Zeolite based Geopolymer from Biomass: a Sustainable Adsorbent for Water Softener

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Abstract. Water quality in several areas in Semarang, especially in Tugu sub-district, is still very low and unsuitable for drinking. Ground water contaminated with Ca$^{2+}$ and Mg$^{2+}$ ions which is commonly known as hard water. This study aims to examine the potential of zeolite-based geopolymer adsorbents, materials which have a zeolite-like structure but are basically geopolymers. Synthesis of zeolite based geopolymers from rice husk ash, kaolin and NaOH activators has been successfully carried out by the sol gel method. Three-dimensional networks have been formed from Silica (SiO$_2$) and Alumina (Al$_2$O$_3$). Activator solution, NaOH, with variations in concentrations of 4 M (Geopolymer 4), 8 M (Geopolymer 8) and 12M (Geopolymer 12) gives significant differences. As the higher the concentration of activator solution, the more silica and alumina dissolved so that the geopolymer becomes amorphous. These results are consistent with XRD and FTIR data. Geopolymer 12 has an adsorption capacity of 97.4% is the best adsorbent in adsorbing Ca$^{2+}$ and Mg$^{2+}$ metal ions with operating conditions at 40°C for 60 minutes. This shows that there is a close relationship between synthesis methods, structural characterization and geopolymer adsorption activities. The higher concentration of NaOH gives amorphous geopolymers. NaOH will activate the silica and alumina surfaces on the geopolymer, making it easier for adsorbents to absorb and interact with the adsorbate molecules, namely Ca$^{2+}$ ions and Mg$^{2+}$ ions.

1. Introduction

Water is an important natural resource in life. The human body contains about 60 % water. No human can survive more than 4-5 days without drinking water[1]. However, some people in the world can not consume cleans, safe and healthy water. Based on World Health Organization, over 760 million people were without adequate drinking water supply [2]. In fact, water quality in some areas in Central Java, in particular, is still very low or unsuitable for drinking. Ground water is often contaminated with a number of ions or minerals such as Calcium (Ca$^{2+}$) and Magnesium (Mg$^{2+}$) ions. Water contaminated with Ca$^{2+}$ and Mg$^{2+}$ ions is known as "hard water"[3]. Hard water is found in the Jerakah area, Tugu District, Semarang City. Residents use ground water for daily needs. Examination of water quality in PAMSIMAS 1 Jerakah Village shows an Mg$^{2+}$ ion content of 186.15 mg/ L[4]. This amount exceeds the requirements or drinking water quality standards according to Indonesia's Minister of Health Regulation (PERMENKES) No 492 of 2010 which is 150 mg / L. Even at PAMSIMAS 2 the levels were higher ie 216.97 mg/L [5]. Magnesium cannot be degraded so it can easily accumulate [6]. The presence of Mg content causes cooking utensils to crust and deposits on metal pipes. When used for washing, the use of detergent or soap will become more and more wasteful. In the health field, the presence of high dosage Mg$^{2+}$ in water will accumulate in the body making kidney stones, dermatitis
and even prostate cancer[7]. So that ground water needs to be treated so that Mg$^{2+}$ levels are below the drinking water quality limit. There are several studies on efforts to reduce the levels of Mg$^{2+}$ ions in hard water have been carried out. Among them are ion exchange[6], [8], electrochemical, filtration[9] and adsorption techniques[6]–[8], [10]–[14]. Ion exchange means replacing the Mg$^{2+}$ ion with another ion such as Na$^+$ through a resin. This method is effective for removing Mg$^{2+}$ ions, but this method has several disadvantages. When Mg$^{2+}$ is replaced by Na$^+$, the number of Na$^+$ ions will become more (even more than Mg$^{2+}$ ions). The result is certainly not good health, for example hypertension. Besides that the price of ion exchange resins is quite expensive and is not suitable if applied to the public, although it can also be applied in the industrial field.

