Synthesis of zeolite NaX using elephant grass (*Pennisetum purpureum*) as a silica source and its characterization

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Abstract. Zeolite NaX is a synthetic zeolite with faujasite framework that has large pores, which it is largely used as adsorbents. Zeolite NaX was synthesized using silica (SiO₂) which was extracted from elephant grass (*Pennisetum purpureum*). The silica was isolated from elephant grass using its ash with conventional ignition method, with NaOH as solvent. The extracted silica purity is 86.33%. Zeolite NaX was synthesized with 3.5 Na₂O : Al₂O₃ : 2.9 SiO₂ : 150 H₂O as molar ratio in hydrothermal condition at 90 °C for 15 hours. Synthesized zeolite was then characterized using FTIR to confirm the formation of zeolite based on chemical bonding that appears on the spectrum, XRD to confirm the framework structure of the formed zeolite, and SEM to obtain its morphology. Based on those analysis, it is known that the result of synthesis process is zeolite with NaX crystal structure and octahedral morphology with crystal sizes range 1-5 µm.

1. Introduction

Zeolites are frequently synthesized because of their multifunctionality. Recently, the zeolite synthesis progress focuses on the methods and the inexpensive alternative material or waste used to precursor, for examples are aluminum scrub and rice husk for aluminum and silica (SiO₂) sources, respectively [1,2,3,4]. Besides rice husk and bamboo leaves [5,6], elephant grass is a weed that having the high silica content [7,8]. So that silica extracted from elephant grass can potentially be a silica source to synthesize zeolite.

One obstacle to using silica from plants is the process of ignoring. Although the percent content of silica in the plant ash is large however it still has a very small value compared to the weight of the plant. This causes the need for a large amount of plants to produce the silica. The process of ignition which is usually carried out in a furnace is inefficient because of its small capacity. Therefore, ignoring elephant grass is done by conventional combustion processes. The silica extraction process from plant is carried out by an extraction process [9,10] where elephant grass is immersed into NaOH solution for a certain time so that the silica contained in elephant grass can be dissolved in NaOH solution [8].
Zeolite is widely applied to adsorbent that utilize the surface area and the porous structure, for an example is faujasite. In this study, silica extracted from elephant grass was then used to synthesize one of the faujasite zeolites, that is NaX. The synthesis of zeolite NaX has been done a lot, but sometimes requires a long crystallization time up to several days. In this research, zeolite NaX synthesized at low temperatures and at relatively short time, less than one day.

2. Methodology
Chemicals used in this research was HCl (37%, Merck®), NaOH (Merck®), aluminum tape (0.3 mm thick, 30 mm wide, Merck®) and aqua DM.

2.1. Silica extraction from elephant grass
Elephant grass as a silica source is washed and dried, then burned by conventionally until it becomes ash. The ash is dissolved in aqua DM (100 mL/20 g of ash) and added HCl by dropwise until pH 7, then stirred for 2 hours at room temperature. Then the ash is filtered and soaked into 1 M NaOH solution while stirring for 1 hour. The mixture is filtered, the resulting filtrate is added with 1 M HCl until pH 7 and forms a gel. Then the gel formed is washed with hot aqua DM until it is white. Then the gel is heated at 90 °C for 12 hours. After that, the dried gel is crushed to powder. Then the silica powder is washed with aqua DM until pH 7 then dried at 105 °C for 15 hours. The formed zeolite NaX was filtered and washed with aqua DM until pH 7 then dried at 105 °C for 3 hours. The resulted silica was characterized by X-Ray Fluorescence Spectrometry (XRF) to know the percentage of silica (SiO₂) contained. Next, the silica powder is used as a source of silica for synthesis of zeolite NaX.

2.2. Synthesis of zeolite NaX
Zeolite NaX is synthesized with a mol ratio of 3.5 Na₂O : Al₂O₃ : 2.9 SiO₂ : 150 H₂O [11]. Aluminum solution is prepared by dissolving aluminum tape into NaOH solution, while heating and stirring until dissolved, then cooled to room temperature. In the same way, silica solution is made by dissolving silica from elephant grass into NaOH solution. Then the silica solution is mixed into the aluminum solution while stirring at room temperature for 40 minutes. The mixture is put into a Teflon-lined stainless-steel autoclave and then heated at 90 °C for 15 hours [11]. The formed zeolite NaX was filtered and washed with aqua DM until pH 7 then dried at 105 °C for 15 hours. The crystallinity of the zeolite NaX was investigated by X-Ray Diffraction (XRD) analysis. The functional groups in the zeolite NaX was analyzed using Infrared Spectroscopy (FTIR). The morphology of the zeolite NaX was analyzed by Scanning Electron Microscopy (SEM).

