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Synthesis of Zeolite Based Material with Aluminum Sources from Used Beverage Cans for Hard Water Desalination

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Abstract

Hard water contains high mineral content, especially calcium (Ca) and magnesium (Mg). Hard water can cause health problems and damage to household appliances within a certain period of time. In this study, zeolite-based materials have been synthesized as adsorbent materials to reduce the concentration of Ca^{2+} and Mg^{2+} in the hard water obtained from Brondong district of Lamongan, East Java. Zeolite based material was synthesized with aluminum sources derived from beverage cans and silica from silica gel. In this study, zeolite was prepared by microwave (ZM) and without the microwave method (ZNM). The amount of ZM was 10.8121 grams, or 99.1% of the yield, and ZNM was 10.5387 grams or 99.15% of the yield. The FTIR results indicate some characteristic peaks of T-O and T-O-T bonds (T = Si/Al) at 460, 670, 726, and 980–1100 cm^{-1}. The diffractogram show that ZNM is still dominated by silica-based materials, while ZM although it still shows dominant amorphous silica peaks, some characteristic zeolite peaks also appear. The SEM results show the shapes of agglomerated tiny particles for both materials. In this study, the synthesized zeolite can reduce the concentration of Ca^{2+} ions by 84–97% and Mg^{2+} ions by 23-51%. The optimal time obtained in this study was 30 minutes, while the optimal mass obtained was 0.5 grams for all materials.

Keywords: *hard wate;, desalination; zeolite; aluminum cans; adsorption*

Introduction

Water is the most crucial natural resource for life, and humans and other living creatures use it extensively. In 2018, the Java-Bali region had the best performance, with consumption numbers of 41 percent, compared to 20-25 percent on other islands. With a consumption rate of 26%, the Nusa Tenggara area received the cleanest water in 2019. (BPS, 2020).

Groundwater is a practical and cost-effective source of clean water (Kilo, 2018). Some communities continue to rely on groundwater for basic needs like bathing, cooking, and washing. Meanwhile, the consumed groundwater likely has a high water hardness level (Sulistyani *et al.*, 2012). The presence of minerals such as calcium (Ca) and magnesium (Mg) in the water affect its hardness. The high mineral content has a detrimental impact, including water supply and domestic facilities degradation. Not only

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that, but drinking water with high mineral content can lead to kidney stones, muscular tissue damage, and urolithiasis (Latuconsina and Lima, 2020). As a result, treatment is required before high-mineral water is used or consumed (Astri Zulfa *et al*., 2020).

Hard water is usually treated with filtration (Dewi *et al*., 2018) or heating (Maran and Pare, 2019). This method, on the other hand, is less important. The creation of crust, for example, occurs during the heating process. Aside from that, the heating procedure is ineffective in big quantities. Other methods such as photocatalysis and biodegradation are inefficient since they are less cost-effective and take a long time. Adsorption is a useful technique. Adsorbents with high adsorption capabilities, selectivity, and the ability to regenerate (Wang *et al.*, 2020). Furthermore, many types of adsorbents can be used as an alternate synthesis process. Zeolite is one form of adsorbent that can be employed.

Zeolites are aluminosilicate compounds with oxygen-linked tetrahedral connections. Cations can neutralize the negative charge of Al atoms. The zeolite's adsorption capacity is influenced by the exchangeable cations. Furthermore, the zeolite's ability is determined by the Si/Al ratio, surface area, and pore size. The zeolite's capacity to absorb water is increased due to its large surface area and pores that are near to the size of a water molecule (0.1 nm) (Djaeni, Kurniasari, and Sasongko, 2015). Zeolite is a mineral with the chemical properties of silica and alumina that can be found naturally in the soil or produced in the laboratory (Zewail and Yousef, 2015).

Researchers can use the simple zeolite synthesis method to create a variety of materials and procedures. According to several studies, zeolites can be made from materials including silica and aluminum. According to Susmanto *et al.*, (2019) aluminum solid waste can be used as one of the raw ingredients in the production of zeolites. Cans for food containers (biscuits) or soft drinks are among the garbage or solid waste containing high aluminum content. Food packaging and used beverage cans have been increasing recently (Iryani *et al*., 2017). The percentage of aluminum in used beverage cans is estimated to be 95% (Adans *et al.*, 2016). Thus, zeolite can be synthesized from used can materials, as demonstrated by Abdelrahman *et al*., (2021) and VH Putranto *et al*., (2016).

