

THE IMPROVEMENT OF MECHANICAL PROPERTIES OF HYDROGEN FILTER BASED ON NATURAL ZEOLITE FROM PAHAE AND CLAY ADDITION

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ABSTRACT

The application of natural zeolite as a filtration material has resulted in the reduction of mechanical properties. Thus, in improving the mechanical characteristics, it requires an alternative material such as clay. This research aims to investigate the use of clay in improving the hardness property of the composite zeolite-clay. Physical and chemical treatments were performed to activate both zeolite clay which involved temperature at 150°C and acid condition respectively. The mixture of zeolite and clay was performed via mechanical mixing, while the composite was fabricated by using a mold-compressing technique, which was followed by sintering in various temperatures. The results showed that an increase in porosity values and Si/Al ratio was obtained from 3.53 to 3.82, so a medium level of the adsorbent level was achieved. The XRD analysis confirmed that filler clay increased the crystallinity characteristic which improved mechanical properties.

Keywords: Zeolite Pahae, Zeolite Clay, Adsorbent Materials, Hydrogen Based Filter, Mechanical Properties

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INTRODUCTION

The implementation of zeolite as filtering material has been extensively used particularly as water vapor adsorbent^{1,2}. Different types of zeolite have varied characteristics, such as natural zeolite from Pahae, North Sumatera, and it has been reported to have absorption level around 48.05% and 68.05% for 60 mesh and 200 mesh respectively, and the other zeolite from Cikalong has been recorded to have 42.60% and 51.60% for 60 mesh and 200 mesh respectively. Thus, the zeolite from Pahae can be utilized as an alternative material for filtering as it has better water adsorption than that from Cikalong. However, this zeolite has a drawback in the insufficient mechanical feature when it was fabricated in the form of powder.¹ To overcome this issue, a composite filter has been designed in form of solid by adding cacao skins as a filler, however, the hardness level is still low (35 N/m²) even though it has adsorption level for 53.82%.² Therefore, a new composite filter made of new materials consists of improved mechanical and adsorption properties², and zeolite can be utilized as ethanol purification with distilled adsorption.³

One of the materials that can be used to enhance the mechanical (hardness) property is clay.⁴ This material is also an affordable material which has varied characteristics, and it has been widely applied for several purification processes in bleaching vegetable oil, medications, catalyst, textiles, petroleum treatments as well as water filtration.⁵ Meanwhile, clay also is composed of calcium⁶, and it has the ability in enhancing hardness features when it is mixed by other materials such as zeolite. Nevertheless, the clay reinforcement is not only able to improve the mechanical property, but also it can act as fillers to cover the zeolite pores.⁷ In this study, clay usage as fillers to fill the porous structures is proposed. The mixing process that is carried out is investigated to determine the mechanical and adsorption properties. Respectively, the characterizations are conducted by performing the X-Ray Diffraction (XRD), while the morphological characteristics are investigated throughout Scanning Electron Microscope Energy Dispersive (SEM-EDX).

EXPERIMENTAL

This study utilized two materials in fabricating the composite filter, and they were natural zeolite as matrixes collected from Pahae, North Sumatera, and clay as a filler. The amount of zeolite was supplied

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from Pahae, Tarutung, Tapanuli Utara without initial treatments. The chemical reagents were supplied by Mallinckrodt Lab Guard, with analytical grade.

Zeolite and Clay Activation

The zeolite and clay powder were activated by performing chemical treatments by using sulphuric acid (H_2SO_4). First, the amounts of zeolite powder were added by 6% of H_2SO_4 at 70°C for 4 hours within constant stirring. Afterward, some distilled water was added into the mixture to reach pH 7, and then it was heated inside the oven at 105°C for 3 hours. Finally, the dried powder of chemical-activated zeolite was obtained. The same procedure was applied to clay to activate it.

