Isothermal approach to predict the removal efficiency of β-carotene adsorption from CPO using activated carbon produced from tea waste

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Abstract. Adsorption of β-carotene in crude palm oil (CPO) was studied using activated carbon produced from tea waste (ACTW) an adsorbent. Isothermal studies were carried out at 60 °C with the ratio of activated carbon to CPO were 1:3, 1:4, 1:5, and 1:6, respectively. The ACTW showed excellent performance as the percentage of adsorption of β-carotene from CPO was > 99%. The best percentage removal (R) was achieved at ACTW to CPO ratio equal to 1:3, which was 99.61%. The appropriate isotherm model for this study was Freundlich isotherm model. The combination of Freundlich isotherm equation and mass balance equation showed a good agreement when validated to the experimental data. The equation subsequently executed to predict the removal efficiency under given sets of operating conditions. At a targeted R, CPO volume can be estimated for a certain initial concentration β-carotene in CPO C₀ and mass of ACTW adsorbent M used.

1. Introduction
Indonesia is the largest producer of crude palm oil (CPO). In 2012, the production of CPO in Indonesia reached 23.5 million ton [1]. Domestic CPO is used for food industry especially cooking oil industry and non food industries such as cosmetics and pharmaceuticals. CPO consists of major ingredient, namely triglyceride (94%) and minor ingredients are tocopherol, sterol, phosphatide and carotenoid [2]. CPO is raw material in cooking oil production. In Indonesia, consumers prefer yellow and clear cooking oil color than reddish one. Carotenoid forms reddish color of CPO thus in cooking oil. In order to meet consumer preference, a bleaching process on CPO is applied to remove carotenoid compounds. The bleaching process is conducted by adsorbing carotenoid compounds [3].

CPO contains carotenoid compounds in 500-700 ppm (0.5-0.7 kg per ton) [4] and is potential to be the huge source of provitamin A and antioxidants as carotenoid compounds consists of 80% β-carotene. Also, many by-products of CPO processing can be used as a base in the chemical industry while β-carotene is needed in food, pharmaceuticals and cosmetics industries [5]. Therefore, carotenoid compounds in CPO are important to be recovered. Unfortunately, normal CPO processing into cooking oil resulted in 80% broken carotenoid. This is due to bleaching processes of carotenoid takes place at the temperature > 240 °C [6]. Broken carotenoid is discarded as waste.
Various methods to get carotenoid compounds in CPO were performed such as extraction using supercritical fluid [7] and adsorption using adsorbents [6]. Adsorption is a bleaching method that is widely used as it is fast and easy. Carotenoids in CPO are bound to the adsorbent. Since there is no chemical reaction, then CPO does not change. Also, adsorption process can be performed at room temperature. Many adsorbents were used to adsorb β-carotene in CPO such as rice husk ash, silica gel, alumina, clay, oil palm shells and activated carbon [3].

Several studies have reported the manufacture and utilization of activated carbon for β-carotene adsorption. Tea waste is the potential raw material for activated carbon production. Tea waste consists of cellulose (29.42%), lignin (36.94%), ash (4.53%) and extractive (15.22%) [8]. One of the considerations for manufacturing activated carbon from tea waste is its high level of holocellulose (60.81%). The previous study showed that the activated and carbonized tea waste had high fixed carbon content of 57.1%. The maximum capacity of the adsorbent to adsorb nitrophenol was 142.85 mg/g [9]. Also, tea wastes adsorption capacity for heavy metal i.e. Ni (II) varied in a range of 50 - 100%. This condition was affected by contact time, and the amount of adsorbent used [10].

The research on isothermal adsorption of β-carotene from CPO using bentonite and activated carbon was also reported. The study showed that the value of activation energy were 74.28 kcal/mole and 30.04 kcal/mole for bentonite and activated carbon, respectively and was able to adsorb β-carotene as high as 79.05% [11]. Furthermore, a study on β-carotene and phosphorus adsorption from CPO using modified natural clays was also reported. The adsorbents used in the study were able to adsorb β-carotene and phosphorus as high as 90% [6]. The previous studies mentioned above showed that activated carbon of tea waste had excellent capacity in heavy metals adsorption. Here, we investigated the utilization of activated carbon from tea waste to study its potential as the adsorbent of β-carotene in CPO.

