



Modified Natural Zeolite into Hydrophilic Zeolite for Desalination of Brackish Water and The effect of Long Time of Stirring

Alex A.Lepa^{1*}, Ilham Salim²

¹Department of Chemistry Education, University of Cenderawasih, Jayapura, Indonesia

²Department of Chemistry, University of Cenderawasih Jayapura, Indonesia

Abstract : Desalination of brackish water using modified natural zeolite (MNZ) that had hydrophilic character and the effect of long time of stirring has been studied. The MNZ was synthesized by destructing the natural zeolite with 6M HCl solution, followed by treating with Al(OH)₃, CTAB and distilled water. The mixture was regulated to pH of 12. The mixture was then poured into a reactor for hydrothermal process at 140 °C for 24 h. The dealumination of natural zeolite was characterized using X-Ray Fluorescence spectrometry(XRF) and the MNZ was characterized using Fourier Transform Infra Red, X-Ray Diffraction, and surface area analyzer. This research was conducted in batch with variation of adsorbent weight and long time of stirring. The Absorption of brackish water using MNZ was carried out in the variation of ratio of zeolite (g) to brackish water (mL) in Batch method. The filtrate results of absorption were analyzed using Atomic Absorption Spectrophotometry (Na⁺ contents) and Mohr Method (Cl⁻ and NaCl contents).The resulted showed that the dealumination of natural zeolite had Si content of 39.28%, and Al of 3.27 %. The results of measurements with XRD produced a different form of chromatogram and type of zeolite. The dominant mineral was faujasite. The MNZ had Surface area, total pore volume and pore diameter of MNZ zeolite were 285.538m²/g; 0.303 cm³/g; and 7.892 nm respectively. The absorption results of Na⁺ and NaCl contents in brackish water were 93,7 %, and 95.9 %at ratio of 2.5 g zeolite to 50 mL of brackish water that was obtained at 2 h of long time of stirring.

Keywords : natural zeolite, modified, absorption, desalination, brackish water.

Introduction

Brackish water is water that has more salt than freshwater, but not as much as seawater. Brackish water can occur due to seepage of sea water that penetrates the soil layer so that the water from this seepage mixes with ground water or mixes with collection of fresh water then the taste of this mixed water becomes slightly salty (brackish). The salinity of brackish water describes the dissolved salt content in brackish water. Brackish water is water that comes from a mixture of fresh water and sea water/salt water. A water can be said to be

brackish if the mineral salt content in each liter ranges between 0.5-30 grams¹. Brackish water can usually be found in river mouth areas. Salinity is generally caused by the presence of sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chloride (Cl⁻), sulfate (SO₄²⁻) and bicarbonate (HCO₃⁻) in water². This brackish water can bring harm if it is used for certain activities, for example dangerous for health if used as drinking water. One alternative to desalination of brackish water is to use hollow materials that can be either natural zeolites or synthetic zeolites. Zeolites are microporous aluminosilicate minerals which could be used as ion exchanger in domestic and commercial water purification, softening and other applications³. Substitution of silicon by aluminum atoms in the crystal framework leads to extra negative charge to be balanced by surrounding counter ions (such as Na⁺, K⁺, Ca²⁺, and Mg²⁺), and these counter ions are easily exchanged by other surrounding cations in a contact solution⁴. Zeolite materials allow an introduction of new functional groups through several processes of modification, improving substantially its activity and selectivity on the removal of several substances^{5,6}. Many authors show the use of modified natural zeolite on environmental applications, mainly anions uptake from effluents by adsorption processes^{7,8}.

Zeolites, crystalline aluminosilicates with a well-defined pore/channel structure, have gained significant research attention as potential materials for desalination processes, because they could theoretically provide perfect separation of molecules of different sizes and adsorptive properties⁹.

Zeolites have in its internal structure channels and cavities interconnected of molecular dimensions where compensation cations allowing the ion exchange¹⁰. Natural Zeolites are charged negative by having an active group cation exchange in the form of alkali cations or alkaline earth for example Na⁺, K⁺, or Ca²⁺. This active group acts as load balancer that can be exchanged with other cations for example cationic surfactant¹¹. Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades¹². Natural zeolite can not be directly used as a catalyst or adsorbent due to non-zeolite material content is high. So far it has made efforts to acquire natural zeolite with a high purity zeolite and can be used as a catalyst or adsorbent¹³. Natural zeolite has silica content (SiO₂) and alumina (Al₂O₃) that is still fused and chemically bonded in the natural zeolite. Modification of natural zeolite from Wonosari Yogyakarta by using HCl solution was carried out and then used in paraffin hydrocracking¹³. Interaction of natural zeolite with brackish water can reduce the Na⁺ content of 35,19%¹⁴. Activated zeolite was able to absorb Na⁺ content of 80% in brackish water¹⁵. Desalination of brackish water with surfactant-modified zeolite can reduce salinity up to 52% of its initial value¹⁶. Modification of natural zeolites to adsorb Fe²⁺ and Mn²⁺ in water (Barloková and Ilavský¹⁷). Modification of natural zeolites for adsorption of heavy metals in water¹⁸. Modification of natural zeolites for adsorption of nitrates and ammonium ions from water.¹⁹, modification of natural zeolites for adsorption of nitrates.²⁰. Removal of NaCl from aqueous solutions by using clinoptilolite zeolite²¹.