In this study, zeolite will be synthesized using cans and silica gel as aluminum and silica sources respectively. Abdelrahman conducted the similar study using the hydrothermal method (2018). The microwave method was used in this study to accelerate the synthesis of zeolite (Chen *et al.*, 2021). This method was used in this study due to the cconventional methods take longer. (Tanaka *et al.*, 2008). The synthesized zeolite will be used as an adsorbent for the primary metal ions in hard water, $Ca^{2+,}$ and Mg^{2+}. Another advantage of using cans waste as a source of aluminum in this study is to optimized canned waste for more valuable thing, especially to treat the hard water to meet the Minister of Health of the Republic of Indonesia's regulations Number 5 of 2017 concerning Sanitary Hygiene, Swimming Pools, Solus Per Aqua, and Public Baths, as well as Environmental Health Quality Standards and Water Health Requirements. The standard of water hardness is 500 mg/L.

Research Methodology

Materials

Beverage cans, Sodium hydroxide (NaOH), silica gel, aluminum foil, filter paper, and a universal pH indicator were among the materials used. FTIR (Magna-FTIR-560, USA), XRD (Bruker D2 Phaser), SEM-EDX (Phenom Desktop ProXL). The solution sample was evaluated by AAS.

Producing Zeolite with Aluminum Made of Used Beverage Cans

To produce a sodium aluminate solution, used cans were cut into bits and dissolved in a 10% NaOH solution while stirring until producing sodium aluminate ($NaAlO_2$). Afterward, the solution is filtered, and solution 1 is produced. Meanwhile, solution 2 is made by dissolving silica gel in 10% NaOH to form a sodium silicate

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(Na_2SiO_4) solution. After that, progressively add solution 2 to solution 1 while stirring continuously for 1 hour, until a uniform precipitate forms. white in color Two different treatments was used to create the gel. The initial treatment used both microwave and no microwave to heat the food. The gel was placed in the microwave and heated for 15 minutes at 170 W in the treatment microwave. The microwave was the final product (ZM). The second treatment eliminates the heating step, resulting in a non-microwaveable final product (ZNM). After that, the zeolite was filtered, rinsed with distilled water, and dried overnight at 110 °C.

Zeolite Characterization

The resulting zeolite was then characterized with Fourier Transform Infrared (FTIR) instruments to determine the zeolite functional group, X-Ray Diffraction (XRD) to determine zeolite crystallinity, and SEM and EDX to determine zeolite morphology and structure.

The Adsorption Process of Ion Ca^{2+} and Mg^{2+} in Hard Water

The adsorption process was conducted by using the batch method at neutral pH. The sample used was hard water obtained from Lamongan, East Java. Several parameters used were contact time (0, 5, 10, 30, and 60 minutes) and adsorbent doses (0.05, 0.1, 0.3, and 0.5 mg/50 ml). Hard water samples were tested with AAS to determine the final concentrations of Ca^{2+} and Mg^{2+}.

Percentage of adsorption obtained through the formula

$$\% \text{ adsorption} = \{(Co - Ct)/Co\} \times 100\% \quad (1)$$

The adsorption reduction curve was obtained by plotting the % adsorption with time for determining the optimal time and the % adsorption on the mass of the adsorbent for determining the optimal dose/mass.

Results and Discussion

The Physical Character of Zeolite

In this study, zeolite was obtained in the form of a fine white powder. ZM obtained as much as 10.8121 grams or a yield of 100.2%, and ZNM as much as 10.5387 grams, or 99.15%.

FTIR Characterization

FTIR characterization used *Fourier Transform Infrared* (FTIR) in the wavenumber range of 4000-400 cm^{-1}. The purpose of this characterization is to determine the presence of functional groups from the zeolite framework.

