Adsorption of Free Fatty Acid (FFA) in Low-Grade Cooking Oil Used Activated Natural Zeolite as Adsorbent

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Abstract. Adsorption of free fatty acid (FFA) in low-grade cooking oil using active natural zeolite adsorbent was done as an effort to improve the quality of low-grade cooking oil so that it can fulfill the standard of fried oil which has been set on SNI 01-3741-2013. Adsorption was carried out with natural zeolite which activated with HCl and NaOH solution followed by the calcination process. The results showed that the NaOH activated zeolite decreased FFA content in low-grade cooking oil more than the HCl activated natural zeolite, with optimum NaOH concentration was 0.75 M. In the adsorption equilibrium analysis with temperature variation (25 °C, 40 °C, 80 °C), obtained that adsorption of FFA with NaOH activated natural zeolite follows Adsorption Isotherm Freundlich Model with equilibrium constant value was 20,5873; 0,9629 dan 0,8053.

1. Introduction
Cooking oil is one of the important foodstuffs used to process foodstuffs. Cooking oil serves as a heat conductor, provides calorific value, and provides a savory taste in food. The main content of cooking oil is triglycerides (triacylglycerol) formed from glycerol and various fatty acids [1]. In addition to triglycerides, cooking oil also contains small amounts of complex lipids, sterols, free fatty acids (FFA), waxes, oil-soluble pigments, and hydrocarbons [2]. Based on the number of the refining process, there are two types of cooking oil on the market, they are packaged cooking oil and low-grade cooking oil. Low-grade cooking oil has low quality because it only has one filtering that causes the color is not clear and contains FFA higher than packaged cooking oil. Budiyanto, et al. [3], Tangkudung, et al. [4], and Lempang, et al. [5] have also proved that low-grade cooking oil has high FFA content, even exceeding the upper limit of FFA levels set at SNI 01-3741-2013 i.e. 0.3%.

The content of free fatty acids in oil is one measure of the quality of cooking oil, where FFA is expressed by the acid number. The high content of FFA can cause cooking oil to become rancid faster, where FFA can react further into aldehyde and ketone which is an indication of the occurrence of rancidity on cooking oil. In addition to causing rancidity in oil, the high consumption of cooking oil with a high free fatty acid content will increase levels of Low-Density Lipoprotein (LDL) or bad cholesterol in the blood.

The data from the government obtained in 2015 indicates that consumption of low-grade cooking oil is about 70%, and the rest already use packaged cooking oil [6]. The amount of low-grade oil consumption is not matched with the quality of low-grade cooking oil, it is necessary to improve the quality of low-grade cooking oil that meets the SNI standard with low operating cost. In general, the separation of FFA from the oil is carried out by reacting with an alkaline solution or another reactant to form a soap, or it may be called a neutralization process. The process of neutralizing cooking oil is...
usually done by using NaOH or Na$_2$CO$_3$. However, the use of NaOH with too high concentrations can result in saponification of small amounts of triglycerides, thereby reducing the yield of oil. While neutralization with Na$_2$CO$_3$, it produces soap that is difficult to separate, because the formation of CO$_2$ gas released from carbonate so as to cause foam in the oil [7]. In addition, when viewed in terms of green chemistry, the neutralization process is still using reagents that are toxic.

Based on that, the alternative to remove FFA from low-grade cooking oil is needed, where the decrease of FFA content in low-grade cooking oil using adsorbent is considered simple, cheap, and efficient. One interesting material to be developed as an adsorbent is a natural zeolite that has a large surface area and high selectivity. However, natural zeolites have some disadvantages, due to the irregular impurity and structure of the aluminosilicate framework. The presence of such impurities can reduce the activity of zeolites as adsorbents. To increase the adsorption capacity of natural zeolite, the activation will be done physically and chemically.

Widayat and Haryani [8] used natural zeolites that are only physically activated (crushed) in the study of acid number reduction, peroxide number and absorbance in the process of refining used cooking oil. Handoko et al [9] also improved the quality of cooking oil by using activated natural zeolite. In his research, adsorption was performed with two types of active zeolites, namely NZA and H5-NZA. NZA is a natural zeolite that is physically activated (crushed and heating) and chemically by using HF and HCl acid solutions. While H5-NZA is calcined NZA in Muffle Furnace (calcination without nitrogen gas) followed by a hydrothermal process, calcination with nitrogen gas and oxidation with oxygen gas. Astuti [10] decreased FFA of palm oil (CPO) using natural zeolite of Lampung which was activated using HCl solution.

