Fly Ash zeolite

by Teguh Kurniawan

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Conversion of Indonesian Coal Fly Ash into Zeolites for Ammonium Adsorption

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ABSTRACTS

The synthesis of zeolite from fly ash has been investigated. The method used for the synthesis of zeolite in this research is the smelting method followed by a hydrothermal process. The zeolite synthesis was characterized using XRD and SEM. Based on the research results, it was found that fly ash can be synthesized into Na-P zeolite with morphology like coral, and cancrinite zeolite and sodalite with morphology like seaweed. The optimum condition for zeolite synthesis occurred at a hydrothermal process at 160°C for 24 hours with the formation of cancrinite zeolite. The synthesized zeolite resulting from the separation of 4 M of HCl formed Na-P zeolite and silica phase crystals which had the most optimum absorption of ammonium with an adsorption capacity of 18.025 mg/g with the adsorption kinetics model in the form of pseudo-second-order with a constant rate of 0.557 h^{-1}.

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1. INTRODUCTION

Fly ash released by coal-fired power stations is a kind of solid waste, and its disposal has become a huge concern with substantial environmental consequences (Feng *et al*., 2018). Fly ash is mostly made up of amorphous phases of vitreous and crystalline phases such as mullite and quartz, as well as a trace of unburnt carbon. The amount of fly ash in the globe has been expanding at an alarming rate because of the fast expansion of the power industry. The majority of coal fly has been used in construction materials and cements, where it may bring both technological and economic benefits, but it is a real environmental issue that the remainder of fly ash is disposed of in landfills (Iqbal *et al*., 2019). This suggests that the development of improved recycling technologies for safely handling fly ash is required (Haryati *et al*., 2014).

In recent years, the synthesis of zeolite has emerged as a technologically and commercially feasible use for fly ash. The major constituents of fly ash are silicon and aluminum, which vary little depending on the kind of volcanic rock, allowing for the synthesis of zeolite from fly ash (Amoni *et al*., 2019). Zeolites are used in a variety of agricultural compounds that are used in huge amounts for water purification, soil enhancement, and other purposes. The hydrothermal synthesis of zeolite from fly ash is a well-known technique that has been studied by numerous researchers.

Holler and Wirsching examined fly ash as a starting material for hydrothermal synthesis of different zeolites in 1985 (Fukasawa *et al*., 2018). Following that, several studies were carried out to convert fly ash to zeolites. Essentially all of the proposed techniques are based on the dissolution of Al-Si from fly ash phases with alkaline solutions and subsequent precipitation of zeolitic components. In addition to the conventional hydrothermal alkaline processing, there are other methods for synthesizing zeolites, including the two-step technique (alkali fuse preceded by the hydrothermal process), microwave-assisted process, and sodium aluminate solution led by zeolite synthesis (Querol *et al*., 2002). The research results showed that the various methods enhanced zeolite efficiency and minimized crystallization time. Synthesizing zeolite with fly ash is simple, easy to manage, and cheap. On the other hand, conventional technologies are expensive, wasteful, and inefficient.

Zeolite materials are of substantial essential and industrial relevance and are frequently as commercial adsorbents and catalysts (Panek *et al*., 2021). Zeolites are porous aluminosilicates with crystalline structures generated by tetrahedral $(SiO_4)_4$ and $(AlO_4)_5$. Zeolites are thermodynamic phases of minerals. As the synthesis processes progress, new zeolites are created by varying temperatures, crystallization length periods, and alkali concentrations to varied chemical compositions (Ren *et al*., 2020). Many studies have concentrated on utilizing fly ash as a source of silicon and aluminum to produce various zeolites, including zeolite P, zeolite X, and sodalite. This research examined the experimental synthesis of zeolite from fly ash using hydrothermal treatment (Panitchakarn *et al*., 2014). The calcination temperature and acid leaching conditions were considered during the pretreatment stage of fly ash (Liu *et al*., 2018). The effects of alkali hydroxide concentration, reaction temperature, and Si/Al ratio on the generation of zeolite products were studied in a hydrothermal process. The characterizations used are SEM, and x-ray powder diffraction (XRD).

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2. METHODS

2.1. Materials and Reagents

The coal fly ash used in this research for the synthesis of zeolite taken from the Suralaya PLTU as a source of SiO_2 and Al_2O_3, distillate water (H_2O), hydrochloric acid (HCl), and NaOH pellets (99.9% p.a), NH_4Cl, and universal pH paper.

2.2. Pretreatment of Fly Ash

The fly ash sample was ground using a mortar morselin and sieved using a 200 mesh sieve so that the size was uniform. To remove the water content contained in the fly ash, the fly ash was heated in the oven at a temperature of 110°C for 3 hours.

