Effect of Acid Pretreatment of Coconut Pulp on Peroxides Removal in used Frying Oil

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Abstract. Oxidation process during frying oil produce many compounds such as peroxides which are detrimental to health. One way to improve quality of used cooking oil is using adsorbent. Coconut pulp is one of adsorbent because contain 37.1 % cellulose. In this research, coconut pulp treated by hydrochloric acid (HCl) 0.1 N and acetic acid (CH₃COOH) 0.1 N. Coconut pulp before and after treated by acids were analyzed using FTIR. The adsorption process of peroxides in used cooking oil was carried out using coconut pulp treated by acids. Then, adsorption isotherm and kinetics of coconut pulp treated by acids were analyzed. The results showed that after treated by HCl and acetic acid, some wavelength and intensity of functional groups change and present new functional group. HCl and acetic acid may decomposed of mineral salts in coconut pulp. The highest percentage reduction of peroxide value is obtained after adsorption onto HCl treated coconut pulp while percentages of reduce is 56.206%. The adsorption of peroxides using coconut pulp treated by HCl and acetic acid are included to pseudo-second-order and were well described with Freundlich isotherm model. Adsorption capacity of coconut pulp treated by HCl is 0.686 mg/g while adsorption capacity of coconut pulp treated by acetic acid is 0.454 mg/g.

1. Introduction

One way to process food is by frying. Frying can be done with various types of vegetable oil, such as palm oil, coconut oil, corn oil, etc. The simultaneous heat and mass transfer of oil, food, and air during deep-fat frying produces the desirable and unique quality of fried foods [2]. Usually, cooking oil is used more than once. Sometimes the colour of used frying oil is black because it is used repeatedly.

During the frying process, various chemical reactions occur such as oxidation, hydrolysis and polymerization. These reactions can produce harmful substances and cause unpleasant taste in fried foods when exceeding a certain threshold. One of the substances produced from oxidation reactions is peroxide which can cause oxidative stress when consumed. Oxidative stress and inflammation together contribute to the pathogenesis of many diseases like Rheumatoid Arthritis (RA), cancer, Coronary Artery Disease (CAD), diabetes, Non Alcoholic Fatty Liver Disease (NAFLD) etc. [1].

One way to improve quality of reheating or used frying oil is using adsorbent. Coconut pulp powder contain 37.1 % cellulose [8]. Activated carbon from coconut pulp could improve physical quality of the water [5] and used as adsorbent for heavy metals. Therefore, coconut pulp is one of potential adsorbent. In this research, coconut pulp with acid pretreatment used as adsorbent for peroxides removal in used frying oil.
2. Materials and methods

2.1. Materials
The materials were coconut pulp that were collected from Tasikmalaya and used frying oil was palm oil with fifteen repetitions of frying.

2.2. Methods
2.2.1. Preparation of acid treated coconut pulp
Coconut pulp that does not contain coconut milk is dried in the oven for 1 hour at 100 °C. It was made into powder then sieved with a 100 mesh size sieve. After that, coconut pulp was macerated by n-hexane and dried in oven at 65 °C for 15 minutes [4].

Coconut pulp powder was treated by HCl 0.1 N and CH₃COOH 0.1 N. 5 gram of coconut pulp was added into beaker glass containing 100 ml HCl 0.1 N and CH₃COOH 0.1 N (in different beaker glass) for 24 h. Then rinsed with distilled water and oven for 24 hours at 105°C.

2.2.2. Preparation of used frying oil
The used frying oil was 2 liters palm oil with 15 repetition of frying for frying 30 pieces of tofu at 160-180 °C for 10 minutes. The used frying oil passed through nylon filter.

2.2.3. Adsorption of peroxides in used frying oil
Each 74.25 gram of coconut pulp treated by HCl and acetic acid were poured into 500 mL of used frying oil for 72 h. After that, the used frying oil passed through nylon filter and then analyse to determine peroxide value.

2.2.4. Determination of peroxide value
The procedure to determin of peroxide value follow the procedure on SNI 7709:2012. Determine peroxide value (mek O₂/Kg) used the equation:

\[
\text{Peroxide value (mek O}_2\text{/Kg)} = \frac{1000 \times N \times (V_0-V_1)}{W}
\]  

(1)

2.2.5. Adsorption isotherm of acid treated coconut pulp
Acids treated coconut pulp were poured into 25 mL H₂O₂ standard solution in different concentrations (2000, 2500, 3000, 3500, 4000, 4500, and 5000 ppm) at room temperature for 90 minutes. Then, passed through nylon filter and then analyse to determine peroxide value.

2.2.6. Adsorption kinetics of acid treated coconut pulp
Acids treated coconut pulp were poured into 25 mL H₂O₂ standard solution with optimum concentration in adsorption isotherm analysis for 3, 12, 24, 48, 72 h. Then, passed through nylon filter.