The prediction of the interaction between FFA and surface of adsorbent delivered by some researchers [9] [11] states that the carboxyl group in FFA interact with the active side of the adsorbent so that FFA can be absorbed on the adsorbent. The active side of the zeolite that can interact with the FFA molecule is the hydroxyl group which is the Bronsted site and the cations contained in the silica-alumina framework of zeolite.

Acid-activated zeolites such as HCl or H$_2$SO$_4$ will undergo a dealumination process, i.e. the process of reducing the alumina atoms from the zeolite framework causing an increase in the Si/Al ratio and the acidity of the zeolite. While base activation causes bond dissolution due to Si extraction from the zeolite framework (desilication) resulting in a decrease of Si/Al ratio in zeolite. Zeolites with low Si/Al ratios tend to be more hydrophilic [12]. Treatment with acids on zeolites is also shown to cause the zeolite to become more hydrophobic so that the adsorption capacity of the polar compound will decrease [13]. The carboxyl group is a functional group having polar properties, so if the active side of the adsorbent is hydrophilic then FFA can be absorbed optimally. In this study comparing the adsorption power of FFA in natural zeolite without activation and that activated with HCl and NaOH, where the active natural zeolite having better adsorption will be determined the optimum condition and its equilibrium constant.

2. Methods
2.1. Activation of Natural Zeolite
The natural zeolite from Klaten was washed with distilled water periodically, then decanted and dried in an oven at 100 °C. Natural zeolite was then washed, crushed, and sieved with 100-mesh filtration. Natural zeolite powder was activated with 1 M HCl and NaOH solution with stirring for 24 hours at 25 °C. Active natural zeolite washed with distilled water to neutral and calcined at 400 °C for 3 hours.

2.2. FFA Adsorption Using Activated Natural Zeolite
Natural zeolite and activated natural zeolite were mixed with low-grade cooking oil in a vial bottle with 2:8 ratio and put in a shaker. IT was mixed in a shaker for 5 hours at 25 °C. Samples of adsorbed low-grade oil were then taken for analysis of their FFA amount. The better zeolite in having FFA adsorption was analyzed equilibrium by adsorption on low-grade cooking oil with a variation of acid/base solution concentration and adsorption temperature (25 °C, 40 °C, 80 °C).

2.3. Analysis
2.3.1. Analysis of free fatty acid content (% FFA)

The free fatty acid amount was determined by titration of an alcoholic oil solution. A one-gram sample of low-grade cooking oil is weighed in Erlenmeyer and added with neutral ethanol and 3 drops of PP indicator, then heated to boiling on an electric heater. The sample solution is titrated with 0.01 M NaOH solution until the color change from clear to pink and it is not lost for 30 seconds. The free fatty acid content is calculated by the following calculations

\[
\%\text{FFA} = \frac{M_{\text{NaOH}}V_{\text{NaOH}}M_{\text{FFA}}}{m_{\text{sample}}} \times 100\%
\]

where:
\begin{align*}
M_{\text{NaOH}} & : \text{NaOH concentration (M)} \\
V_{\text{NaOH}} & : \text{Volume of NaOH (mL)} \\
M_{\text{FFA}} & : \text{The molecular weight of FFA (oleic acid = 282 g/mol)} \\
M_{\text{sample}} & : \text{Sample weight of low-grade cooking oil}
\end{align*}

2.3.2. Analysis of isothermal adsorption

The data obtained from the research were FFA concentrations at equilibrium \(C_e\), and the \(q_e\) value (fraction of FFA adsorbed on the pore surface of zeolite) can be calculated using the following equation

\[
q_e = \frac{V(C_0-C_e)}{m}
\]

Then make a plot between \(C_e\) and \(q_e\) to get the isothermal adsorption curve. The obtained graph was compared with the equilibrium equation used to obtain an isotherms adsorption model which according to the experiment. The determination of the isothermal adsorption model is performed by comparing the relative coefficient of each isothermal adsorption linear graphics.

3. Results

3.1. Characterization of Natural Zeolite

Character changes after treatment of both thermal and alkaline activation were proved by characterization methods using FT-IR and EDX instruments. The spectra of infrared spectroscopy result against natural zeolite without activation, thermal activation and acid-activated are shown in Figure 1.