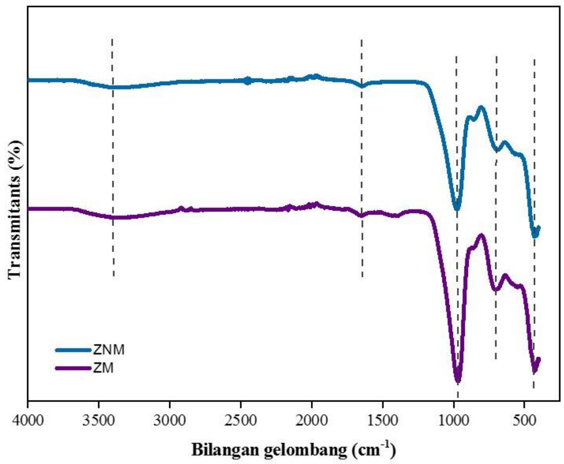

Figure 1: FTIR Spectra of Microwave Zeolite (ZM) and Non-Microwave Zeolite (ZNM)

Based on Figure 1, the absorption that appears can be seen that the synthesized zeolite has been formed. At a wavelength of 400–1400 cm-1, specific zeolite characteristic functional groups can be observed (Mozgawa *et al.*, 2011). The peak in the wavelength region of 460 cm^{-1} indicated the peak belonging to the T-O bending (with T = Si/Al), while the peak in the 670–726 region showed *symmetric stretching* of the T-O-T bond. A similar bond is also characteristically shown at wave number 980–1100 cm^{-1}, originating from the *symmetric stretching* of the T-O-T bond. These peaks were also found in the results of the study (Kumar and Jena, 2022)), which

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concluded that the zeolite formed resembled type A zeolite. However, areas of identical but wider peaks were also found in other types of zeolites, such as zeolite-X and *cancrinite.* In general, in this study, the peak intensities of several bonds were found to be higher and sharper, especially at ZM, which indicates that identical bonds have been clearly and conclusively identified.

XRD Characterization

To determine the crystallinity of the materials, zeolite was characterized with XRD. The results of the characterization of synthetic zeolite with XRD are presented in Figure 2.

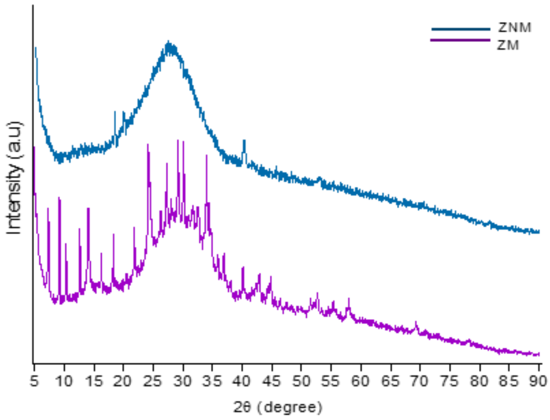

Figure 2. Microwave and non-microwave zeolite diffractogram patterns

Figure 2 shows the diffractogram pattern for the ZM sample, which has sharp peaks at 2 values of 7.33^0, 10.32^0, 12.59^0, 16.26^0, 21.78^0, 24.37^0, 26.25^0, 27.28^o, 29.16^o, 30.07^0, 33.970^0, and 34.31^0. The resulting diffractogram pattern is compared with JCPDS data 38-024183-2319 (*Joint Committee on Powder Diffraction Standard).* It is known that the resulting diffractogram pattern is similar to synthetic zeolite A with a cubic crystal form. The similarity of the diffractogram pattern was also found in the zeolite, which was successfully synthesized by El-nahas *et al.*, (2020). However, the results show that there is still amorphous silica material in ZM. As shown in Figure 2, the peaks of amorphous silica and zeolite seem to overlap. Meanwhile, for the ZNM sample, a few peaks are formed, namely 18.75^0, 18.81^0, 35.53^0, and 58.19^0. The ZNM peak has only one peak in common with the JCPDS reference, and it indicates that the zeolite crystal is not completely formed due to the lack of heating using a *microwave*. The calculation results show that the zeolite crystal size of the ZM sample is 45 nm and that of the ZNM sample is 48 nm. Based on the results of the XRD characterization, it can be proven that the ZM sample zeolite has better crystallinity than the ZNM sample.

SEM-EDX Characterization

SEM was used to examine the morphology of the materials, EDX was used to determine the distribution of elements (*mapping*) and determine the percentage of elemental content in the materials. The results of the characterization using SEM can be seen in Figure 3.