2.2.7. Functional Group Analysis
Coconut pulp before and after treated by HCl 0.1 N and CH₃COOH 0.1 N were analysis using Fourier-Transform Infrared Spectroscopy (FTIR) to determine functional groups.

3. Results and discussion
3.1. Adsorption capacity of coconut pulp after treated by acid
Peroxide value of used frying oil before and after adsorption onto coconut pulp shown in table 1.
Table 1. Peroxide value of used frying oil before and after adsorption

| Used frying oil                               | Peroxide value (mek O2/Kg) | % reduce  |
|-----------------------------------------------|----------------------------|-----------|
| Before adsorption onto coconut pulp           | 18.852                     | -         |
| After adsorption onto HCl treated coconut pulp| 8.256                      | 56.206    |
| After adsorption onto acetic acid treated coconut pulp | 9.172                      | 51.345    |

The result shows that used frying oil before adsorption onto coconut pulp has peroxide value about 18.852 mek O2/Kg. This value does not meet SNI 7709:2012 requirements (max 10 mek O2/Kg). But, after adsorption onto acid treated coconut pulp, the peroxide value of used frying oil fulfil SNI 7709:2012 requirements. The highest percentage reduction of peroxide value is obtained after adsorption onto HCl treated coconut pulp while percentages of reduce is 56.206%.

Adsorption isotherm of liquid usually use Freundlich and Langmuir type. The adsorption isotherms of coconut pulp treated by HCl and acetic acid were shown in figure 1.

![Figure 1](image-url)

**Figure 1.** Adsorption isotherm model for (a) Langmuir and (b) Freundlich.

Figure 1 shows that isotherm model for coconut pulp treated by HCl and acetic acid were well described with Freundlich isotherm model. At Isotherm Freundlich the adsorption process happens by multilayer adsorption [6]. Based on calculation using Freundlich isotherm model, adsorption capacity of coconut pulp treated by HCl is 0.686 mg/g while adsorption capacity of coconut pulp treated by acetic acid is 0.454 mg/g.

### 3.2. Adsorption kinetics of acid treated coconut pulp

The adsorption kinetics shows the adsorption rate between the active site and the adsorbate molecule [3]. The models which are commonly used to study adsorption kinetics are Langmuir-Hinshelwood, Santosa and Ho. The Langmuir-Hinshelwood kinetics model assume that initial concentration of adsorbate ($C_0$) affects the rate of adsorption while for Santosa kinetic models assume that initial concentration of adsorbate ($C_0$) does not affect reaction rate but affected by adsorbate concentration in certain t states ($C_a$). Ho’s kinetic model shows pseudo second order [2]. The results of adsorption kinetic of acid treated coconut pulp were shown in Figure 2.
Figure 2. Adsorption kinetic model for (a) Langmuir-Hinshelwood, (b) Santosa and (c) Ho

Figure 2 shows that Ho kinetics model gave the best $R^2$ value for coconut pulp treated by HCl and acetic acid. It means that kinetics model follow pseudo-second-order from Ho with adsorption rate constant for coconut pulp treated by HCl is $4.761 \text{ g.mg}^{-1}\text{hour}^{-1}$ while adsorption rate constant for coconut pulp treated by acetic acid is $12.813 \text{ g.mg}^{-1}\text{hour}^{-1}$.

3.3. Functional group analysis

Functional group analysis of coconut pulp before and after treated by acids are showed in Figure 3.
Figure 3. FTIR spectrum of coconut pulp (a) before treated by acid, (b) after treated by HCl 0.1 N and (c) after treated by acetic acid 0.1 N.

Figure 3 showed that coconut pulp before treated by acid have several peaks such as hydroxyl, carbonyl and C-H groups. After treated by acetic acid, intensity of –OH and C-H groups changes and present C≡C functional group at 2361, 19 cm$^{-1}$, and after treated by HCl some wavelength of functional groups change and present C≡C functional group at 2363.20. HCl and acetic acid may decomposed of mineral salts in coconut pulp.

4. Conclusion
Coconut pulp treated by HCl and acetic acid can used as adsorbent for peroxides removal in used cooking oil. Before and after treated by acid, some intensity and wavelength of functional groups change which are indicated that acids cause decomposition of mineral salts in coconut pulp. The highest percentage reduction of peroxide value is obtained after adsorption onto HCl treated coconut pulp with percentages of reduce is 56.206%. Isotherm model for coconut pulp treated by HCl and acetic acid follow Freundlich isotherm model with adsorption capacity of coconut pulp treated by HCl is 0.686 mg/g while adsorption capacity of coconut pulp treated by acetic acid is 0.454 mg/g. The kinetic model of coconut pulp treated by acid follow pseudo-second-order from Ho.

5. References
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