![Infrared Spectra of (a) No Activation, (b) Acid Activated and (c) Base Activated Natural Zeolite](image)

It can be seen that there are some major absorptions that arise as a result of the vibration of the functional groups in samples of natural zeolite. In the spectra of natural zeolite, there is an absorption on the wavelength 462.92 cm\(^{-1}\) indicating the presence of Si-O-Al vibration, whereas in the spectra of acid and base activated natural zeolite has shifted to 470.63 and 455.20 cm\(^{-1}\). The shift proves that there is a change of character of Si-O-Al in the framework of natural zeolite where the activation process is capable of causing desillation and dealumination reactions on the aluminosilicate structure.
Interpretation of the covalent bonds of the functional groups composing the natural zeolite framework is presented in Table 1.

| Wave Number (cm\(^{-1}\)) | Interpretation of Vibration Absorption Type from Functional Group |
|---------------------------|---------------------------------------------------------------|
| 462.92                    | Si-O-Al                                                      |
| 794.67                    | Si-O                                                        |
| 1211.29                   | TO\(_4\) internal asymmetric stretch vibration               |
| 1049.28                   | Si-O-Si                                                     |
| 3448.72                   | stretch vibration of O-H from H\(_2\)O, Si-OH and/or free OH |

The change of Si/Al ratio is determined by analysis using Electron Dispersion X-ray Spectroscopy (EDX). This technique of analysis was performed to detect the composition of the elements contained in the sample of zeolite. By characterization of Si and Al elements contained in natural zeolite structure using EDX, data of Si/Al ratio change on natural zeolite before and after activation shown in Table 2. It can be seen that in HCl activation there is an increase of Si/Al ratio, whereas at NaOH activation decreased Si/Al ratio.

| Adsorbent              | Si/Al Ratio of Natural Zeolite before and after activation |
|------------------------|-----------------------------------------------------------|
| Natural Zeolite        | Si/Al                                                     |
| No Activation          | 7.599                                                     |
| HCl activated          | 8.128                                                     |
| NaOH activated         | 6.788                                                     |

### 3.2. Adsorption of FFA with Natural HCl and NaOH Activated Zeolite

In this study, free fatty acids on low-grade cooking oil were adsorbed using natural zeolites that had not been activated, and which were activated using HCl and NaOH. The results of free fatty acid content analysis before and after the adsorption process are shown in Table 3.

| Adsorbent   | FFA content (%) before adsorption | FFA content (%) after adsorption |
|-------------|-----------------------------------|----------------------------------|
| Natural Zeolite | 0,4                               | 0,33                             |
| ZAA HCl 1 M   | 0,4                               | 0,2                              |
| ZAA NaOH 1 M  | 0,4                               | 0,15                             |

In Table 3 it can be seen that the greatest decrease in FFA content in low-grade cooking oil is by using activated NaOH zeolite as the adsorbent. Decreased amount of FFA with NaOH activated zeolite can reach up to 62.5%, whereas with natural zeolite without activation and HCl activated zeolite has the percent decrease only 17.5% and 50%. Natural zeolites are a porous natural mineral that has a large surface area and high selectivity. However, natural zeolites have disadvantages, due to the impurity and the irregular structure of alumina-silicate framework, the adsorption capacity of natural zeolite was very low. The existing impurities of organic, inorganic and water molecules in the natural zeolite cover the active site on the pore surface so that the adsorbate molecule cannot be absorbed. This is evidenced by the low FFA adsorbed on natural zeolite without activation. Activation zeolite by the acid solution can lead to dealumination where the Si/Al ratio will increase, and the zeolite becomes hydrophobic. While natural zeolite which is activated with a base can cause desilication where the ratio of Si / Al will decrease, and zeolite become more hydrophilic. Free fatty acids are carboxylic compounds which are having a polar side, that is in the carboxyl group (-COOH) which also is electropositive (acid) [14]. Based on this it can be explained that the FFA will be more interested in the surface of hydrophilic
adsorbents, which in this study is a natural zeolite that is activated with NaOH base solution. The Prediction of interactions between FFA molecules with the polar zeolite side is shown in Figure 2.

![Figure 2 The Prediction of interactions between FFA molecules with natural zeolite](image)

3.3. Adsorption of FFA with NaOH Concentration Variation for Natural Zeolite Activation

It is known that the NaOH activated natural zeolite has a better adsorption capacity against FFA compared to natural zeolite without activation and activated natural zeolite by HCl. A variation of NaOH concentration was performed to determine the optimum concentration for the activation of natural zeolite. The effect of NaOH concentration on the FFA adsorption process in low-grade cooking oil is shown in Figure 3.