2.3. Zeolite Synthesis

The zeolite synthesis from fly ash was carried out using the smelting method followed by the hydrothermal crystallization process. The smelting process is carried out by reacting fly ash with NaOH, which decomposes silica and alumina into sodium silicate and sodium aluminate. In the smelting process, aluminate and silicate salts will be produced as a source of Si and Al used for zeolite synthesis. The smelting reaction occurs between the components of fly ash (SiO_2 and Al_2O_3) with NaOH.

In this study, the result of smelting was in the form of a brown to gray solid, which was initially black from fly ash. **Figure 1** shows fly ash has been a smelting reaction between the components of SiO_2 and Al_2O_3 in the fly ash, using reacts with NaOH to form an alkaline salt in the form of sodium silicate and sodium aluminate.

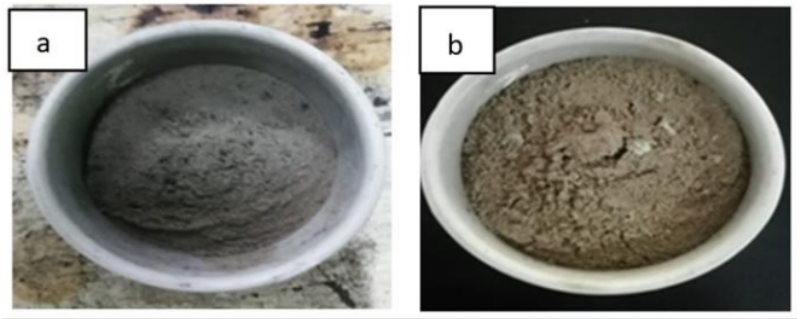

Figure 1. Photograph images of samples: (a) before and (b) after the result of the smelting process.

The next step is fused fly ash using distillate water to obtain dissolved silicate and aluminate. The solid mixture was stirred for 4 hours to obtain a homogeneous mixture of Si and Al. After that, the aluminosilicate solution was formed for 2 hours to crystallize the zeolite to form a crystal core.

The solution is put into an autoclave for the hydrothermal crystallization process. In this study, the hydrothermal process was carried out for 24 hours with temperature variations of 100, 130, 160, and 190°C. The result of the hydrothermal process is a light brown solid. The next process was washed with distilled water to remove impurities and excess NaOH still attached. The zeolite was dried in an oven at 105°C for 24 hours to reduce the water still bound to the synthesized zeolite solids so that white synthetic zeolite solids were obtained. **Figure 2** shows the result of the synthesis of zeolite.

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Figure 2. Zeolite synthesis after dried in an oven at 150°C for 24 hours.

3. RESULTS AND DISCUSSION

3.1. Morphological Analysis by Scanning Electron Microscope

Characterization using SEM aims to determine the morphological shape of the structure of the sample. The samples analyzed using SEM are before and after synthesized in the zeolite. Zeolite synthesis samples were carried out with hydrothermal temperature variations of 100, 130, 160, and 190°C, and zeolite samples were synthesized from the separation with HCl. **Figure 3** shows fly ash before synthesis.

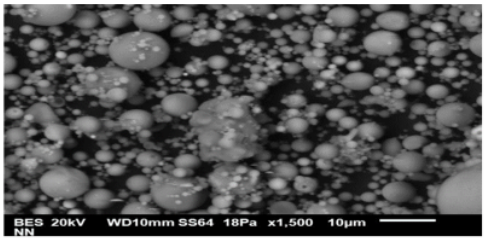

Figure 3. SEM analysis of fly ash before synthesis.

Based on the results of the SEM analysis in **Figure 3**, the raw material of fly ash before being synthesized into zeolite has a uniform round morphology like a ball. Its surface texture is relatively smooth, and particle SiO_2 is found in the ash. The surface smoothness of the fly ash particles is still in the form of amorphous phase particles. The hydrothermal process at 100°C in **Figure 4** shows a morphological form of quartz crystal particles of SiO_2. It can be seen that the particles are distributed, but it a less homogeneous particle shape and size.

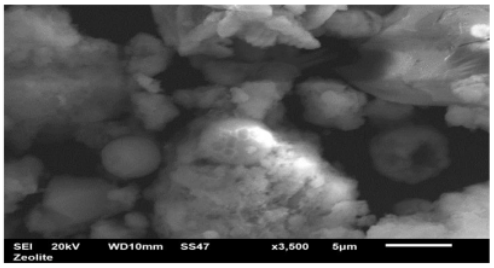

Figure 4. Results of SEM Analysis of Synthetic Zeolites with Hydrothermal Temperature 100°C for 24 hours.

