

Synthesis Of Zeolites From Lombok Pumice As Silica Source For Ion Exchanger

Mega Putri K.¹, Regina G.L.D.¹, Ade L.N.F.¹, Haiyina H.A.¹, Nura H.H.¹, Darminto^f

¹Physics Department, Math and Science Faculty, Institute of Tehnology Sepuluh Nopember (ITS), Surabaya, Indonesia

*e-mail : mega.putri12@mhs.physics.its.ac.id

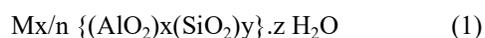
Abstract— Hard water is the mineral content in the water such as calcium and magnesium which have a negative impact of these minerals in the kidney. The hardness level can be lowered through the principle of ion exchange. Zeolite has been known as a good adsorbent to be used as an ion exchanger. However, natural zeolites can't be modified. Therefore, it is made of synthetic zeolites using pumice as a substitute for silica from Ijobalit, East Lombok (0-30 masl) and Karang Sidemen, Central Lombok (500-1000 masl). This study used other variations of the level of grain size of pumice, which is 60 mesh and 80 mesh. With BET, pore size pumice from the first location is 3,2 nm. While the pore size pumice from the second location is 3,207 nm. Pumice mixed into a solution of sodium hydroxide to form sodium silicate. Meanwhile, Al (OH)₃ was mixed into a solution of sodium hydroxide to form sodium aluminate. Then sodium silicate and sodium aluminate is mixed with stirring for 1 hour and temperature of 160°C. Electrical conductivity test showed that the smaller grain size pumice produce the greater conductivity. The conductivity value of 1A80, 1A60, 3A80, and 3A60, respectively was 96.9 mS/cm, 248 mS/cm, 335 mS/cm and 205 mS/cm. 3A80 synthetic zeolites potentially has the ability in ion exchange to reduce the level of water hardness.

Keywords— ion exchanger, pumice, synthetic zeolite.

INTRODUCTION

Hard water is formed when water passes through limestone rock area so that calcium and magnesium ions dissolved in water[1]. Calcium and magnesium ions in temporary hard water can be removed by heating. While, on permanent hard water necessary chemical reaction[2]. These chemical reaction can use ion exchange principle where calcium ion was removed by sodium ion[3]. Ion exchanger have various materials used. The materials different from physical or chemical composition, natural or synthetic[4]. Most of ion exchanger used synthetic organic exchanger. This kind available on several shapes like powder or grain. Hydrocarbon bonding of this material could be random and flexibel. The advantages of synthetic organic are high capacity and low cost[5]. One of these kind is synthetic zeolite made by hydrothermal process[6].

Zeolite is a mineral form of crystalline silica-alumina which consists of three components, namely exchangeable cations, alumina silicate framework and water that make porous structure[7][8]. Al-O-Si bonding form a crystal structures while the alkali metal is a source of exchangeable cations[9]. Cations in the zeolite framework can be exchanged and substituted without changing the original framework structure[10]. This was caused by the Al atom that causes tetrahedral alumina negatively charged, thus requiring a cation to neutralize[8]. The empiric equation is presented below.



Mx/n is exchangeable cation; $\{(AlO_2)_x(SiO_2)_y\}$ is silica-alumina framework; z H₂O is water content; and y>x[11].

The advantages of synthetic zeolite are; purity of synthetic zeolite is higher than natural zeolite and the ratio of silicon can be arranged as needed, thus affecting the properties of the material[12]. Synthetic zeolite can use as adsorbents and catalysts[13]. It has highly rated in their molecular sieving and ion exchange[14]. Zeolites as ion exchanger having alkali metal cations that can be move freely and can be exchanged with other metal cations by the same amount[15]. The main frame structure of the zeolite is occupied by silicon or aluminum atoms with four oxygen atoms at each corner. These structure causes zeolite has the ability as an ion exchanger[16]. There are several types of synthetic zeolites, which one is zeolite type A. Zeolite type A (the next called zeolite A) has the ability in high selectivity towards ion adsorption Ca²⁺ and Mg²⁺[16]. Addition to composition, thermodynamic variables such as pressure, temperature and time also influences the formation of synthetic zeolites[17]. Main composition of synthetic

zeolite is silica and alumina[19]. One silica source could from pumice.