In the electrochemical method, an electric current will be used to reduce the levels of Mg$^{2+}$ ions. The effectiveness of electrochemical methods is greatly influenced by the electrical voltage used. Generally, the greater of voltage makes the result better. However, high voltage means that it requires a large amount of electrical energy and consequently the costs are also large. Membrane filtration is also an alternative to reducing hard water [15]. However, just like electrochemistry, the cost of making and applying it to water on a large scale requires relatively high costs. The adsorption can be applied to remove hard water. In the adsorption method required adsorbents or filters. The production costs can be reduced by using cheap and sustainable adsorbents [9].

In this research, an adsorption method will be used to reduce the levels of Mg$^{2+}$ ions in groundwater, especially in the Village of Jerakah. There are several things that need to be considered including choosing the right adsorbent. Adsorbents that are widely used include activated carbon[3], [16], [17], zeolites [6], [18], and silica [19]. The material can be used because of its porous structure, large surface area so that more metal ions are absorbed, easily available and relatively inexpensive.

One of the things that can be done is to make geopolymer materials. Geopolymers are amorphous aluminosilicate compounds [10], [20], [21]. The crystalline aluminosilicate material is called zeolite. This research will combine the two materials, namely zeolite based geopolimer. a material which is chemically similar to the structure of zeolite will be made but basically the material is a geopolymer. Zeolites are widely known as adsorbents in various metal ions. Zeolites also have the ability to exchange ions. Zeolites in nature still have a lot of impurities so zeolite synthesis is easier and more practical to apply. However, the price is relatively expensive and to make zeolites is not easy because crystalline compounds are usually formed at high temperatures. Geopolymers are easier to make because they do not require a crystallization growth stage. The basic ingredients of making zeolite-based geopolymers are materials that are very easy to obtain, namely kaolin (limestone) and silica which can be derived from rice husk ash. By using these materials, it is expected that production costs will be cheaper [17,18, 19]. To make zeolite based geopolymer activator solution is needed, namely NaOH solution. Activator concentration is an important factor in geopolymer synthesis. This study was aim to examine the effect of activator concentration on the properties of materials.

2. Methodology

The material used in this study is rice husk from Batang, Central Java. Kaolin and Aquades were obtained from Indrasari Chemical, Semarang. NaOH, Na$_2$EDTA, ZnSO$_4$, Buffer pH 10 solution, EBT indicator was obtained from E. Merck. The artificial waste used was Ca$^{2+}$ 150 ppm solution, Mg$^{2+}$ 200 ppm solution.

2.1 Sample preparation

The synthesis of zeolite based geopolymers begins with the synthesis of silica and metakaolin. The synthesis of silica from rice husk ash was adapted from[22]. Rice husk cleaned and dried under the sun for 3 days. The dried rice husk are calcined using furnaces at a temperature of 800°C to obtain gray rice husk ash. The ash are dissolved in 4 M NaOH in stop erlenmeyer. The mixture is stirred while heated at 109°C. The residue is 500°C to whitish brown. The resulting substance was then dissolved in mineralized water into a yellowish brown of sodium silicate solution. The solution of silicic acid is added HCl 1 M dropwise until it has pH 7. The solution is then allowed to stand for 72 hours until gel
is formed. The formed gel is then washed with demineralized water and the residue is dried in an oven at 80° C. The formed silica is then crushed and sieved with 100 mesh sieve. Silica has been heated at 400°C for 4 hours. In other hand synthesis metakaolin adapted from [23]. Kaolin was calcined at 700°C for 10 hours to become metakaolin.

2.2 Synthesis of Geopolymer
Silica (3 gram) form rice husk was dissolved in 20 mL NaOH at various concentrations of 4M, 8M and 12 M. To the mixture, 6 grams of Metakaolin was added. The mixture is stirred slowly until it is homogeneous. The mixture is heated to the bath until the water content is reduced. After the water content is reduced, the mixture is at 100°C for 12 hours. The mixture was then calcined at 200°C for 3 hour. Zeolite based geopolymers are ready to be characterized.

2.3 Characterization of geopolymer
Material characterization in this study includes the characterization of the structure using the X Ray Diffraction (XRD) Philip PW-1710. Analysis was done using Cu Kα radiation in the range of 5–100°(2θ). Fourier Transform Infra Red (FTIR) Shimadzu Prestige-21 use to analyzed functional group of material.