Fabrication of Composite Zeolite-Clay

Activated zeolite and clay was fabricated by performing mixing and sintering process. These two materials were mixed and this mixture was placed inside a shaker Yami 550 cc YM1832. This mixture was then shaken for 10 minutes with varied compositions, and they were 100%: 0%; 95%:5%; 90%:10%; 85%:15%; and 75%: 25% (%w). Then, these mixture samples were added by several drops of distilled water and they were stirred several times. Next, the sample was placed into the moulding of Hydraulic Press Ytd27-200t with 5 tonnes of pressure for 10 minutes, and the same pressing treatments were done for the other compositions. Afterward, the samples were allowed to stand for 1 week in the open air to ensure their dryness which would be ready to be sintering. Finally, the dried samples were placed into a furnace for sintering treatments with 700° , 800°C , and 900°C within 4 hours of holding time. The sintering process was conducted repeatedly for other compositions of samples.

Characterizations

Measurement of Porosity

The investigation of porosity was performed to determine the amounts of sample pores due to their influence in adsorption property. These amounts have a value that is proportional to the characteristics of adsorption which can be considered as a ratio between the amount of pore volume of space and the amount of volume of a solid. The ratio can be determined in the form of percentage as the following equation:

$$\% \text{ of Porosity} = \left(\frac{m_b - m_k}{\rho_{\text{air}} - V_t} \right) \times 100\% \quad (1)$$

Adsorption Characteristic

The ability of zeolite in absorbing water produced by the electrolysis process can be determined through adsorption level tests on the hydrogen filter. Samples were immersed in water for 24 hours, and then they were allowed to stand in the open air for 24 hours. Next, the samples were placed into a water-hydrogen converter instrument equipped with a hydrogen sensor as it is described from the previous study¹.

RESULTS AND DISCUSSION

Porosity Measurements

The measurement of porosity in this study aims to investigate the effects of the diameter sizes of pores on the surface filter based on the different temperatures of sintering. The porosity of the filter was determined by performing weigh measure for both wet mass and dried mass of filter. The following Fig.-1 displays the porosity levels of samples for all varied temperatures of sintering and compositions.

According to Fig.-1 below, the highest percentage of porosity is displayed in a sample with 95%:5% of compositions at 900°C which contributed to 66.23%, while a sample which had only 100% of zeolite contributed a smaller percentage of porosity at the same temperature for 23.10%. In Fig.-1, it also can be seen that at the sintering process of 900°C , three compositions had the highest percentage of porosity among the compositions. However, the smallest percent weight of zeolite contributed to the highest percentage, which implied to the oxygen presence. This also implies the interaction of Silicon and oxygen which produces small hollow spaces in the same sizes or smaller sizes than the structures.⁸ Meanwhile, clay is a soil material that has microscopic and sub-microscopic scales, which let clay to fill zeolite hollow spaces.⁸ However, the use of clay as additive material must concern the composition, and based on the data obtained, the composition with the highest proportion of porosity level was that in the composition of 95%:5%.⁸