Pumice is mineral rocks that erupted from volcanic mountain (pyroclastic rock) that content glass, called glass silicate volcanic rock[20][21]. This material is often called the scattering material that released during a volcanic eruption[22]. Volcanic activity depend on magma composition, most from volatile character that erupted from water become steam. Main gases when eruption are carbon dioxide and sulphur[20]. Indonesia is located on the ring of fire that resulted this country has several volcanoes, one of which is Mt. Rinjani in Lombok (last erupted, 2016). Pumice included into extrusive igneous rock types containing silica as main compound. It has a lightweight structure with small pore size, so that yields huge surface area.

MATERIALS AND METHODS

a. Pumice Resources and Characteristics

The variable of this study is location of source deposit was obtained from Ijobalit (0-30 masl), east region and Karang Sidemen (500-1000 masl), middle region of Lombok island. Another variable is grain size of pumice, 80 mesh (0,177 mm) and 60 mesh (0,25 mm). Lombok pumice has a characteristic; the colour is grey-white to brown, big gravel with size 5-20 cm, and also has a huge potential for prosperity people with the detail is in the Table 1. The highest potensial location is in Labuhan Haji district. That's because the scattered deposits from Rinjani mountain carried by winds to the east region and then make sedimentation for along time. Especially, in east region also available rotary machine that used for washing and sorting by each size. Since a long time ago, pumice be used stone wash for jeans clothes.

Table 1. Potential of Pumice in East Lombok[23]

District	Availability		
	Volume (m ³)		Area (Ha)
	Early	Present	
Montong Gading	4.698	3.751	1,17
Masbagik	50.400	25.200	6,3
Suralaga	84.135	25.240	16,7
Labuhan Haji	665.201,75	265.160,75	74

Composition of pumice with XRF; SiO₂, 58,3%; Fe₂O₃, 12,4%; Al₂O₃, 12%; Fe₂O₃, 12,4%; K₂O, 7,73%; CaO, 6,75%; TiO₂, 1,45%; MnO, 0,42%. Fig 1. shows the peaks of X-ray diffraction has large peak width and diffraction peaks is slope slightly (not steep). It explains

that the arrangement of atoms in materials is not periodic. So it can be said that pumice is the amorphous.

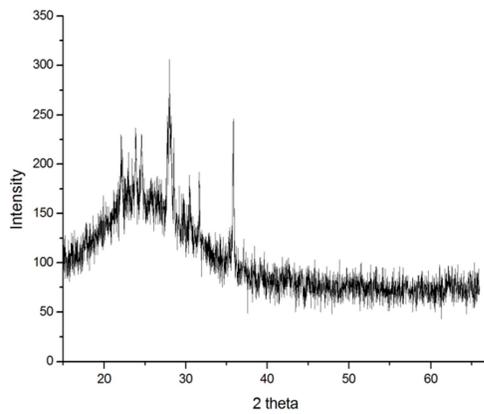


Fig 1. X-Ray Diffraction (XRD) of Lombok pumice from second location

b. Synthesis

Sodium silicate formed by 5 g pumice powder (washed and dried) mixed with 20 g NaOH (diluted with distilled water). The mixture was stirred with heating 350°C for ± 45 minutes and become a solids that was then added 200 ml of distilled water with stirring for 1 hour at room temperature. Furthermore, the mixture is allowed to stand for 12 hours then filtered using spherical filter and the distillate is concentrate form. While, sodium aluminate formed by NaOH (diluted with distilled water) mixed with Al(OH)₃ at temperature 100°C for 1 hour and generate sodium aluminate (liquid). Then both of them mixed at temperature 160°C for 1 hour using ratio of based on recently experiment[8] ratio of sodium silicate : sodium aluminate, 15:15 (ml), that obtained zeolite type-A with conductivity value is 0,383 mS/m. Then all samples were washed using distilled water until a neutral pH. Furthermore, samples were filtered and dried using the oven at 100°C. This research was conducted for each sample with different mesh and locations. After that, all samples was characterized using X-Ray Diffraction (XRD) and conductivity meter.