![Figure 3 The effect of variation NaOH concentration on decrease of FFA amount](image)

The results are shown in Figure 3 state that the optimum concentration of NaOH for the activation of natural zeolite is 0.75 M. It can be seen that the higher the NaOH concentration the more FFA molecules adsorbed on the zeolite pore, which is indicated by the less FFA content contained in the low-grade cooking oil. However, at concentrations of 1 M and 1.25 M NaOH levels of FFA in low-grade cooking oil after adsorption increased again. Concentrations of 1.0 and 1.25 M have made the viscosity of the NaOH solution to be very high or become more viscous so that the diffusivity of the solution into the pores of the zeolite will decrease. Decreasing the diffusivity of NaOH solution into the pores causes a lot of impurities in the pores so that the zeolite surface area will decrease and cause the adsorption power to be small [15]. In addition, the activation of natural zeolites with high NaOH concentrations may result in deformation of structural deformation structures or substantial loss, i.e. the presence of a small portion of Al^{3+} that is detached due to the high concentration of NaOH resulting in decreased micropore surface area.

3.4. Analysis of isothermal adsorption

The isothermal adsorption data is expressed as the amount of adsorbate absorbed by the adsorbent as a function of concentration and temperature so that in this research isothermal adsorption analysis is used initial concentration of FFA and temperature as an independent variable. The adsorption equilibrium
depends on the interaction between the adsorbents (polar, non-polar, hydrophilic, hydrophobic, etc.) and operating conditions such as temperature, pressure and concentration [16], while the adsorption capacity of the adsorbent involves the interaction of 3 factors, i.e. the concentration of adsorbate in fluid, the concentration of adsorbate in solids and system temperature [17].

The isothermal adsorption is the relation of the number of molecules was absorbed in the adsorbent with the concentration absorbate on the fluid. Many isotherms adsorption models have been found to model a variety of adsorption equilibrium. Theoretical models are used to approach the experimental results from theoretical concepts. To evaluate the adsorption data, an appropriate isotherm equation is required for an adsorption system. From some existing isotherms equations, each has its limitations. In this research used some isotherm equations include:

*Henry’s Isothermal Adsorption Model*

\[ q_e = H \cdot C_e \]  

*Langmuir’s Isothermal Adsorption Model*

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

*Freundlich’s Isothermal Adsorption Model*

\[ q_e = K_F C_e^{\frac{1}{n}} \]  

Based on FFA concentration data at equilibrium \( (C_e) \) it can be obtained \( q_e \) (Equation 2) and plot isothermal adsorption curve based on isothermal adsorption model Henry, Langmuir and Freundlich presented in Figure 4. The correlation coefficient obtained from the three isotherms model, on the adsorption of FFA using NaOH-activated zeolite shows that the experimental data is closest to the Freundlich model. The Freundlich approach indicates that the heterogeneous surface of the heterogeneous activated zeolite has an unequal FFA adsorption capability. This may occur because there are two possible interactions between the FFA molecules and the active site on the pore surface of the zeolite, i.e. with the hydroxyl groups at the Bronsted site and Na\(^+\) ions. In addition to indicating the occurrence of heterogeneous adsorption, the Freundlich model approach also indicates the formation of a multilayer coating on the zeolite pore surface. Long carbon chains in FFA molecules are nonpolar, allowing to have an affinity with the nonpolar side of other FFA molecules which then form a multilayer coating.

The Freundlich adsorption isotherm model is the closest approximation of the FFA adsorption equilibrium data using the alkaline activated natural zeolite, where Freundlich’s frequency linearization is performed to obtain the equilibrium constant value shown in Table 4.

| Parameter Value of Linear Equations Model of Freundlich Isothermal adsorption |
|---------------------------------|--------|--------|--------|
| Parameter          | Temperatur Adsorpsi | 25 °C | 40 °C  | 80 °C  |
| \( R^2 \)           | 0.9492    | 0.9271  | 0.9628 |
| \( K_F \)           | 0.5873    | 0.9629  | 0.8052 |
| \( n \)             | 1.2931    | 1.2297  | 1.3706 |

The \( K_F \) value shows the active natural zeolite capacity, while \( n \) is an indicator of the efficiency of the adsorption process at various FFA concentrations. Increasingly larger values of \( n \) indicate that more and more zeolites absorb FFA with rising temperatures.
4. Conclusions
The adsorption capacity of FFA in low-grade cooking oil using NaOH activated zeolite is better than natural zeolite without activation and HCl activated natural zeolite which can achieve decrease of FFA content up to 62.5%. The optimum concentration of NaOH in the activation of natural zeolite as FFA adsorbent in low-grade cooking oil is 0.75 M. The free fatty acid adsorption equilibrium model on the NaOH activated zeolite follows the Adsorption Isotherm Freundlich Model with equilibrium constant is 0.5873; 0.9629 dan 0.8053 and n value is 1.2931; 1.2297 dan 1.3706.

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