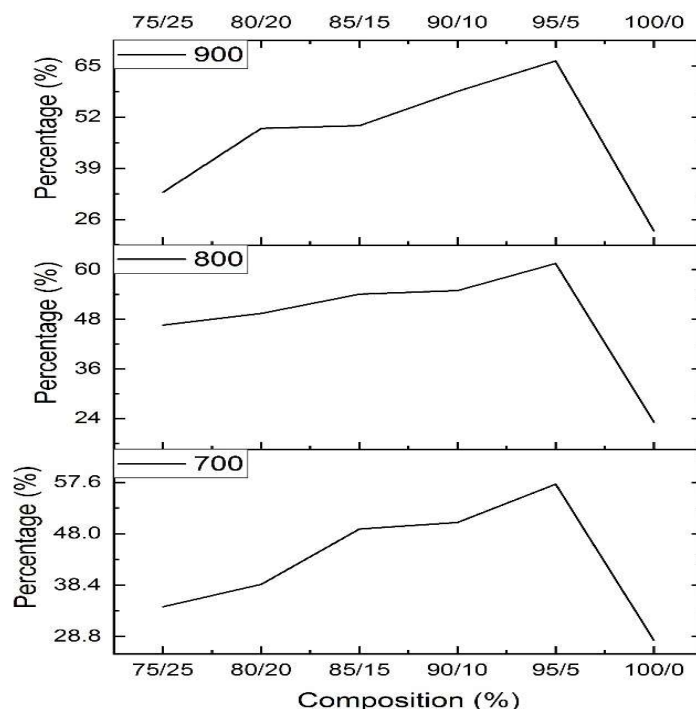


Fig.-1: Comparison of Porosity Percentage for Different Temperature of Sintering

Hardness Test

The investigation of the mechanical property was in the hardness feature. In this study, Hardness Vickers Tokyo instrumentation was performed to measure the hardness characteristic of samples. The clay as a filler is aimed to improve the hardness property which implies to use it in a longer time. As the best temperature of sintering occurred at 900°C, we measured the hardness property only for this temperature. The following Fig.-2 below and Table-1 highlight the hardness value of samples based on the compositions.

Table-1. Hardness Test Results Based on Varied Compositions

No.	Temperature	Composition (Z+C) (%)	Hardness (N/m ²)
1.	900°C	75 Z + 25 C	224.36
2.		80 Z + 20 C	205.88
3.		85 Z + 15 C	187.19
4.		90 Z + 10 C	143.09
5.		95 Z + 5 C	136.61
6.		100 Z + 0 C	136.46

Figure-2 illustrates an increasing trend based on clay composition in every sample to the hardness property of samples. Based on the line graph, the highest hardness value occurred in the composition of 75%:25% which accounted for 224.36 N/m², and the lowest hardness value was in the sample with no clay within the composition for 136.41 N/m². This was caused by the rising bulk of clay which affects the sizes of pores diameters of composites to be denser.⁹ On the other hand, both clay and zeolite have almost similar chemical compositions, in which clay is composed by Al₂Si₂O₅(OH) with tetrahedral structure¹⁰, and it has been reported to contain mostly of silicon dioxide with percentage up to 50%, followed by aluminum oxide for over 30%, and water.¹¹

Zeolite also has a tetrahedral structure which is mainly composed of AlO₂, AlSi₂, and H₂O, and it contains another metal oxide including SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O, and K₂O.⁶ However, clay has more stabilized chemical and mechanical properties which are better to be used as filler in forming physical and chemical interaction among elements within zeolite.^{12,13} In this study, the usage of clay as reinforcement into zeolite increased the density, the physical interaction and chemical bonds, and hardness property, so in the land, it enhances the hardness property of soil to be optimum.¹⁴

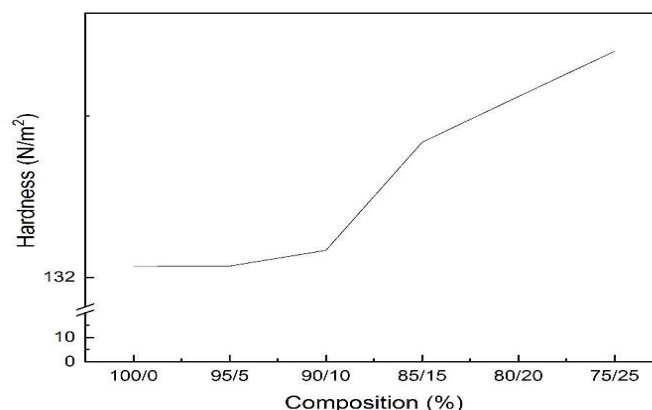


Fig.-2: Hardness Measurements of Samples at 900°C

SEM-EDX Characterisations

SEM results confirmed that at 900°C, both zeolite and clay were distributed evenly. Based on the photographic image of SEM, the diameter of the pores observed on the surface of the samples had different sizes of pores. The diameters of samples in five variations were 4.764 μm for 75%:25%, 4.764 μm for 80%:20%, 3.667 μm for 85%:15%, 3.464 μm for 90:10, 2.805 μm for 95%:5%, and 1.822 μm for 100%:0% in average. Samples added by filler increased the diameter of the pores compared to those without clay as a filler.

