Layer interaction adsorption isotherms model of mango seed as biosorbent in reducing free fatty acid and peroxyde value in crude palm oil refining

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Abstract. The activated mango seed was used to reduce FFA (Free Fatty Acid) and PV (Peroxyde Value) content in CPO (Crude Palm Oil). This study was begun with biosorbent modification. With size 140 mesh, 1% biosorbent of CPO with 35 minutes contact time, and shaking speed 200 rpm shown that the FFA and PV reduction percentage were 28.97% and 51.6%. The surface layer interaction model results follow Freundlich isotherm. The $R^2$ of kinetics equation model results are 0.9879 on FFA adsorption and 0.9923 on PV adsorption. This model involves the assumption that the pore surface of the biosorbent is different or heterogeneous. The Freundlich Isotherm model is also based on the assumption that there is a pore size distribution on the adsorbent and is applicable to more than one surface layer (multilayer) adsorbed by biosorbent. The ability of activated mango seed to adsorb more organic compound shows its potential as an alternative for bleaching earth substitute.

1. Introduction

Adsorbent/biosorbent is a material that can be produced from various sources that one of which is biomass and also certain plant like seeds of mango Arum Manis (Mangifera Indica L). Most of the mango are edible, but the seeds are mostly untapped. Agriculture Ministry reported that the mango production level is one of the primary commodities in horticulture for the decade 2004 to 2014 with an average of 21.95% per year. Mango seed contents carbohydrate (69-72%), fat (8-16%), tannin (10-15%), fiber and ash. Tanin has an active ingredient that functions as a cause of coagulation and precipitation. Just like as starch is a natural polymer that functions as a floculent [1]. Carbohydrates are organic compounds that are included in starch as a polymeric material. This bond is formed with a unit of glucose hydroxyl (-OH) in a cellulose molecule. It has a high potential to become an adsorbent because it contains -OH which can interact with the adsorbed [2]. The application of mango seeds as an adsorbent by activating it chemically has been carried out by a number of researchers [3,4].

The palm oil industry has multifunction that gives double benefit to the Indonesian economy as well as the world as a whole. Until 2017, Indonesia has succeeded in developing oil palm plantations around 12.3
million hectares with CPO production of 35.4 million tons. With the production of CPO of that size, Indonesia managed to become the world's largest CPO producer [5].

2. Method

The mango seeds were collected from markets in Medan city and Deli Serdang district. Chloric acid (HCl) used as chemical activators and Iodine analysis solution purchased from Merck KgaA, Darmstadt, Germany. CPO was obtained from Oil Palm Research Center, Sumatera Utara, Indonesia.

In the preliminary step, pure water is used to wash the mango seeds. The seeds are then dried in an open space. The dried seeds were crushed to powder form and sieved to separate to get 140 mesh sizes. The powder then was activated using 3N HCl in certain ratio (1:1; 1:2; 1:3 and 1:4) (g/ml), and then put in heater about 2 hours under temperature controlled at 70°C. The powder was then cooling to room temperature. To remove residual acid, the powder was washed several times with deionized water (aquadestilator, W41 Water Still Favorit, Indonesia). In order to increase the surface area of adsorbent, it was activated physically (calcinating) by putting them in the oven (Memmert UN 55) on 2 hours at variation temperatures such as: 90°C, 100°C, 110°C, 120°C, 130°C, 140°C [2]. The final preliminary step was conducted to measure the iodine number of each biosorbent (Europe Standard Method, EN 14111). The existence of unsaturated bonds in the form of double bonds interact with iodine, this can be used to measure the amount of unsaturated bonds in a compound. The amount of iodine reacting is the mass of iodine (mg) which is absorbed by 100g of its chemical compound.

Batch adsorption operation was running in beaker glass (0.5 L) which was shaken for five variations time (25, 30, 35, 40, 45 minutes) and three variations dose ratio of biosorbent of CPO (0.5; 1.0; 1.5%) with 200 rpm in 100 to 110°C. Free fatty acid and peroxide value analyze are tested in Oil Palm Research Center Laboratory, Sumatera Utara, Indonesia. The adsorption operation data were used to evaluate the layer interaction of adsorption isotherms model.

The equations of adsorption percentage (1) and capacity of adsorption (2) expressed as follows [6][7]:

\[
\%\text{ adsorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \tag{1}
\]

\[
q_e = \left(\frac{C_0 - C_e}{m}\right) V \tag{2}
\]

with Co is initial and Ce is equilibrium concentrations of FFA and PV (mg/L). v is total volume and w is weight of adsorbent. The Freundlich isotherm model is generally used to measure heterogeneous surface energy systems with non-uniform distribution of sorption heat. The Langmuir isotherm model is always used to determine a monolayer adsorption at specific homogenous [8][9][10]. Equation (3) is the Freundlich and equation (4) is the Langmuir expression:

\[
\frac{C_e}{q_e} = \frac{1}{K_f q_m} + \frac{C_e}{q_m} \tag{3}
\]

\[
Log q_e = log K_f + \frac{1}{n} log C_e \tag{4}
\]

with qm represent of monolayer sorption capacity (mg/g) and KL symbolize the Langmuir equilibrium constant (L/g). Kf and n are both the Freundlich constants. The Kf is adsorption capacity while n is
biosorption intensity and qe is amount of FFA and PV per unit mass of adsorbed (mg/g). Ce is the equilibrium concentration (mg/L). The adsorption operation data were used to evaluate the layer interaction of adsorption isotherms model, based by the correlation coefficient (R²) which is closer to 1.