2. Materials and Method

2.1 Equipment and materials

The equipments used in this study were tray dryer, ball mill, sieve of 50 mesh, pyrolysis reactor equipped with N₂, hot plate, electric motor and stirrer. Whereas the main materials used were CPO, tea waste, and 85% phosphoric acid (H₃PO₄).

2.2 Activated carbon production

Tea waste used in this study was collected from Acehnese restaurants in Medan. The activated carbon was prepared in the same procedure as published previously in [12]. Tea waste was dried using tray dryer at 40 °C. Later, tea waste was milled using a ball mill and was sieved using a 50 mesh sieve. Subsequently, it was activated with a solution of 85% H₃PO₄ for 24 hours with a weight ratio of it and H₃PO₄ was 1: 2. The carbonization process was conducted in a pyrolysis reactor at 500 °C for 15 min using N₂ stream. The activated carbon acquired was rinsed using hot water (85 °C) and was dried in the oven at 110 °C. Activated carbon is then pulverized using a mortar.

2.3 Adsorption experiments

CPO and activated carbon were prepared in ratios of 1:3, 1:4, 1:5 and 1:6 in beaker glasses. The mixture was heated using a hot plate at 60 °C and was homogenized using an electric motor at 120 rpm for 2 hours. The mixture was filtered using Whatman filter paper #1. The filtrate was put into a plastic bottle and analyzed using UV-VIS spectrophotometer to determine the content of β-carotene.

2.4 Adsorption isotherms model and mass balanced

Adsorption isotherm models were used to determine the distribution between liquid and solid phase adsorbents as a measure of equilibrium position in the adsorption process. The models were represented by Langmuir and Freundlich isotherm models [6].
Langmuir isotherm model defines that the maximum adsorption capacity is the result of a single layer (monolayer) on the surface of the adsorbent adsorbate [13]. The linear form of the Langmuir isotherm equation is shown in the Equation (1) [6].

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left( \frac{1}{q_m} \right) C_e
\]

(1)

where \( q_e \) is the amount of adsorbate per mass of adsorbent, \( C_e \) is the equilibrium concentration adsorbate, \( K_L \) and \( q_m \) are the Langmuir constants related to adsorption capacity and rate of adsorption.

Freundlich isotherm model is the model used for the non-ideal adsorption and multilayer adsorption [13]. The Relationship between amount of adsorbed substances and concentrations is shown in the Equation (2) [6].

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

(2)

where \( q_e \) is the amount of adsorbate per mass of adsorbent, \( C_e \) is the equilibrium concentration adsorbate, \( n \) is the intensity of adsorption and \( K_f \) is the constant of Freundlich isotherm.

The isotherm model combined with a mass balance can be used to predict the adsorbate efficiency removal and the required mass of the adsorbent for the desired removal efficiency based on the previous modeling for adsorption study [14]. Firstly, at a given initial concentration and amount of adsorbent, the concentration at equilibrium is calculated using Equation (3) and (4) for Langmuir isotherm and Freundlich isotherm, respectively.

\[
K_L C_e^2 + \left( 1 + \frac{K_L q_m M}{V} - K_L C_0 \right) C_e - C_0 = 0
\]

(3)

\[
\frac{K_f M}{V} C_e^{1/n} + C_e - C_0 = 0
\]

(4)

where \( M \) is the mass of adsorbent and \( V \) is the volume of adsorbate.

The percent removal is determined by the following equation [13]:

\[
R = \frac{C_0 - C_e}{C_0}
\]

(5)

where \( R \) is the percentage of removal, \( C_e \) is the equilibrium concentration of adsorbate and \( C_0 \) is the initial concentration of adsorbate.

For a given initial solute concentration and target removal efficiency, the equation to predict the required mass of adsorbent can be calculated using Equation (6) and (7) for Langmuir isotherm and Freundlich isotherm, respectively.

\[
M = \frac{VR}{K_L q_m (1 - R)} + \frac{VR}{q_m} C_0
\]

(6)

\[
M = \frac{VR}{K_f (1 - R)^{1/n}} C_0^{1 - \frac{1}{n}}
\]

(7)

Equation (6) and (7) can also be rearranged to get the volume of CPO that could be processed at a given mass of adsorbent.