RESULTS

a. BET Result

BET result (Quantachrome NovaWin; Version 10.01) show pore size of pumice from the first location is 3,2 nm and from the second location is 3,207 nm, similar since location between both of them is quite near. Relationship of volume and relative pressure of adsorption and desorption is illustrated in Figure 2. Nitrogen adsorption occurs at low relative pressures (P/P₀) that causes the volume of adsorbed nitrogen is little, even nothing. It show in the relative pressure at 0,02 with total volume of absorbed nitrogen is 0 cc/g. Nitrogen adsorption occurs when the relative pressure increase to ± 0,05 where the volume is ± 0,05 cc/g. It show that the first nitrogen adsorption occur on the microporous region then move into the mesoporous region. Thus, higher relative pressure adsorbed, also increase nitrogen adsorbed. In Figure 2, the adsorption-desorption isotherm graph shows the relative pressure difference, called hysteresis curve. Adsorption-desorption isotherms met on one point when the relative pressure cross to the value of relative pressure (P/P₀) is 0,7 and the value of volume is 4,927 cc/g. In this state, the amount of adsorbed nitrogen will reach a peak (saturation point), while desorption process begins[24]. But, the point also mean when the gas should adsorbed, there were also events desorption. These could happen

remember pumice has huge pores and small particles. So, there is not the gas was absorbed again, but themselves.

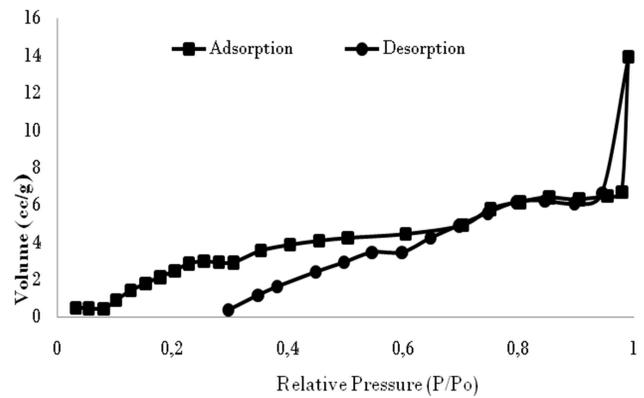


Fig 2. Adsorption-Desorption of Lombok pumice from second location

The average pore size show that pumice has large specific surface area, that is 19,23 m²/g. Surface area influence of the porosity and density, where the greater the porosity, the density gets smaller. It because, the higher density means the particles is getting closer to each other. When particles tightly, the ability value of adsorbed gas is getting smaller.

b. XRD Result

Results of XRD, shows the relationship between the intensity and angle of each samples that combined using Origin software shown in Figure 4. Peak similarities can be seen between the four samples with zeolite type A (Figure 3). Where the value of 2θ of four samples at 12,48°, the value of 2θ zeolite type A is equal 12,49°. Meanwhile there is also 2θ of 24,04° similar to 2θ zeolite type A[15].