3. Results and discussion

3.1. Silica extraction from elephant grass and its characterization
In this study, silica was obtained from the extraction of elephant grass. Elephant grass is dried into an oven at 100 °C to remove water. Dry elephant grass is burned to ashes. The ash is black which shows incomplete combustion results. Then the ash is put into aqua-DM which is added HCl, which aims to dissolve the metals contained in the ash. This process is aided by stirring to accelerate the metal dissolution process. After the washing process uses HCl, then the ashes are immersed in 1 M NaOH solution while heated for 2 hours to extract silica from the ashes. The process of dissolving silica in a NaOH solution produces sodium metasilicate (Na₂SiO₃) which is soluble in water.

From this extraction process obtained a brownish yellow filtrate, which is caused by the presence of organic impurities. Then the filtrate is added 1 M HCl until a gel is formed (pH 7). The addition of HCl aims to reduce pH so that the solubility of silica in NaOH to decreases and forms silica hydrogel. The hydrogel is then washed with hot aqua DM until it is white, to remove salt and organic impurities. The silica hydrogel is then dried at 105 °C to produce silica xerogel. The xerogel was crushed and washed with aqua DM then dried at 105 °C for 4 hours. The XRF result of silica sample are shown in Table 1.

This extracted silica has a low percent yield, which is around 10% of the elephant grass ash. This is because the ash content produced from conventional combustion is mostly carbon. Although the ash has
a low percent yield, but the purity of silica can achieve to 86.33%. Besides silica (SiO₂), other metal oxides contained in extracted silica are sodium oxide (Na₂O). The Na₂O content may be derived from NaOH solution which is used as an extraction solvent. The content of LOI (Lost of Ignition), which is a compound lost through combustion or an organic compound, is 11.01%. The content is quite normal because silica is extracted from organic matter.

### Table 1. Results of XRF analysis in silica sample extracted from elephant grass.

| Oxide      | Total (%) | Element | Total (%) |
|------------|-----------|---------|-----------|
| SiO₂       | 86.3300   | Si      | 40.3600   |
| TiO₂       | 0.0158    | Ti      | 0.0095    |
| Al₂O₃      | 0.1540    | Al      | 0.0814    |
| Fe₂O₃      | 0.0180    | Fe      | 0.0126    |
| CaO        | 0.1840    | Ca      | 0.1320    |
| MgO        | 0.0743    | Mg      | 0.0448    |
| Na₂O       | 1.6100    | Na      | 1.2000    |
| K₂O        | 0.2240    | K       | 0.1860    |
| P₂O₅       | 0.0821    | P       | 0.0358    |
| SO₃        | 0.0610    | S       | 0.0012    |
| LOI        | 11.0100   | -       | -         |

### Table 2. Comparison of the peak NaX diffractogram from synthesis and NaX Standard [12].

| No. | 2 theta (°) | d-spacing (Å) | 2 theta (°) | d-spacing (Å) |
|-----|-------------|---------------|-------------|---------------|
| 1   | 6.09       | 14.500        | 6.12        | 14.450        |
| 2   | 9.94       | 8.891         | 10.00       | 8.849         |
| 3   | 11.70      | 7.555         | 11.73       | 7.546         |
| 4   | 15.38      | 5.756         | 15.43       | 5.742         |
| 5   | 18.38      | 4.823         | 18.42       | 4.817         |
| 6   | 20.05      | 4.425         | 20.07       | 4.424         |
| 7   | 22.46      | 3.956         | 22.47       | 3.957         |
| 8   | 23.34      | 3.808         | 23.58       | 3.773         |
| 9   | 24.64      | 3.610         | 24.64       | 3.612         |
| 10  | 26.65      | 3.343         | 26.65       | 3.345         |
| 11  | 29.21      | 3.055         | 29.21       | 3.258         |
| 12  | 30.94      | 2.888         | 30.94       | 2.890         |
| 13  | 31.99      | 2.796         | 31.98       | 2.798         |
| 14  | 32.64      | 2.741         | 32.59       | 2.747         |
| 15  | 33.60      | 2.665         | 33.59       | 2.668         |
| 16  | 35.14      | 2.552         | 35.13       | 2.554         |
| 17  | 37.35      | 2.406         | 37.34       | 2.408         |
| 18  | 39.91      | 2.257         | 39.95       | 2.257         |
| 19  | 40.81      | 2.210         | 40.79       | 2.212         |

### 3.2. Zeolite NaX synthesis and its characterization

In this study, zeolite NaX was synthesized using a method that adapted from the synthesis previously carried out [11] with little modification from the method. The method has two main steps, that are the precursor mixing step, with a mol ratio of 3.5 Na₂O : Al₂O₃ : 2.9 SiO₂ : 150 H₂O, and the crystallization step at the hydrothermal condition. The modification of method is done at the mixing step, where the silica powder does not enter directly into the aluminum solution, but the silica is previously dissolved...
into NaOH solution with the heating process to forming silicate ions. The silica solution is then mixed into the aluminum solution with rapid stirring for 40 minutes at room temperature. When the two solutions are mixed, a grayish white gel is formed. The gel formation is caused by copolymerization between silicate ions and aluminate ions. While stirring is done to homogenize the solution. The next step is crystallization under hydrothermal conditions. Zeolite crystallization begins by the process of forming a crystal nuclei (nucleation), which is a change of the compound structure from amorphous to crystalline. Then proceed with the process of crystal growth, where the molecules in the solution attach to the crystal nuclei so that the size of the crystal to increases.