2.5 Parameter determination and model calculation

Isotherms were fitted to experimental data for activated carbon with the Equation (1) and (2) to determine the isotherm parameters. Equation (3) and (4) were solved using numerical analysis based on the Newton-Raphson method.

3. Results and Discussion
3.1 The ability of ACTW to adsorb β-carotene

The concentration of β-carotene initially contained in CPO was 509 ppm. The concentration of β-carotene decreased significantly after contacting with 14 g of activated carbon produced from tea waste (ACTW) at 60 °C for 120 min. Table 1 showed the concentration of β-carotene in various ratios activated carbon to CPO after the adsorption process. The best percentage removal of β-carotene of 99.61% was obtained at ratio 1:3 with the final concentration of β-carotene of 2 ppm. At the same amount of adsorbent, the increment of CPO volume resulted in a decrease of adsorption capacity although not significant.

Table 1. Removal efficiency of β-carotene using activated carbon produced from tea waste

| Ratio of ACTW to CPO (w/w) | Mass of CPO (g) | Volume of CPO (mL) | Final Concentration of β-Carotene (ppm) | Percentage removal, R (%) |
|---------------------------|-----------------|-------------------|----------------------------------------|--------------------------|
| 1:3                       | 42              | 46.94             | 2                                      | 99.61                    |
| 1:4                       | 56              | 62.58             | 3                                      | 99.41                    |
| 1:5                       | 70              | 78.23             | 4                                      | 99.21                    |
| 1:6                       | 84              | 93.88             | 5                                      | 99.02                    |

The ability of ACTW to adsorb β-carotene from CPO in this study is better compared to the ability of modified natural clay. Modified natural clay was able to adsorb β-carotene and phosphorus by 90% [6]. This study also showed the higher performance of ACTW compared to bentonite and activated charcoal to adsorb β-carotene from CPO which has 79% adsorption [11]. The ACTW showed excellent performance since the percentage removal of β-carotene from CPO were > 99% for all of the variables under this study.

3.2 Determination of adsorption isotherms model

Isothermal models fitness determination was conducted by plotting the related variables as shown in Equation (1) and (2) for Langmuir and Freundlich isotherm models, respectively. The experimental data form a linear graph with excellent correlation (Figures 1 and 2). From the linear equation obtained, can be determined the constants associated with each isothermal models (Table 2).

Table 2. The adsorption isotherm model parameter of β-carotene from CPO

| Model isotherm | Parameter       | Parameter value |
|----------------|-----------------|-----------------|
| Langmuir       | $q_m$ (mg/gr)   | 10              |
|                | $K_L$ (L/mg)    | 0.1             |
| Freundlich     | $K_f$ (L/mg)    | 1.0020          |
|                | $n$             | 1.3368          |
Therefore, the isotherm model corresponds to this study is the Freundlich isotherm model. The correlation coefficient in the Freundlich isotherm model is better than the Langmuir isotherm models, which is of $R^2 = 0.999$. Results of previous research on the study of the adsorption isotherm of β-carotene from crude palm olein using bentonite also showed that the appropriate model was Freundlich isotherm corresponding to the value of the correlation coefficient ($R^2$) of 0.9899 [11].

### 3.3 Validation of calculation of R and V prediction with R and V experimental

Since the appropriate isotherm model for this study was Freundlich isotherm, then Equation (4) and (5) would be executed to predict the adsorbate efficiency removal ($R$) or the percentage of adsorption. Table (3a) shows a comparison between the experimental and the predicted value of $R$. In the adsorption process, the same initial concentration of β-carotene in CPO ($C_0$) of 509 mg/L and the mass of ACTW adsorbent ($M$) of 14 g were used for the entire experiments. When the ratio of ACTW to CPO = 1:3, thus the mass of CPO was 42 g or the volume of CPO became 0.04694 L. The removal efficiency was predicted to be 99.60%, and the experimentally determined value was 99.61%, and thus the prediction error was 0.0038%. For other ratios of ACTW to CPO, the errors were in the range of 0.0049 to 0.0111%. The predictions for CPO volume to obtain the desired $R$ value were shown in the Table (3b) based on the calculation using Equation (7). With the same initial concentration of β-carotene as shown in Table (3a) and desired $R$ was 99.61%, the predicted volume of CPO was 0.0466 L, and thus the error was 0.72%.