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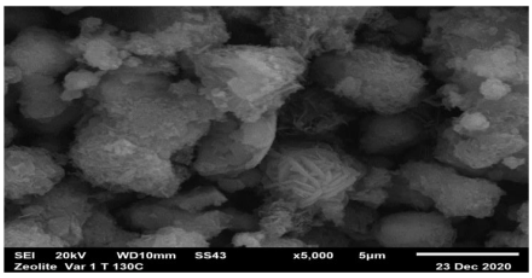

Figure 5. SEM analysis zeolite synthesis at 130°C.

The result shows the particles like a rock stone. This morphological structure was identified from the XRD analysis of the morphology of the Na-P zeolite. While in **Figures 6 and 7**, the hydrothermal process used temperatures of 160 and 190°C, respectively.

In **Figure 6**, the SEM surface micrograph of hydrothermal synthesis zeolite at 160°C is a type of cancrinite zeolite in the form of a shape like seaweed. This morphology is also the same as the morphology of sodalite zeolite as shown in **Figure 7**. SEM micrograph of the surface of hydrothermal synthesis zeolite at 190°C is shaped like seaweed with small crystalline particles of sodalite. And then in **Figure 8**, the SEM surface micrograph of zeolite synthesis (separation of 4 M of HCl) shows particles shaped like a rock stone. This morphological structure was identified from the XRD analysis of the morphology of Na-P zeolite.

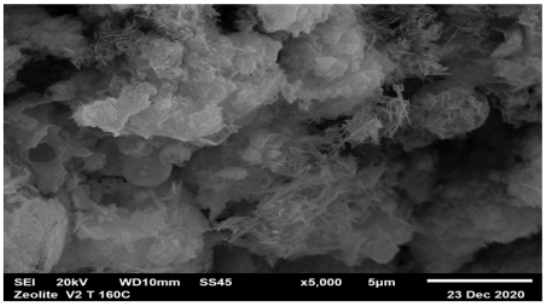

Figure 6. Results of SEM Analysis of Synthetic Zeolite with Hydrothermal Temperature 160°C for 24 hours.

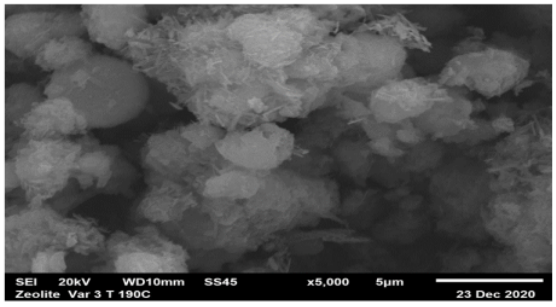

Figure 7. Results of SEM Analysis of Synthetic Zeolite with Hydrothermal Temperature 190°C for 24 hours.

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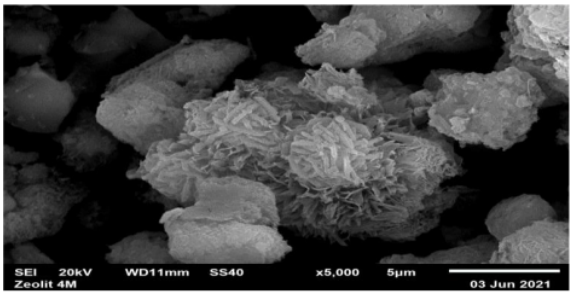

Figure 8. Results of SEM analysis of synthetic zeolite (Separation Results of 4 M of HCl) with a Hydrothermal Temperature of 160°C for 24 hours.

3.2. X-Ray Diffraction (XRD)

The XRD test was conducted to determine the crystalline phase and the intensity formed from the zeolite synthesis. The diffractogram describes the crystallinity of the material. The presence of a crystalline phase can be seen from diffraction peaks. In this study, the hydrothermal process was carried out with temperature variations of 100, 130, 160, and 190°C for 24 hours to determine the best zeolite crystallization process was formed. The results of the XRD characterization can be seen in **Figure 9**.

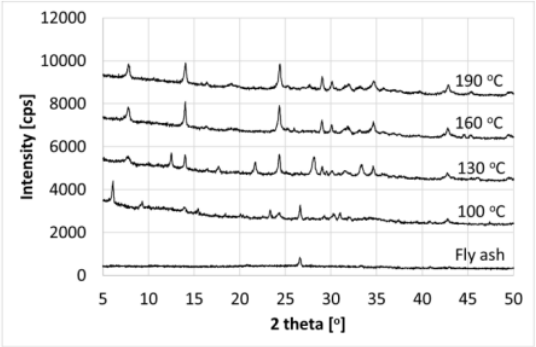

Figure 9. Diffractogram of fly ash and zeolite synthesis results with variations in hydrothermal temperature 100, 130, 160, and 190°C.