2.4 Adsorption test
Adsorption Test is carried out under the following conditions:
- Concentration of Ca²⁺ solution: 150 ppm
- Concentration of Mg²⁺ solution: 200 ppm
- Temperature: 40-50°C
- Time: 15, 30, 45, 60 and 75 minutes
- Adsorbent mass: adsorbate volume = 1: 1000 (g / mL)

Hard water analysis using complexometry titration using EDTA. The efficiency of adsorption / removal efficiency (RE) is formulated

\[ \text{RE} = \frac{C_0 - C}{C_0} \times 100\% \]

3. Result and Discussion
3.1 Synthesis of zeolite based geopolymers
Metakaolin is produced from the mineral kaolin. When kaolin is heated, dehydroxylation will occur according to the following reaction[10][24][25]:

\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O} \]

The calcination temperature in this study was 700°C. This temperature is relatively high because the termination reaction of hydroxyl ions which are chemically bound with alumina and silica is endothermic reaction. At this temperature there is also a recrystallization of amorphous kaolin crystals into quarsa and mullite.[23]. Metakaolin has twice the pozzolan (clay) properties compared to its original material. [10], [23], [26], [27]

The synthesis of geopolymer material in this study was carried out by the sol gel method. In geopolymer synthesis silica, alumina and activator solutions are needed. The source of silica and alumina in this study was metakaolin that had been prepared previously. In addition, silica added from rice husk ash. Based on analysis by X-ray fluorescence (XRF) silica content in metakaolin is 49.60% while the alumina are 34.2%. The rice husk ash has a silica content of 99.5% This is consistent with the previous research by [25] [28]. The use of rice husk ash is an effort to optimize the use of biomass so it does not become waste for the environment. The addition of silica from rice husk ash in this study aims to increase the Si/Al ratio of the resulting geopolymer. This Si/Al ratio is important to the mechanical properties and adsorption ability of geopolymer materials[26][29][30][31][32].
The geopolymerization process, is also influenced by the concentration of an alkaline solution as an activator[33]. In geopolymer synthesis, base activator is needed in the dissolution of Si and Al from the initial material [28][34]. So that it becomes aqueous phase. The type of alkaline solution affects the dissolution process. In this study, the alkaline solution used was NaOH because compared to KOH, the activity was better and it dissolved silica and alumina. In addition, concentration of activator will affect characterize and performance of geopolymer. Based on previous research concentrations of alkaline solutions made variations namely 4M, 8M and 12M [33]. The resulting geopolymers are named Geopolymer 4, Geopolymer 8 and Geopolymer 12.

After silica is dissolved in NaOH then metakaolin is added so it looks like a watery slurry. This aqueous mixture is then stirred until cooked in a bath in order to remove the solvent. In the process of removing the solvent, it shows a different process in each geopolymer. Geopolymer 4 (with 4M NaOH concentration) decreases the number of solvents the fastest while the longest lost solvent is Geopolymer 12.

After removal of the solvent the geopolymer sample is then dried at 100°C for 10 hours. According to [10] geopolymers have been produced in this process. It is also in accordance with [31] research, that the drying temperature of 85-200°C has formed geopolymers. However, in this study showed different results, at that temperature produced geopolymers that have not been dry, especially in geopolymer 8 and geopolymer 12. This shows the concentration of NaOH is very influential on the geopolymerization process as in previous studies.

To obtain a dry geopolymer the researchers finally calcined at 200°C for 4 hours. At this temperature dry of geopolymer are produced. The material is then mashed with mortar and pastel. During grinding, Geopolymer 4 produces the most coarse texture (like sand). The geopolymer 8 is still rough but slightly softer than geopolymer 4. The geopolymer 8 has a smooth texture like flour.