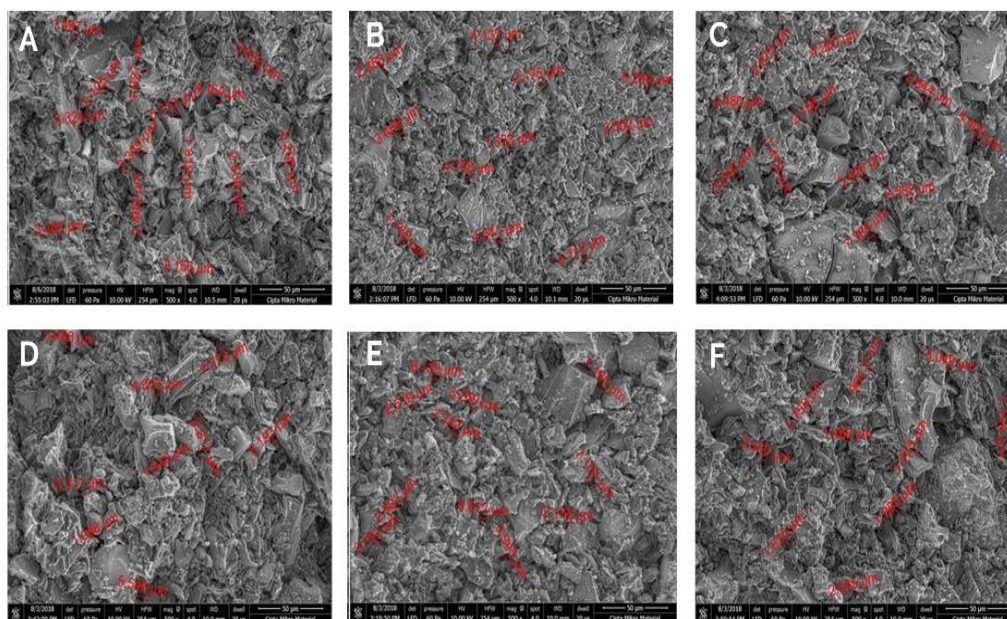


Fig.-3: SEM Microstructure Analysis of Samples; (A) 75/25; (B) 80/20; (C) 85/15; (D) 90/10; (E) 95/5; (F) 100/0

Figure-4 shows the elemental composition of all samples, and mostly they were contained by oxygen, silica, aluminium, iron, potassium, calcium, carbon, sodium and magnesium. The SEM-EDX also confirmed that oxygen was the highest element in all samples, and this suggested the presence of metal oxides which indicated the characteristics of zeolite. Such as silicon oxide (SiO_2) affected the pores into a smaller size which were distributed evenly on the surface as it is indicated by Fig.-4E. This results also implied to the ability of oxygen in generating uniform small holes so that they could provide adsorption ability to the samples.

Based on the element composition, it can also be determined the ratio of Si/Al as it is influenced by the adsorption level of samples.⁵ The EDX results for all five samples, the ratio of Si/Al were accounted for

3.55 (75%:25%), 3.75 (80%:20%), 3.82 (85%:15%), 3.82 (90%:10%), 3.53 (95%:5%). These ratios ranged from 2-5, which is classified to be intermediate adsorbent with modernite types of zeolite.⁵

