Indonesian Natural Zeolites as potential Adsorbent in Waste Cooking Oil Regeneration

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Abstract—This study aimed to know the effect of zeolite modification toward density and water content of waste cooking oil after adsorption and to know the optimum temperature of waste cooking oil adsorption using natural zeolite. Natural zeolite was prepared by dipping in aquadest for 1 hour then dried in oven at 120°C for 2 hours. Zeolite was activated by dipping in HF solution (1%v/v) with volume ratio 1:2. Sample was filtrated and washed using aquadest followed by calcinations at 500°C. Adsorption process was done in batch system at various temperature (50, 60, 70, 80, 90 and 100°C). After adsorption, waste cooking oil was separated from zeolite then was characterized to determine the density, % free fatty acid (FFA), and water content. The results showed that: modification zeolite using HF caused FFA and water content of waste cooking oil decreased. The optimum temperature of waste cooking oil adsorption was 70°C with value of density, % FFA and water content respectively were 0.8593 g/mL, 0.056%, 0.200%

Keywords: adsorption, waste cooking oil, zeolite

I. INTRODUCTION

During frying, cooking oil made of palm oil is heated in the presence of air. This process causes degradation reaction in cooking oil. The degradation reaction is caused by heat, oxygen from the air, and water. Hydrolysis occurs in the presence of water. The reaction yield free fatty acids, monoglycerides, diglycerides and glicerols. Oxidation occurs in the presence of oxygen. Some carbyol compounds are formed in this process [1]. The degradation reaction will make the quality of the oil drops and cause bad effect to humans. Several parameter is usually used as quality indicator of the oil. The parameter are free fatty acid, iodine value, peroxide value, viscosity, specific gravity.

Waste cooking oil can flow to the water environment and cause environmental problems so it is important to reduce amount of waste cooking oil [2,3]. The better method to reduce amount of waste cooking oil is make another product from waste cooking oil for example biodiesel. Some treatments is needed to increase quality of waste cooking oil before the waste cooking oil is changed to another product.

Adsorption is widely used to increase quality of waste cooking oil. This method is relatively easy and cheap so it brings economical benefit. Indonesian natural zeolite can be used as adsorbent. Natural zeolites is easily found in Wonosari Indonesia so the price is low. Unfortunately the natural zeolites contain some impurities. Some efforts is needed to increase the quality of natural zeolite. The activation process should be done before use natural zeolite as adsorbent. Activation using acids is commonly used in activation process. For nonpolar adsorbate such as waste cooking oil it is important to increase the Si/Al ratio of natural zeolite due to better interaction of adsorbate-adsorbent.

II. EXPERIMENTAL PROCEDURES

A. Preparation of Zeolite

Natural zeolite was obtained from Wonosari Indonesia. The zeolite samples were prepared in 100 mesh particle size then washed with aquadest and dried in oven at 120°C for 2 hours. Zeolite was calcined at 500°C for 4 hours then ZA was obtained. ZA was immersed in 1% v/v HF for 10 minutes; using zeolite : acid ratio = 1: 2 v/v. After that, the mixture was washed with aquadest to remove excess acids. The mixture was dried in oven at 120°C for 2 hours and calcined at 500°C for 4 hours then ZA-HF was obtained.
B. Characterization of zeolite

Determination of Si/Al ratio. The values of Si/Al ratio were determined by AAS.

Determination of Acidity. Acidity of zeolite was determined using gravimetric method using ammonia as adsorbate. Sample were placed in a crus and heated at 120°C for 2 hours. The weight of the sample was measured and noted as W. Sample was placed in vacuum dessicator ad let ammonia flow into dessicator until the dessicator was full of ammonia. Sample was kept in that condition for 24 hours. The weight of the sample was measured (W1). Acidity was amout of ammonia which was adsorbed for a gram sample.

\[ \Delta W = (W1 - W) \text{ (mgram)} \]

\[ \text{acidity} = (\Delta W / M_{NH_3}) \text{ mmol} \]

where \( \Delta W \) is weight of adsorbed ammonia, \( M_{NH_3} \) is Molecular weight of ammonia

C. Adsorption of Waste Cooking Oil

Waste cooking oil was obtained from fried food producer in Yogyakarta Indonesia. Fifty grams of waste cooking oil and 10 grams of various zeolite (ZA and ZA-HF) were mixed in beaker glass. The mixture was heated and stirred at various temperature (50,60,70,80,90,100°C). Adsorption was carried out for 60 hours. After cooling at room temperature, the mixture was poured into funnel with filter paper (whatman 42) under vacuum.