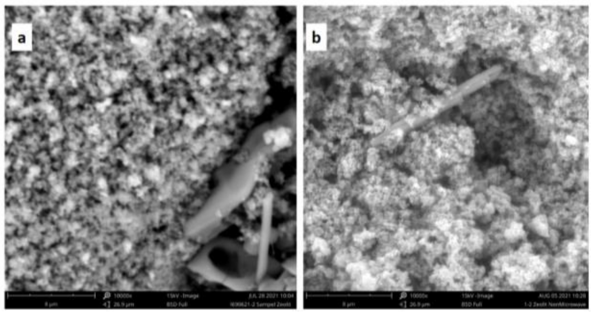

Figure 3. (a) Surface morphology of ZM and (b) ZNM

Figure 3 (a) depicts the SEM morphology of ZM at various magnifications. Based on the micrograph at a magnification of 10,000 times, it was observed that the ZM particles consisted of grains of non-uniform size, and some of the zeolite particles experienced agglomeration. In addition, ZM particles have an irregular shape as well as are porous. Figure 3 (b) is an SEM morphology for ZNM at a magnification of 10,000 times. It was observed that ZNM particles have a morphology similar to that of ZM. Abdelrahman et al. (2018) also show

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the shape of the material in the form of small spherical particles in the results of research.

The results of the analysis with EDX found that the percentage of the elemental content of the two types of zeolite was quite different. ZNM, through SEM results, appears to contain more aluminum and silica elements than ZM. The most elemental component in both materials is oxygen.

Table 1: The percentage of elemental content in zeolite derived from the synthesis

Elements	%	
	Microwave	Non-Microwave
O	56.60	65.94
Al	5.38	14.92
Si	3.97	5.72
C	11.78	9.91
Na	22.26	3.42
Ca	0.01	0.06
Fe	-	0.04

Meanwhile, the distribution of elements on the surface of the zeolite is shown through *mapping* using EDX. The results of this *mapping* can be seen in Figure 4.

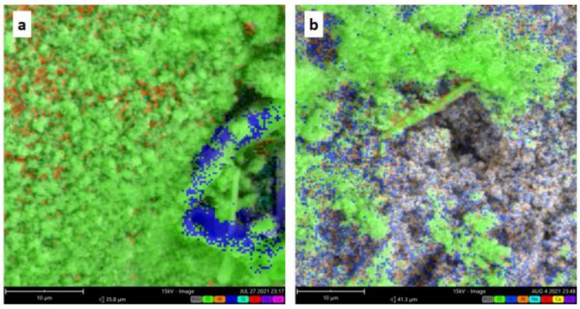

Figure 4. (a) Distribution of elements in ZM and (b) ZNM

Figure 4 shows the distribution of ZM zeolite elements is uneven and there are still many oxygen atoms, while the ZNM element distribution is more even and the number of oxygen atoms is not as high as in ZM. This could be because rinsing ZM with distilled water was not good enough.

The Analysis of Analisis Calcium and Magnesium Content of Hard Water

Analysis of the calcium and magnesium content in hard water was carried out using the AAS instrument. Time and dose were assessed in this study. The results of the characterization can be seen in Figure 5.

The adsorption process in this study was carried out at certain water pH conditions so that the hard water used was not added with other pH-regulating reagents. Research conducted by Aragaw et al. (2018) revealed that the optimal pH conditions for the adsorption of Ca^{2+} and Mg^{2+} using zeolite were between 6.5 and 7, close to the natural conditions of the water (Aragaw and Ayalew, 2019).

The effect of contact time on the removal of Ca^{2+} and Mg^{2+} was carried out in time variations of 5, 10, 30, and 60 minutes. The initial concentrations of Ca^{2+} and Mg^{2+} in the hard water samples used were 58.59 ppm and 72.63 ppm, respectively. The results are shown in Figures 5 (a) and 5 (b). At the beginning of the adsorption process, between the contact times of 0 minutes and 5 minutes, the zeolite showed a very large increase in adsorption ability. This was because at the beginning of the adsorption, up to 5 minutes, the surface conditions of the zeolite were still clean. Therefore, the adsorption process happened very quickly and then increased slowly. However, after reaching the optimum contact time (5 minutes), there was a decrease in the absorption of metal ions Ca^{2+} and $Mg^{2+,}$ which was caused by the interaction between metal ions and the oversaturated zeolite where metal ions Ca^{2+} and Mg^{2+} were adsorbed in the minute 5. It revealed collisions between the adsorbate and the adsorbent particles rapidly and continuously, so there would be a possibility that the adsorbate would be released again by the adsorbent in the next minute.

The adsorption capacity was strongly influenced by the adsorbent in the solution or the solid/liquid ratio. The removal of Ca^{2+} and Mg^{2+} was affected by the solid/liquid ratio as illustrated in Figure 5 (c) and (d). The number of adsorbent solids varied from 0.05 g, 0.1 g, 0.3 g, and 0.5 g, and the volume of constant hard water was 50 mL. Based on the results, the removal of Ca^{2+} and Mg^{2+} increased as the solid/liquid ratio increased. Adsorption of Ca^{2+} and Mg^{2+} occurred at a

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dose of 0.5 g of zeolite in 50 mL of hard water.