Figure 9 shows that the diffractogram in fly ash has not seen any diffraction peaks, which means that there is no crystallinity of zeolite growth so no diffraction peaks are formed. There is also the formation of diffraction peaks. It is a quartz crystal phase of SiO_2 that comes from fly ash seen in the 2θ=26.58° region. In the XRD diffractogram of the fly ash obtained, it can be seen that the fly ash is still in the amorphous phase, which is indicated by the diffraction pattern in the form of a diffraction irregular intensity. while the sharp diffraction peak is the form of the quartz crystal phase of SiO_2 at an angle of 2θ = 26.58°. In the synthesis of zeolite at a hydrothermal temperature of 100 °C, the diffraction pattern still gives an amorphous phase, and a diffraction peak of the SiO_2 crystal phase is formed, which is the main component derived from fly ash, while the crystallinity diffraction peak of zeolite growth has not yet been formed. At 130°C, the presence of a diffraction pattern has formed a crystal structure of the most dominant Na-P1 synthetic zeolite, which is found at an angle of 2θ = 12.37 with an intensity of 698.9; angle 2θ = 17.57 with an intensity of 288.2; angle 2θ = 21.56 with an intensity of 605.2; angle 2θ=28.02 with intensity 950.5; angle 2θ=33.19 with an intensity of

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600.8. In the synthesis of zeolite at a hydrothermal temperature of 130°C, the crystallinity of zeolite growth is still relatively low, and there are still diffraction peaks from the impurity material. Compared to samples at hydrothermal temperatures of 160 and 190°C, the diffraction peaks of zeolite crystals increase when compared to temperatures of 100 and 130°C.

At 190°C, a diffraction pattern of the dominant synthetic zeolite crystal structure was formed, which was found at an angle of 2θ=14.03° with an intensity of 878.7; angle 2θ=19.02° with an intensity of 130.08; angle 2θ=24.40° with intensity 1000; angle 2θ=27.66° with intensity 148.4; angle 2θ=30.10° with intensity 328.7; angle 2θ=32.67° with an intensity of 76.3; angle 2θ=34.67° with an intensity of 423.4, while the other diffraction peaks formed are from impurities. From the variation of hydrothermal temperature carried out in zeolite synthesis, the optimum hydrothermal temperature was 160°C.

In the zeolite synthesis, the results of the separation of impurities with 4, 8, and 12 M of HCl using a hydrothermal process at 160 °C for 24 hours it shows in **Figure 10**. the diffraction pattern formed is the crystal structure of the Na-P type zeolite synthesis, which is found at an angle of 2θ = 12.37; 17.57; 21.56; 28.02, and 33.19°. In addition, a crystalline diffraction peak of alpha quartz (SiO_2) was formed, which increased sharply at an angle of 2θ = 26.58°.

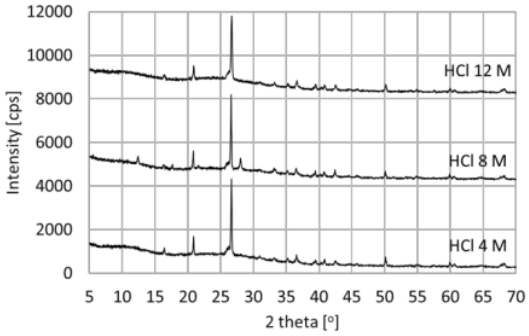

Figure 10. Diffractogram of synthesized zeolite from metal separation with 4, 8, and 12 M of HCl.

In the synthesis of zeolite as a result of this separation, when synthesized by a hydrothermal process at a temperature of 160°C for 24 hours, the amorphous quartz phase has reacted a lot to turn into Na-P type zeolite and the form of quartz crystal phase is indicated by the diffractogram that appears. The zeolite synthesized from the separation with HCl has increased the crystallinity as indicated by a sharp increase in the diffraction peak at an angle of 2θ = 26.58 θ.

The diffraction pattern of the synthesized zeolite showed an increase in intensity compared to the diffraction pattern in fly ash, which identified that the amorphous phase had turned into a crystalline phase. It could be indicated by the pattern of diffraction peaks that appeared. The strong acid HCl had released the metal impurities present in the fly ash during preparation before the zeolite synthesis was carried out, leaving only more silica which is the main component in the formation of zeolite crystals.