In the process of synthesis of Geopolymers the following reactions occur:

a. The process of dissolving raw silica alumina with NaOH.
Al and Si dissolution is critical in geopolymerization because it is the first step that releases aluminate and silicate by alkali attack on raw aluminosilicates. Dissolution of starting material has a dual role. First, the formation of polysialate species is released from the starting material in the same way in the formation of zeolite precursors. Second, the dissolving process will activate the surface and the binding reaction takes place making a significant contribution to the final strength of the structure. Dissolution if silica and alumina can be write as the reaction at figure 1.

\[
\begin{align*}
\text{Si}_2\text{O}_5\text{Al}_2\text{O}_3 + \text{NaOH} & \rightarrow \text{Si}_2\text{O}_5\text{Al}_2\text{O}_2\text{n} + 4\text{H}_2\text{O} \\
4\text{SiO}_2\text{vapour} + 2\text{Al}_2\text{O}_3\text{vapour} + 4\text{O}_2 & \rightarrow (\text{Si}_2\text{O}_5\text{Al}_2\text{O}_2)\text{n} \\
2\text{SiO} + \text{O}_2 & \rightarrow \text{SiO}_2 \\
\text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Al}_2\text{O}_3 \\
\text{SiO}_2 \text{ dan Al}_2\text{O}_3 \text{ form a three dimensional network at geopolymer.}
\end{align*}
\]

b. Drying and calcination process

\[
\begin{align*}
2(\text{Si}_2\text{O}_5\text{Al}_2\text{OH}_4) & \rightarrow 2(\text{Si}_2\text{O}_5\text{Al}_2\text{O}_2)\text{n} + 4\text{H}_2\text{O} \\
4\text{SiO}_2\text{vapour} + 2\text{Al}_2\text{O}_3\text{vapour} + 4\text{O}_2 & \rightarrow (\text{Si}_2\text{O}_5\text{Al}_2\text{O}_2)\text{n} \\
2\text{SiO} + \text{O}_2 & \rightarrow \text{SiO}_2 \\
\text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Al}_2\text{O}_3 \\
\text{SiO}_2 \text{ dan Al}_2\text{O}_3 \text{ form a three dimensional network at geopolymer.}
\end{align*}
\]
Overall mechanism of geopolimerization is

$$\text{SiAl materials} \quad +2n\text{SO}_2+4n\text{H}_2\text{O}+n\text{NaOH}$$

Figure 2. Geopolymerization mechanism

3.2 Microstructure of Zeolite based geopolimer

Analysis of microstructure adsorbent that have been synthesized, was carried by X Ray diffraction. The result of XRD analysis shown in figure 3. Based on Figure 1 a. Silica show the specific peak for SiO$_2$ lies at 22.49°. This shows that the synthesized sample is really SiO$_2$. The diffractogram obtained show widening peak indicating amorphous phase of silica. Based on the metakaolin diffractogram (1b), there are three highest peaks, i.e. at 26.6, 19.992 dan 19.998°. This shows that metacaolin has tridinite, aluminum oxide (Al$_2$O$_3$) and quartz (SiO$_2$) phases. The baseline of the diffractogram in the form of a widening of 2 theta 10-40 shows metacaloline in the amorphous phase.

Figure 3. X-Ray Diffraction of Adsorbent (a. Silica b. Metakaolin c. Geopolymer 4 d. Geopolymer 8 e. Geopolymer 12)
The process of geopolymer synthesis (fig 1c) shows 2-phase quartz (SiO2) at around 24.50; 34.72; and 38.07° with small intensity. Based on this difractogram, specific peak of silica still there. While ini figure 3 d (geopolymer 8) and e (geopolymer 12) there was not show silica and alumina specific peak. This is show that NaOH activator dissolves silica and alumina. The greater the concentration of NaOH used (12M), the dissolution process will be more effective and produce amorphous geopolymers. This is consistent with what was conveyed by Davidovits (1989), a scientist who introduced the term geopolymer. This results are corresponded with previous studies [24,25]

![Figure 4. FTIR Spectra of of Adsorbent (a. Silica b. Metakaolin c. Geopolymer 4 d. Geopolymer 8 e. Geopolymer 12)](image)