D. Characterization of Waste Cooking Oil

Density \((\rho)\). Density of water cooking oil was measured using picnometer.

\[ B = B_2 - B_1 \]

\[ \rho = \frac{B}{V} \]

Where \( \rho \) is density (g/mL), \( B_1 \) is mass of empty picnometer, \( B_2 \) is mass of waste cooking oil + picnometer, \( V \) is volume of waste cooking oil [4]

Water Content. Water content determined by hot plate method. Five grams until 20 grams waste cooking oil in beaker glass was stirred and then heated using hot plate. The beaker glass was rotate slowly. Temperature of waste cooking oil less than 130°C. Waste cooking oil was cooled at room temperature after there was no gas came out from the oil. Weight of waste cooking oil was measured [5].

\[ \text{Water content(%) } = \frac{\text{lost mass (g) x 100}}{\text{Mass of initial sample (g)}} \]

Free Fatty Acid (FFA). About 28.2 of well mixed oil added with 50 mL alcohol and phenolphthalein. The mixture is then titrated with 0.1 N NaOH with vougorous shaking until a permanent faint pink appeared and persisted at least for 1 minute

\[ \% \text{FFA} = \frac{V \times \text{NaOH} \times N \times \text{NaOH} \times M}{m \times 1000} \times 100\% \]

Where \( m \) is the mass of the test portion, \( N \) the normally of NaOH , \( V \) the volume of NaOH consumed, in mililiters, \( M \) the molecular weight of free fatty acid [5]

III. RESULT AND DISCUSSION

A. Si/Al ratio of zeolite

Table 1 showed that Si/Al ratio of ZA-HF was higher than Si/Al ratio of ZA. It means that modification using HF affect Si/Al ratio. After immersed in HF solution, the Si/Al ratio of natural zeolite was higher. HF reacted with zeolite caused the framework Al was extracted from zeolite. This treatment lead to the increase of Si/Al ratio.

<table>
<thead>
<tr>
<th>Nama Sampel</th>
<th>Keasaman (mmol/g sampel)</th>
<th>Rasio mol Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA</td>
<td>699,941</td>
<td>4,950</td>
</tr>
<tr>
<td>ZA-HF</td>
<td>755,529</td>
<td>5,132</td>
</tr>
</tbody>
</table>
Modification of zeolite to get higher Si/Al ratio was important for hidrophobic adsorbate. If the Si/Al ratio was high, the charge density of the zeolite framework was low, due to insufficient number of cations within the pore system[7]. This condition caused hidrophobic molecule has stronger interaction with zeolite. Fig. 1 showed the reaction of zeolite with HF solution.

![Figure 1. Dealumination zeolite using HF](image)

### B. Acidity of Zeolite

The term acidity here was total acidity consist of Lewis acid and Bronsted acid. Table 1 showed that dealumination using HF caused acidity of zeolite increase from 699,411 to 755,529 mmol/g. A decrease in the Al content (rise in Si/Al) decreased the charge density of the anion framework of zeolite. Thus, the hydroxyl groups were subjected to less intense interaction with the framework, which should decrease the force constant of the OH oscillator and facilitate the deprotonation i.e enhance the acidity strength[7]. Lewis acid sites in zeolite might occur as three fold-coordinated aluminum or silicon and/or extraframework aluminum. Lewis sites formed upon dealumination of zeolite[7]. The increase in acidity of zeolite was important because the acid site of zeolite act as active site which did interaction with adsorbate.