3.3. The Adsorption of Ammonium Using Zeolite Synthesis

One of the liquid wastes that result from the process of industrial activities and domestic

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is nitrogen-ammonia. Ammonia in surface water comes from urine, feces, and the decomposition of substances microbiologically organic comes from the natural water or wastewater industry (Kotoulas *et al*., 2019). In surface water, the level of ammonia is less than 10 ppm while in wastewater usually reaches 30 ppm or more (Lu *et al*., 2018). Waste accumulation when it reaches the water. It will have a negative impact on the environment that influences and cause ecological and health issues for the surrounding community.

The performance of ammonium adsorption from fly ash depends on the porosity on the surface of the fly ash. In fly ash, there is an active group SiO_2 that can interact with ammonium. Based on the data in **Table 1**, the adsorption value increased in the synthetic zeolite because of separation with 4 M of HCl by 18.025 ppm, because the synthetic zeolite sample separated with 4 M of HCl has more pore formed so it can increase the surface area becomes large so it would affect the adsorption of ammonium ions (NH^{4+}) into the zeolite.

Table 1.The comparison of adsorption ammonium with zeolite synthesis.

Sample	Co(ppm)	Ce(ppm)	qe(ppm)
Fly ash	100	71.3	7.175
Zeolite Synthesis 160°C	100	43.5	14.125
Zeolite Synthesis 160°C – HCL 4 M	100	27.9	18.025
Zeolite Synthesis 160°C– HCL 8 M	100	35.7	16.075
Zeolite Synthesis 160°C– HCL 12 M	100	28.3	17.925

The larger the surface area of the zeolite, the more negative charge on the zeolite will be so that more ammonium ions will be bound to the zeolite. In zeolite synthesized, the adsorption process occurs not only in the active group of the zeolite but also can occur through a cation exchange mechanism. In quartz, there is a functional group SiO_2 that will bind ammonium ions and the presence of Na-P zeolite will exchange cations with the zeolite because the synthetic zeolite purified with 4 M of HCl has a higher adsorption capacity value than the other samples.

Based on calculations using chemical kinetics in **Figure 11**, the longer the contact time between the adsorbate (ammonium ion) and the adsorbent (synthetic zeolite), the amount of adsorbate (ammonium ion) that interacts with the active site of the adsorbent (synthetic zeolite) will increase until it reaches equilibrium. At the initial contact time, many sides of the adsorbent are still empty so that the tendency of the adsorbate (ammonium ion) to be absorbed into the adsorbent is higher, with increasing contact time until equilibrium is reached.

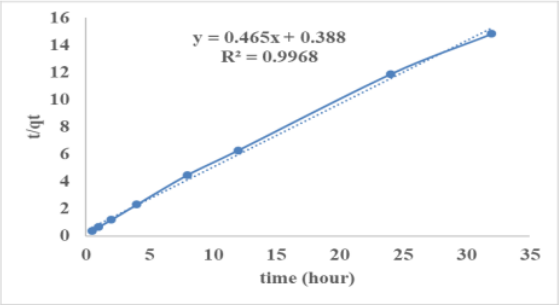

Figure 11. The plot of the pseudo-second-order kinetic model on ammonium adsorption by synthetic zeolite (separation result with 4 M of HCl).

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Based on the results of this research, showed that the adsorption capacity increased along with the length of adsorption time, this was related to the longer the time, the greater the interaction between the adsorbate solution and the synthetic zeolite adsorbent. **Figure 11** shows that the adsorption kinetics of zeolite synthesis (separation with 4 M of HCl) follows the pseudo-second-order model, this is because the second-order pseudo model has a correlation factor (R2) of 0.9968, which is closest to the value 1 between the first-order model and the second-order model intraparticle, with a rate constant of pseudo-second-order, which is 0.557 per hour. Thus it shows that 99.68% of the data can be explained by the equation of the pseudo-second-order kinetic model. In the adsorption kinetics test, the reaction order is the number of reactant concentration factors that affect the reaction rate.

4. CONCLUSION

The zeolite produced from this research is a Na-P zeolite with morphology like coral rock, cancrinite zeolite, and sodalite with morphology like seaweed. The optimum conditions for the synthesis of zeolite are found in the hydrothermal process at a temperature of 160 °C for 24 hours with the formation of crystalline cancrinite zeolite which has the highest absorption capacity as an adsorbent for ammonium ions. Synthetic zeolite separated by 4 M of HCl produced crystalline Na-P zeolite and crystalline silica phase the most optimal absorption of ammonium with an adsorption capacity of 18.025 mg/g with adsorption kinetics model in the form of pseudo-second-order with a constant rate of 0.557 per hours.

5. ACKNOWLEDGMENT

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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