The FTIR spectra of materials obtained from the alkali treatment are shown in Fig. 4. The broadband at 3400–3700 cm⁻¹ for all of materials is due to the absorption of hydrogen bonded silanol groups (Si-OH). The band at 3419.83-3452 cm⁻¹ and a band at 1632 cm⁻¹ are corresponds to the stretching and bending vibration of H-O-H molecules. However the intensity of absorption band at that region are decreased accorrding the order silica>metakaolin>Geopolymer 4>Geopolymer 8. Geopolymer 12. This isi indicate dissolution of SiO₂ and Al₂O₃ with NaOH solution [32][26][36][28]. The band at between 950-1097 cm⁻¹ with a weak shoulder is assigned to the Si-O-Al asymmetric stretching vibrations. This band shift suggested strongly formation of geopolymers. [31] The intense bands at 800 cm⁻¹ and 474 cm⁻¹ are due to symmetric stretching and bending vibrations of Si-O-Si. At synthesized geopolymer have new and shoulder peak at 690 cm⁻¹. That show symmmetric stretching vibration of T-O and L-O (T are Si or Al) that indicate geopolymer matrix. After geopolymerization, both intensities of these two bands decreased and the new band appeared at about 710 cm⁻¹. The spectral data indicated that the formation of tetrahedral Al [Al-O₄] was found in the resultant geopolymers[31] The bands such as 450, 800, 950, 1100 and 1190 cm⁻¹ are bending vibration of Si-O-Al dan and bending vibration of Si-O that related to fused silica. Also, the absorption bands at 1450 cm⁻¹ are observed in the geopolymer FT-IR spectra of alkali treated samples, which confirms the formation of sodium silicate. This FTIR spectra indicate that the mechanism of geopolymerization in this case is more complex including not only the level of dissolution of the amorphous silica from RHA. Obviously it can be suggested the action of the finer particles of silica from the standard sodium silicate and coarse ones from silica alumina-NaOH. Increasing NaOH concentration, the amount of fine particles increases in relation with the extend of dissolution improving the formation of 3D network [28]. Some peaks that appear on silica
and metakaolin are lost due to the dissolution process by NaOH activator at various concentrations.

Based on the results of the characterization of existing structures prove that the structure of Zeolite Based geopolymers has been formed. The resulting geopolymer has an amorphous phase. This is what distinguishes zeolite from geopolymers as conveyed by Davidovits [15]. With the same structure as zeolite, geopolymers are more easily synthesized because they can be made at temperatures below the zeolite synthesis temperature. This is an advantage of geopolymers.

3.3 Adsorption capacity

Adsorption efficiency of each adsorbent material can be seen in Tables 1, 2 and 3.

Table 1. Adsorption Capacity (%) of adsorbents against Metal Ca\(^{2+}\) ions

| No | Adsorbent | 15  | 30  | 45  | 60  | 75  |
|----|-----------|-----|-----|-----|-----|-----|
| 1  | Geo 12    | 90.2| 92.9| 98.2| 100.0| 99.1 |
| 2  | Geo 8     | 72.3| 72.3| 78.6| 75.9| 79.5 |
| 3  | Geo 4     | 35.7| 35.7| 40.1| 25.8| 25.0 |
| 4  | Metakaolin| 54.4| 49.1| 46.4| 42.8| 40.1 |
| 5  | Silika    | 23.2| 26.7| 19.6| 33.0| 35.7 |

Based on table 1, the best adsorbent for absorbing Ca\(^{2+}\) metal ions is Geopolymer 12. The optimum adsorption time is 60 minutes with an adsorption capacity reach 94.0%. However, the adsorbent which has the lowest absorption capacity is this is metakaolin.

Table 2. Adsorption capacity (%) of Adsorbent against metal Mg\(^{2+}\) ion

| No | Adsorbent | 15' | 30' | 45' | 60' | 75' |
|----|-----------|-----|-----|-----|-----|-----|
| 1  | Geo 12    | 61.9| 72.6| 89.3| 94.0| 92.9 |
| 2  | Geo 8     | 72.6| 77.4| 79.8| 85.7| 80.9 |
| 3  | Geo 4     | 45.2| 52.4| 41.6| 66.6| 69.0 |
| 4  | Metakaolin| 16.6| 26.1| 33.3| 41.6| 38.1 |
| 5  | Silika    | 64.3| 57.1| 61.9| 50.0| 46.4 |

Based on table 2, the best adsorbent for absorbing Mg\(^{2+}\) ions is Geopolymer 12. The optimum adsorption time is 60 minutes with an adsorption capacity of 100.0%. However, the adsorbent which has the lowest absorption capacity is silica.