The results suggested that the constant in the equation of the Freundlich isotherm associated in mass balance equation can be applied to predict the removal efficiency at various initial concentrations of solutes and the volume of CPO. Moreover, for given $R$ and mass of adsorbent, the volume of CPO can be predicted without significant error.

### Table 3. Calculation validation of R and V predictions with experimental R and V

| Initial condition | Experimental $R$ (%) | Predicted $R$ (%) | Error (%) |
|-------------------|---------------------|------------------|-----------|
| $C_0$ (mg/L)      | $M$ (g)             |                  |           |
| 509               | 14 (in 0.04694 L)   | 99.61            | 99.60     | 0.0038    |
| 509               | 14 (in 0.06258 L)   | 99.41            | 99.42     | 0.0084    |
| 509               | 14 (in 0.07823 L)   | 99.21            | 99.22     | 0.0049    |
| 509               | 14 (in 0.09388 L)   | 99.02            | 99.01     | 0.0111    |
**Table 3.** Calculation validation of \( R \) and \( V \) predictions with experimental \( R \) and \( V \) (Cont.)

| Initial condition | \( C_0 \) (mg/L) | \( R \) (%) | Experimental \( V \) (L)* | Predicted \( V \) (L) | Error % |
|-------------------|------------------|-------------|--------------------------|----------------------|---------|
|                   | 509              | 99.61       | 0.0469                   | 0.0466               | 0.72    |
|                   | 509              | 99.41       | 0.0626                   | 0.0632               | 0.98    |
|                   | 509              | 99.21       | 0.0782                   | 0.0786               | 0.47    |
|                   | 509              | 99.02       | 0.0939                   | 0.0931               | 0.83    |

* mass of ACTW adsorbent was 14 g

3.4 Prediction of \( R \) value at given initial concentration and mass of adsorbent

Furthermore, the prediction of ACTW ability to adsorb \( \beta \)-carotene in processing more volume of CPO can be conducted. The initial concentration \( (C_0) \) of 509 ppm and mass of ACTW \( (M) \) of 14 g was applied to Equation (4) and (5), with the various value of CPO volume \( (V) \) based on the various ratios ACTW to CPO (greater than 1:6). This step aimed to determine the maximum volume of CPO that could be processed for the target value of \( R \) was \( \geq 90\% \). From the simulation results, the mass of CPO that can be processed is 532 grams or equivalent to 0.59 L of CPO. In another word, ACTW has the ability to remove 90% of \( \beta \)-carotene until the ratio of ACTW to CPO is 1:37.

![Figure 3.](image)

**Figure 3.** Correlation of \( R \) with mass of CPO (left) and with CPO volume (right) at initial concentration of 509 ppm and mass of ACTW of 14 g

4. Conclusions

Activated carbon produced from tea waste (ACTW) showed excellent performance to absorb \( \beta \)-carotene from CPO. The ability of ACTW was > 99% for various mass ratios of ACTW to CPO under study. At the same initial concentration, the greater ratios of ACTW to CPO will decrease the percentage of removal. Freundlich isotherm model is by the process of adsorption \( \beta \)-carotene from CPO. The combination of Freundlich isotherm equation and mass balance equation can be used to determine the removal efficiency \( (R) \) for a given set of operating conditions. The equation has been validated for accuracy since it can predict the \( R \) value well without a significant error in comparison with the experimental result. These results enabled prediction of CPO volume at greater ratio of ACTW to CPO using the combined equation. For \( C_0 = 509 \) ppm, \( M = 14 \) gr, and \( R \) was targetted \( \geq 90\% \), the maximum ACTW to CPO ratio is 1:37. At that condition, the maximum mass of CPO that can be processed is 532 grams or equivalent to 0.59 L of CPO.
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