From the XRD diffractogram that obtained (Figure 1) and peaks data (Table 2), it can be seen that the synthesized crystal structure is faujasite crystals, which is NaX crystal structure. From the diffractogram peak comparison in Table 2, it can be seen that the shifting in the position of the diffraction peak can be caused by several things, including the composition of the compound (the presence of impurities), lattice stress, and temperature [13].

The most likely factors affecting the occurrence of peak position shifts are changes in composition (presence of impurities) and lattice stress, because the synthesis of zeolite is used silica that extracted from elephant grass with a purity of 86.33% and there are still many impurities from the silica.

![Figure 1. XRD diffractogram of synthesized zeolite NaX.](image)

When compared with the NaX standard diffractogram obtained from the International Zeolite Association (IZA) [12], the peaks in the diffractogram analysis results are slightly wider. This widening is caused by differences in the size of crystal, if the crystal size to be the larger according to the peak width to be the smaller [14].

Based on the XRD diffractogram using calculations to Scherrer equation, the particle size of zeolite NaX crystals is 32.5 nm. However, the results of this calculation cannot be used fully for determining particle size, because Scherrer equation can only determine particle sizes less than 1000 Å or 100 nm [13].

Although there are differences between the intensity ratio with the standard NaX diffractogram, diffractogram pattern of the analysis results is similar to the NaX diffractogram that obtained from the synthesis of Zhang et al. [11], which is used as a reference for the synthesis method in this study.

From the results of XRD analysis, it can be seen that zeolite NaX can be synthesized using silica extracted from elephant grass. The size of the synthesized crystals is slightly smaller than the standard NaX, but almost the same as the results of Zhang et al. [11].
Figure 2. Zeolite NaX infrared spectrum (a) Zhang et al. [11] and (b) synthesis result.

Figure 3. SEM images of synthesized zeolite NaX with magnification (a) 2000 ×, (b) 5000 × and (c) zeolite NaX by Zhang et al. [11].

The infrared spectrum wavelength at 400-1500 cm\(^{-1}\) is a typical spectrum of zeolite, which shows characteristics of zeolite skeletal structure. The spectrum in the range 400-1300 cm\(^{-1}\) is divided into two types of vibrations, i.e. vibrations caused by tetrahedral TO\(_4\) (T = Si/Al), which are zeolite primary constituent units, and vibrations caused by external bonds between tetrahedral units which are influenced by secondary constituent units, such as rings and pores.

FTIR results can be seen in Figure 2. The absorption band at 1600-1700 cm\(^{-1}\) shows the presence of O-H bonds originating from water molecules in the zeolite structure; at 900-1000 cm\(^{-1}\) shows the Si-O-
Al bond, which is a connecting link between tetrahedral silica and tetrahedral alumina; at 700-800 cm\(^{-1}\) shows Si-O-Si bonds in tetrahedral silica; at 600-700 cm\(^{-1}\) shows the Al-O bond in alumina tetrahedral; and absorption bands at 500-600 cm\(^{-1}\) show Si-O-Na bonds \cite{11,15}.

The SEM result of zeolite NaX can be seen in Figure 3. The size and morphology of crystalline particles is almost the same as zeolite NaX from Zhang et al \cite{11}. The morphology of zeolite NaX crystals observed from SEM analysis showed a non-uniform for shape and size, but still showed an octahedral shape as shown in the Figure 3. The non-uniformity of NaX zeolite crystals is caused by agglomeration during the crystallization process. Agglomeration can be caused by many factors, such as temperature and composition of raw materials used so that the size of the crystals formed is not homogeneous.

The shape or morphology of crystal particles is an illustration of its internal atomic structure. NaX zeolite has a truncated octahedron crystal structure so that the shape of the crystal particles can be estimated to be octahedral. From Figure 3 it can also be observed that NaX zeolite crystals have a size ranging from 1-5 µm. This particle size is different from the results of Scherrer equation calculation, that is 32.5 nm, which indicates that the Scherrer equation can only be used to calculate submicron particle size, i.e. particles with a size smaller than 100 nm.

4. Conclusion
Silica has been successfully isolated from elephant grass, which from the result of XRF shows the silica content about 86.33%. Zeolite NaX has been successfully synthesized using silica from elephant grass. This synthesis was done through hydrothermal method at low temperature and at relatively short time. FTIR spectra shows that absorption peaks of NaX sample characterized by vibration of function groups at 900-1000 cm\(^{-1}\), 700-800 cm\(^{-1}\), and 600-700 cm\(^{-1}\) are Si-O-Al bond, Si-O-Si bond, and Al-O bond, respectively. XRD result shows that zeolite of faujasite type confirmed as NaX crystal structure. SEM result follows that the sample of NaX describe octahedral morphology that having the crystal size about 1-5 µm.

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