### C. Density

Waste cooking oil which was used in this research had dark colour. The colour became clearer after adsorption using zeolite (ZA and ZA-HF). By varying the temperature, density of waste cooking oil was observed (Figure 2 and Table 2). Density of waste cooking oil after adsorption was lower than waste cooking oil before adsorption. Waste cooking oil contain many materials from frying food. After adsorption, the impurities material was adsorbed on zeolite so the density of waste cooking oil was lower than before adsorption. The highest density of waste cooking oil was 0.8944 g/mL. It was reached at 80°C. The lowest density of waste cooking oil was reached at 50°C with density 0.8419 g/mL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature(°C)</th>
<th>Density (g/mL)</th>
<th>FFA (%)</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste cooking oil</td>
<td>70</td>
<td>1.0132</td>
<td>1.297</td>
<td></td>
</tr>
<tr>
<td>Fresh cooking oil</td>
<td>70</td>
<td>0.9700</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>50</td>
<td>0.8716</td>
<td>0.078</td>
<td>4.824</td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>60</td>
<td>0.8593</td>
<td>0.057</td>
<td>0.524</td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>70</td>
<td>0.8944</td>
<td>0.056</td>
<td>0.2</td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>80</td>
<td>0.8607</td>
<td>0.085</td>
<td>0.36</td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>90</td>
<td>0.8624</td>
<td>0.058</td>
<td>0.159</td>
</tr>
<tr>
<td>Oil after adsorption</td>
<td>100</td>
<td>0.8419</td>
<td>0.076</td>
<td>1.213</td>
</tr>
</tbody>
</table>
D. Free Fatty Acid (FFA)

FFA in cooking oil or on the surface of fried food used to predict the life of the food with respect to the development of rancidity. FFA were formed from hydrolysis oil. Water caused hydrolysis oil procedure fatty acid and glicerol. The hydrolysis occured rapidly in the presence of acid, base, enzim, and high temperature[2].

Zeolite activation using HF affected the ability of zeolite to decrease % FFA in waste cooking oil. Value of FFA which was adsorbed on zeolite without activation (ZA) was lower than FFA which was adsorbed on activated zeolite (ZA-HF). Effect of ativation using HF toward %FFA was shown in Fig 3. This result due to better interaction of waste cooking oil and zeolite. Activation using HF lead to higher acidity so zeolite had more active site to interact with waste cooking oil. The activated zeolite also had higher Si/Al ratio so the surface of zeolite was more hidrophobic and suitable for hidrophobic molecule such as waste cooking oil and its impurities.

Figure 3. Effect of Activation using HF toward %FFA

Figure 4 showed that FFA value in adsorption at temperature 50-100°C has occupied SNI 01-3741-2002 (below 0.3 %). The lowest FFA value was reached at 70°C with FFA value 0.056 %. Figure 4 showed that FFA value in adsorption at temperature 50-100°C has occupied SNI 01-3741-2002 (below 0.3 %). The lowest FFA value was reached at 70°C with FFA value 0.056 %. At temperature 50-60°C, FFA value decreased if temperature increased but after 80°C, FFA value increased. For physisorpsi, the increase in temperature caused a decrease in adsorption capacity [8].
E. Water content

Result of this research showed that water content for fresh cooking oil; waste cooking oil before adsorption; waste cooking oil after adsorption using ZA; waste cooking oil after adsorption using ZA-HF respectively were 0%; 11.297%; 6.996%; 3.980% (Table 2). Water in waste cooking oil was adsorbed on zeolite so after the adsorption process the water content decreased. The adsorption ability of zeolite treated with HF was higher than natural zeolite without HF treatment. HF cleaned zeolite pores so the pores were opened and the active sites easily interact with water in waste cooking oil as adsorbate. Without activation using HF some impurities did interact with active sites caused adsorbate was not able to do interaction with active sites.

At temperature 50-90°C, water content decreased with increase in temperature. It means adsorption was better at higher temperature. Increase in temperature means an increase in mobility of the adsorbate molecule and an increase in the number of active sites for the adsorption [9]. With chemisorption, higher temperature could improve performance[8]. The enhancement of adsorption capacity of adsorbate at higher temperature due to enlargement of pore size and activation of zeolite adsorbent[10].

As shown at Fig.6, at temperature 100°C, water content was higher than the water content at 60-90°C. During physisorption, increase in temperature caused desorption rate increase. Species that were physically adsorbed to solid could be released by applying heat[8]. Increasing temperature decreased the adsorption capacity because adsorptive forces between adsorbate and the active sites on the adsorbent surface decreased [11].
IV. CONCLUSION

Modification zeolite using HF caused FFA and water content of waste cooking oil decreased. The optimum temperature of waste cooking oil adsorption was 70°C with value of density, %FFA and water content respectively were 0.8593 g/mL, 0.056%, 0.200%

ACKNOWLEDGMENT

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REFERENCES

[6] AOCS, Official Method And Recommended Practice of The AOCS, 6th ed USA