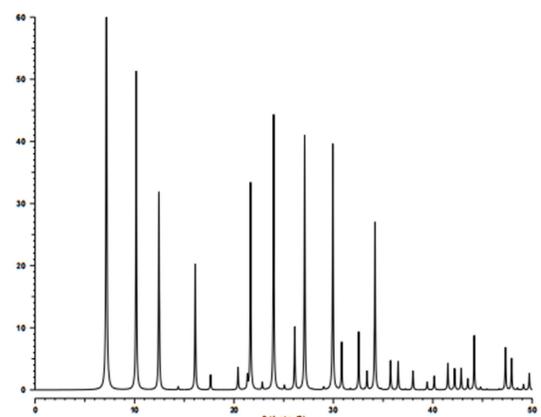


Figure 3. X-Ray Diffraction of zeolite type-A[15]

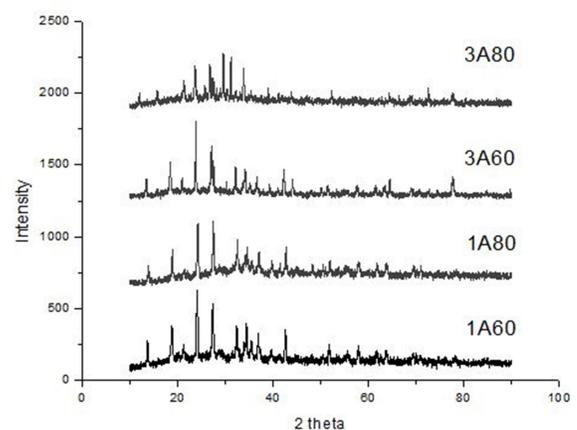


Figure 4. X-Ray Diffraction of samples

The sample's code 1A60 is meaning that sample content pumice from first location, 60 mesh. 1A80; content pumice from first location, 80 mesh. 3A60 and 3A80 is synthetic zeolite from second location of pumice with grain size respectively 60 and 80 mesh.

c. Conductivity Result

The sample from second location with 80 mesh, has the highest conductivity values (shown at Table 2), which is 335 mS/cm. Thus, the sample potentially be used in better ion exchange process than previous studies[8]. Because, the amount of surface area makes chemical bonding that occurs on the surface is getting stronger. It's important in study of composites, where smaller particle size of the material, increase the strength of composite materials. Meanwhile, samples from first location with 80 mesh has smallest conductivity values. Whereas the value should be greater than 60 mesh on the same location, this matter the influence of particle size.

Zeolites with high conductivity has a negative charge comes from the formation of the anion $Al(OH)_4^-$ polymerized on the state of bases. The existence of the aluminum atom the caused the zeolite has a negative charge. Anion in the zeolite framework can move freely and capable of binding cations that can be exchanged. Tetrahedral units of silica and alumina is formed of four oxygen atoms surrounding one atom of Si or Al. Each oxygen atoms are contents two negative charge and each silikon atoms contents four positive charge. These makes tetrahedron alumina has negative charge, so that cations necessary.

Table 2. Conductivity value of samples

Location	Mesh	Conductivity Value (mS/cm)
1	80	96,9
	60	248
2	80	335
	60	205

In this study, the huge surface area makes adsorption of ions maximum. Cation obtained from NaOH for reduce levels of Ca^{+} and Mg^{+} . Sodium ions will replace the presence of Ca^{+} and Mg^{+} ions until balance or saturated state. To maximize the ion exchange happens required large surface contact. The surface area of pumice reached 19.23 m²/g, enable for ion absorption maximum. Maximum ion exchange marked by greater conductivity value. Temperature and residence time are little influence on the nature of the zeolites. The H₂O adsorption capacity is an important parameter in the evaluation of the degree of crystallinity of zeolites. The adsorption capacity is low for products obtained at low residence time and for those derived from pumice with their low crystallinity[4].

CONCLUSION

From this study, can be concluded that Lombok pumice has pore size about 3,2 nm and the specific surface area is 19,23 m²/g. Lombok pumice can be used as silica source for synthetic zeolites and produce zeolite type-A with the greatest conductivity value 335 mS/cm. This is potential as ion exchanger to reduce hard water because of the ability surface area when adsorbed Ca^{+} and Mg^{+} .

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