Table 3. Adsorption Capacity (%) Adsorbent for total Hardness

| No | Adsorbent | 15' | 30' | 45' | 60' | 75' |
|----|-----------|-----|-----|-----|-----|-----|
| 1  | Geo 12    | 89.3| 92.3| 94.4| 97.4| 97.4 |
| 2  | Geo 8     | 72.4| 74.5| 79.1| 80.1| 80.1 |
| 3  | Geo 4     | 39.8| 42.8| 40.8| 43.3| 43.8 |
| 4  | Metakaolin| 38.2| 39.3| 40.8| 42.3| 39.3 |
| 5  | Silika    | 40.8| 39.8| 37.7| 40.3| 40.3 |

Based on table 3, the best geopolymer is Geopolymer 12. The optimum adsorption time is 60 minutes with an adsorption capacity reaching 97.4%. After this time there were no changes in Ca\(^{2+}\) and Mg\(^{2+}\) concentrations. The adsorbent which has the lowest absorption capacity is metakaolin. Based on table 3, the best adsorbent for absorbing hard water is Geopolymer 12. The optimum adsorption time is 60 minutes with an adsorption capacity reaching 94.0%. However, the adsorbent which has the lowest absorption capacity is this is metakaolin.
3.4 Relationship of Material Structure and Adsorption Capacity

Based on the analysis of data in Tables 2, 3 and 4 show that the best adsorbent is geopolymer 12 which is synthesized with 12 M NaOH activator and the lowest is Geopolymer 4. This is consistent with the results of the characterization of the previous structure. When viewed from the structure of this adsorbent has the most amorphous structure compared to other adsorbents. The more amorphous an ingredient, the easier it will be to interact with the adsorbate molecule. The adsorbate molecule will more easily emerge with adsorption with an amorphous surface. As stated by [25][37][38]. NaOH will activate the silica and alumina surfaces that exist in geopolymers. The more surfaces of Silica and Alumina that are active, the more adsorbate molecules are absorbed. The active silica and alumina surfaces are amorphous geopolymers [38]. When compared with existing raw materials, the synthesized geopolymer has better activity. Raw material basically has adsorption capability. This data show in Fig 5. Silica adsorbents have a low adsorption capacity to absorb Mg$^{2+}$ metal ions. Silica in this study has the most crystalline structure compared to other materials. While metakaolin has the lowest adsorption ability to absorb Ca$^{2+}$ metal ions. Even though metakaolin is also amorphous, it has a better crystallinity than the geopolymer produced by synthesis. Adsorbents that have a high crystallinity, the surface is not as active as amorphous material so that fewer adsorption molecules are absorbed on the surface of the adsorbent. It can be said that the interaction is weak and only physical adsorption (physisorption).

![Figure 5. Adsorption capacity of material.](image)

4. Conclusion

Based on the research that has been done, a number of conclusions can be drawn. Synthesis of zeolite based geopolymers has been successfully carried out by the sol gel method. Three-dimensional networks have been formed from Silica (SiO$_2$) and Alumina (Al$_2$O$_3$). Activator solution in the form of NaOH with variations in the concentration of 4 M (Geopolymer 4), NaOH 8 M (Geopolymer 8) and NaOH 12M (Geopolymer 12) gives results that have significant differences. The higher the concentration of the solution, the more silica and alumina dissolved so that the geopolymer becomes amorphous. These results are consistent with XRD and FTIR data. Quartz and alumina are still present in zeolite based geopolymers but have an amorphous phase. Geopolymer 12 has the best adsorption
capacity for total hardness, metal ions Ca\(^{2+}\) and Mg\(^{2+}\). This shows that there is a close relationship between synthesis methods, structural characterization and geopolymer activity. The higher concentration of NaOH gives amorphous geopolymers. NaOH will activate the silica and alumina surfaces on the surface of the geopolymer, making it easier for adsorbents to be absorbed and interact with the adsorbate molecules, namely Ca\(^{2+}\) ions and Mg\(^{2+}\) ions.

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