3. Results and Discussions

3.1. Characteristic of Biosorbent

Figure 1 below shows that the graph of the molecular structure of mango seed is higher after activation compared to before activation. The activation conditions of the process showed a comparison of the amount of 3N Chloric Acid was four times the number of biosorbents in units of g/ml and the calcinations temperature was 110°C.

![Figure 1. FT-IR spectra a. after activation; b. before activation of mango seeds Arum Manis type](image)

The results of this study noted that both mango seeds of Arum Manis variety produced the FT-IR spectra which varied in the range of 4000-500 cm⁻¹ as shown in Figure 1. A small difference in the graph of the two samples appears in the area of hydrogen bonding between molecules, please see in the area of 3200-3400 cm⁻¹. But overall, the results of this investigation illustrate that there is no significantly difference in behavior of Arum Manis mango seeds at the both stages of activation. FTIR result after activation shows that a peak appears on the certain wavelength 1743.65 cm⁻¹. This wave peak confirms the subsistence of unsaturated bond (C=O group). Based on 3N HCl activation, the action of cation exchange has occurred to the minerals with H⁺ from acid and creates the adsorbent becomes negatively changed. It was increased the capacity to adsorb and on the other side. Furthermore, the ion exchange will possible to increase the surface area of the adsorbent [11].

Figure 2 shows the differences surface morphological of mango seed biosorbent before and after activation. The SEM image shows the porous structure of mango seed. After activating process be seen that the biosorbent surface has more pore distribution and more pore cavity than the biosorbent before it is
activated. This is because the chemical activator is capable of dissolving the impurities, so that more pore pores are formed and the ability of removing adsorbed by biosorbent.

![Figure 2](image1.png)  
**Figure 2.** Surface Characteristic of (a) Mango seed powder; (b) Mango seed activated; (c) Mango seed after adsorption

### 3.2. Adsorption Isotherm

The results are presented from experiments for adsorption of FFA and PV. Table 1 shown relationship between adsorption capacities, $q_e$ (%) against contact time ($t$) at several doses. The experimental data was then used to describe the interaction on layer surface of adsorbent with adsorbed by using equation (1), (2), (3), and (4).

| Contact Time (min) | Adsorption capacity, $q_e$ (%) | 0.5 | 1 | 1.5 |
|-------------------|-------------------------------|-----|---|-----|
|                   | FFA                           | PV  | FFA| PV  | FFA | PV  |
| 25                | 7,76                          | 51,46| 7,19| 28,3| 2,93| 14,77|
| 30                | 14,18                         | 61,26| 11,14| 31,83| 6,50| 1,29 |
| 35                | 19,12                         | 67,26| 14,90| 27,43| 8,10| 13,49|
| 40                | 18,80                         | 58,00| 12,64| 20,23| 7,73| 7,30 |
| 45                | 15,88                         | 41,46| 11,90| 14,43| 7,43 | 5,82 |

Table 1 is shown adsorption capacity data. Based on the research data obtained, it is known that the longer the adsorption contact time does not increase the adsorption capacity of biosorbent. Once the adsorption capacity has reached the optimum point for all biosorbent conjugated ratios, it will decrease the adsorption capacity due to adsorption. Desorption occurs due to the saturated on adsorbent surface. In the saturation state of the adsorption the rate was resulting reduced. Based on these results, it is suspected that the adsorption mechanism is dominated by the adsorption of physics interaction.

Reporting on equilibrium studies that give the adsorption capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbed are described by adsorption isotherms. Those are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Figure 3 shows the adsorption result in the relationship between the x and y axis of correlation to the single or monolayer interaction model. The result is obtained using an equation 4 (Langmuir model) and equation 3 (Freundlich model). The data showed that the experimental results were better against the Freundlich
model compared to Langmuir model based on the correlation coefficient ($R^2$) and so do in Fig. 4 shows the relationship between both of axis to the single or monolayer interaction model. The result showed the correlation coefficient of Freundlich model is to closer 1.

![Figure 3](image1.png)

**Figure 3.** (a) Isotherm adsorption Langmuir curve (b) Isotherm adsorption Freundlich curve for FFA adsorption

![Figure 4](image2.png)

**Figure 4.** (a) Isotherm adsorption Langmuir curve (b) Isotherm adsorption Freundlich curve for PV adsorption

In the same concentration ratio indicate that major adsorption occur at low concentration. However by increasing the quantity of adsorbed concentration becomes less significant at higher concentration and the otherwise [12]. R values are close to one (1) in Freundlich isotherm model is 0.9879 for FFA and 0.9923 for PV. The model of Freundlich isotherm is generally applied for heterogeneous surface energy systems [13][14]. Apart from a homogeneous surface, the Freundlich model is also appropriate for a highly heterogeneous surface. This model is also used for an adsorption isotherm lacking a plateau, to indicate a multi-layer adsorption.

4. Conclusion

$R^2$ coefficients of kinetics equation model results are 0.9879 on FFA adsorption and 0.9923 on PV adsorption. The adsorptions occur that follows the model of Freundlich isotherm involves the assumption that the pore surface of the biosorbent is different or heterogeneous. This result is also based on the theory that there is a pore size distribution on the adsorbent and is applicable to more than one surface layer.
(multilayer) adsorbed by biosorbent. The ability of mango seed activated to adsorb more organic compound shows its potential as an alternative of bleaching earth substitute.

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