent Characterization Using SEM (Scanning Electron Microscope)
Characterization of the rubber-fruit shell biosorbent before and after activation is done to determine the shape of the changes on the surface of the biosorbent with 1000x magnification. The SEM results are shown below.

Figure 2. Activated biosorbent FTIR spectrophotometry result

Figure 3. Used biosorbent FTIR spectrophotometry result

Figure 4. Scanning Electron Microscope result of non activated biosorbent
3.3 The Test of Equilibrium Model Used

The value of determination coefficient ($R^2$) determines the equilibrium model used. If the $R^2$ is higher or approaching 1, then the applicable model can be used [10].

The graph of Langmuir isotherm is shown in figure 6 below.

![Langmuir isotherm graph](image)

Figure 6. Peroxide number Langmuir isotherm model

It can be seen that if the active sides on surface of biosorbent was unsaturated yet with adsorbats and then the higher percentage of the decreasing peroxide number would cause the peroxide number adsorbed was higher. It was resulted that the correlation of $R^2$ was 0.9995 and $y = -2.319x + 8.753$.

Langmuir isotherm model assumes that the surface of the adsorbent is homogen and the quality of energy adsorbed in every sites of adsorption is equivalent. The interaction between active sites of adsorbent with adsorbate causes the chemi-adsorption. The interaction happened on monolayer adsorption (single layer adsorption) of the surface of adsorbent cell only [11].

The model of isotherm Freundlich is as follows.

![Freundlich isotherm graph](image)

Figure 7. Peroxide number Freundlich isotherm model
The result showed that the curve is almost linear. Correlation coefficient $R^2$ was 0.995 and formed the linear equation $y = 0.145x - 2.839$.

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 compound is caused by the presence of unsaturated fatty acid. According to the experiment data, the longer the contact time can not increase the capability of adsorbent because of desorption process. Saturated surface of adsorbent causes the desorption. After the adsorption process, the CPO standard peroxide number is zero meq/kg [12]. Using 0.5% dose of biosorbent with 40 minutes of contact time, the removal of the peroxide number was 83.86%.

4. Conclusion
The model of Langmuir and Freundlich isotherm matched the adsorption process with the constant of parameter.

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