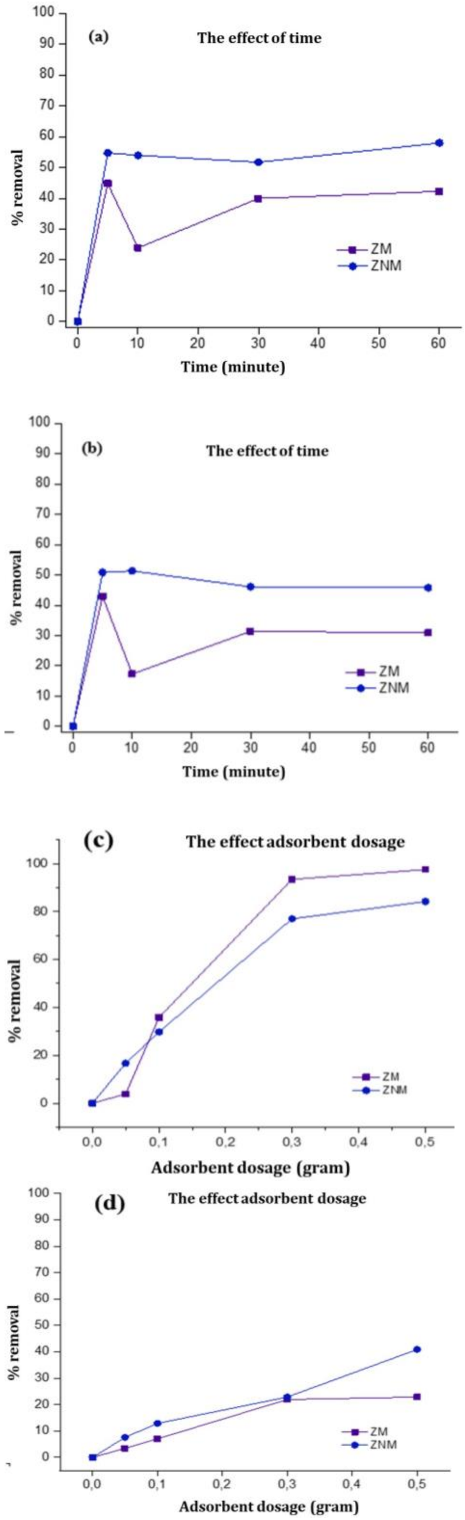

Figure 5: Percent removal for metal ions a) Ca^{2+} b) and Mg^{2+} based on contact time optimization, and dose optimization for metal ions c) Ca^{2+} d) Mg^{2+}

The availability of larger ion exchange sites and various pore types on the zeolite surface caused the increase in adsorption for Ca^{2+} and Mg^{2+} ions. Aragaw et al (2018) investigated the adsorption of Ca^{2+} and Mg^{2+} on zeolite. The result show that the uptake of Ca^{2+} and Mg^{2+} are reach 670 and 750 ppm respectively. Zeolite was had a good potential to decrease the concentration of metal ions in the water, including the presence of Ca^{2+} and Mg^{2+} in the hard water. Hard water from the around of Brondong district of Lamongan, East Java, was evaluated in this study. Due to the samples are not only contain Ca^{2+} and Mg^{2+}, it seems to contain some other contaminants, thus the % removal of the specific metal ions (Ca^{2+} and Mg^{2+}) did not reach 100%. There were be molecule competition to reach the surface of the materials. In addition, rudimentary zeolite may also affect adsorption results, especially parts of the framework that have not been formed perfectly.

Conclusions

The synthesis of zeolites depends on the method used. In this study, non-microwave method produces amorphous silica predominantly material (ZNM). While with microwaves, although amorphous silica is still found, it shows diffractogram peaks that are identical to zeolite peaks (ZM). SEM result confirm both of materials are in the form of agglomerated tiny particles. The proportion of Ca^{2+} and Mg^{2+} adsorption in hard water ranged from 84 to 97 percent for Ca^{2+} and 25 to 51 percent for Mg^{2+}. In this study, the optimal time was 30 minutes, and the optimal mass was 0.5 grams for all materials.

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