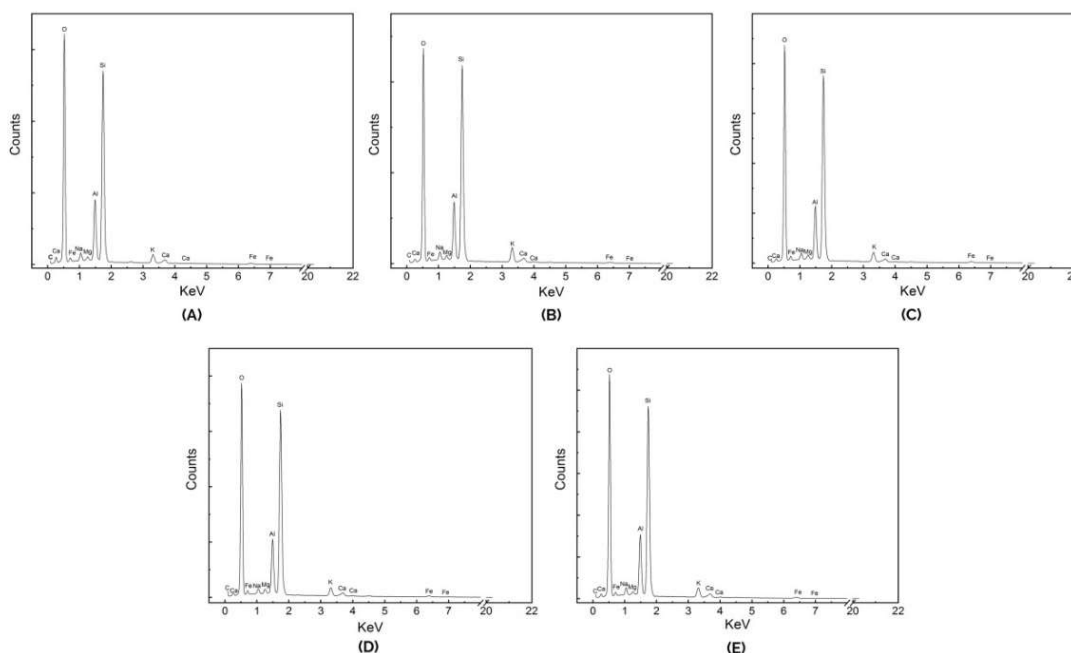


Fig.-4: SEM-EDX Elemental Analysis of Samples (A) 75/25%; (B) 80/20%; (C) 85/15%; (D) 90/10%; (E) 95/5%

XRD Analysis

Figure-5 displays the XRD results of samples. In zeolite, no peak intensity was occurred implying to the amorphous phase. The diffraction spectrum of natural zeolite has been reported to be primarily dominated by amorphous phase.¹⁵ The previous study also has suggested that natural zeolite from Lampung has been reported still to be dominated by amorphous phase.¹⁶

Based on Fig.-5 too, the presence of peak intensity occurred in 30° - 40° which indicated an amount of crystallinity within the spectrum of clay. When the samples were mixed, the peaks shifted, and the peak intensities were reduced. The samples with composition of 75%:25% had peak around 26.5699° ($d = 3.35213 \text{ \AA}$) with wavelength 1.53996 \AA , while the 95%:5% of composition contributed for wavelength 1.54054 \AA with peak around 20.8148° ($d = 4.26413 \text{ \AA}$). The other compositions which are 80%:20%, 85%:15%, and 90%:10% contributed for peaks respectively 26.6033° , 26.4562° , and 22.1395° . The clay reinforcement implies the increase of crystallinity as clay has a higher crystallinity phase compared to those in the zeolite, which also improved the mechanical properties.

The XRD and SEM-EDX results also confirmed that the highest compositions of elements are Al, Ca, Na, O, and Si, formed into andesine, quartz, quartz low. As the increase of clay affected the crystallinity of the samples, it can be determined that the samples of 75%:25% had andesine, quartz and quartz low for 60%, 27.1%, and 12.9% respectively. The results for samples 95%:5% showed 93.9% of anorthoclase with forming elements such as Al, Si, Na, K, O, and Quartz (6.1%) and SiO_2 .

Adsorption Test

In this study, the improvement made by clay as a reinforcer is determined to investigate its ability as an adsorbent. Thus, adsorption ability was performed to measure which samples with the high mechanical property have the ability in adsorbing water vapor. The following Figure 6 below illustrate the adsorption characteristic of samples.

Based on Fig.-6, the most optimal samples that were able in adsorbing was that in a composition of 95%:5%. In this composition, clay contributed to the lowest amount, suggesting that the decrease of adsorption ability occurred due to the increase of clay amount. However, this also implied the smallest value of hardness due to the low intensity of peak based on the XRD analysis. Regarding the control sample which was zeolite,

the adsorption level of the composition 95%:5% was higher than it, suggesting that the porosity proportion contributed an important role as it was higher in this composition too. The zeolite-based filter was able to absorb 822 ppm, while in the zeolite filter with clay filler, the absorption value was 1095.15 ppm. The optimal composition as a filler was obtained at a composition of 95%:5% wt. at 900°C of sintering temperature.

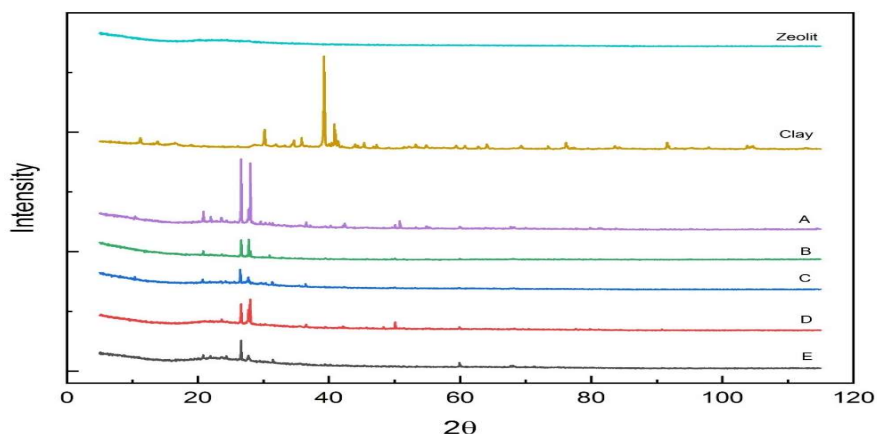


Fig.-5: XRD Analysis of Samples Zeolite, Clay, (A) 75/25%, (B) 80/20%, (C) 85/15%, (D) 90/10%, (E) 95/5%

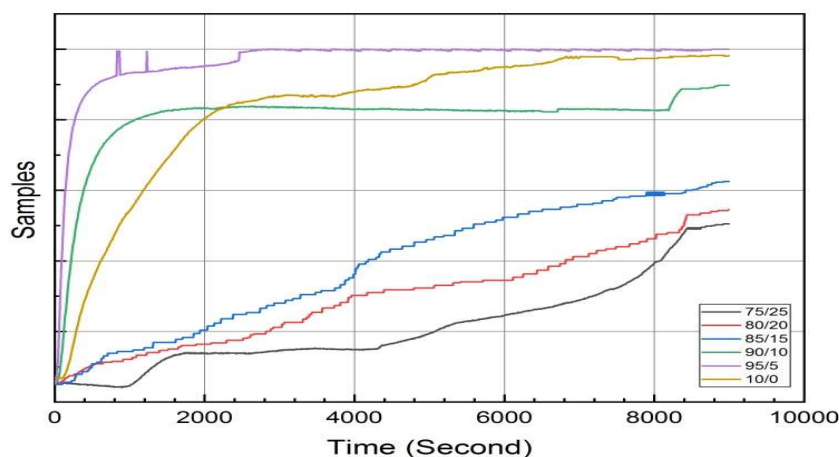


Fig.-6: Adsorption Tests for Samples

CONCLUSION

The use of clay as a filler was able to improve the mechanical property of the composite. From the porosity values from each sample, and the morphological characterizations confirmed the even distribution between zeolite and clay which can increase the diameter of the pores. The SEM-EDX analysis also showed that ratio Si/Al increased which classifies the composite into intermediate adsorbent, and the crystallinity values of samples reinforced by clay improved the hardness characteristics from the XRD analysis. Moreover, the best composition for adsorbing criteria was a sample with the lowest amount of clay, and there was a significant difference.

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