Experimental

Materials

Natural zeolite was obtained from Klaten, centre of Java, Indonesia. The chemicals used were HCl 37%, Al(OH)₃, NaCl, AgNO₃, K₂CrO₄, pH universal paper that purchased from E. Merck, and cetyltrimethyl ammonium bromide (CTAB) from (Aldrich). Aquadest was purchased from Chemistry Laboratory, Department of Chemistry Faculty of Science and Mathematics, Cenderawasih University, Jayapura, Indonesia. Brackish water was purchased from brackish water sources on the coast of Argapura, City of Jayapura, Indonesia.

Instrumentation

X-Ray Fluorescence spectrometry (XRF): Bruker S2 Ranger, Fourier Transform Infra Red (FTIR): Shimadzu Prestige 21, X-Ray Diffraction (XRD): Shimadzu-6000 XRD, Atomic Absorption Spectrophotometry (AAS): Shimadzu 6650F, Surface area analyzer: NOVA1200 (QUANTACHROME).

Procedure

Modified natural zeolite (MNZ) and modification of natural zeolite to zeolite with ratio Si/Al of ± 1

After being washed and separated with water then dried in oven at temperature of 120 °C for 4 h, the natural zeolite was grinded and sieved (100 mesh). The natural zeolite (20 g) was destructed (dealumination) using 50 mL of 6M HCl at 100 °C followed with refluxing mixture for 6 h. The natural zeolite was filtered and washed using deionized aquadest until neutral condition, dried on the oven at 120 °C for 4 h. Furthermore, synthesis treatment was carried out as follows:

Dealuminated natural zeolite (10.0 g) was mixed with Al(OH)₃ (8.5g), CTAB (0.3 g) and distilled water was added to adjusted pH of 12 while stirring for 48 h at room temperature. Then the samples were hydrothermally treated at 140 °C for 24 h. The synthesized zeolite (ZSNZ) was then washed using aquadest until the solution reached pH of ± 6 , then filtered, followed by dried on the oven at 120 °C for 4 h and calcined at 350 °C for 3 h.

Absorption process

Modified zeolite was interpreted with brackish water with variation of 0.5 g : 50 mL; 1 g : 50 mL ; 1.5 g : 50 mL ; 2 g : 50 mL and 2.5 g : 50 mL respectively. Each of variation was mixed and stirred using magnetic stirrer for 1, 2 and 3 h, then separated (filtered) between the zeolite and the filtrate (absorption results) using Whatman paper of 42. The filtrate was collected in container. The contents of Na⁺ were determined using AAS, while the contents of Cl⁻ and NaCl were determined using the Mohr method²².

Determination of Na⁺, Cl⁻ and NaCl contents

The contents of Na⁺ were determined using AAS, while the contents of Cl⁻ and NaCl were determined using the Mohr method. The procedure for determining of Cl⁻ as follows:

Initial treatment

Standardization of the standard solution of AgNO₃ with 0.0141 N. NaCl (25 mL), entered into Erlenmeyer flask of 100 mL. The blank solution was made using 25 mL of distilled water, then added 2 mL of indicator solution of 5% K₂CrO₄ (w/v) and stirred. Then it was titrated with AgNO₃ solution until the color changes (brownish red color) and the volume of AgNO₃ solution used for the sample (A-mL) and blank (B-mL) was recorded. Calculation of the normality of the standard solution of AgNO₃ using formula :

$$N \text{ of AgNO}_3 = \frac{V_1 \cdot N_1}{V_A - V_B} \dots \dots \dots (1)$$

With the understanding:

N of AgNO₃ = the normality of standard solution of AgNO₃ (mgrek / mL)

V_A = the volume of AgNO₃ standard solution for titration of NaCl solution (mL)

V_B = the volume of AgNO₃ standard solution for blank titration (mL)

N₁ = the normality of the NaCl solution used (mgrek / mL)

V₁ = the volume of NaCl solution used (mL)

Procedure of test

Taken 100 ml of sample water and used it in duplicate, then water sample was put into the Erlenmeyer flask of 250 mL. In the test sample, 2 mL of indicator solution of 5% K₂CrO₄ was added, then titrated with the standard solution of AgNO₃ until the end point of the titration was indicated by the formation of brownish red deposits from Ag₂CrO₄, then recorded the volume of AgNO₃ used. Blank titration of 100 ml of distilled water was carried out. The titration was repeated twice and averaged the volume of AgNO₃ obtained. The desalination water was measured by chloride content using the formula equation:

$$\text{Content of Cl}^- \text{ (mg / L)} = \frac{(A-B) \times N \times 35.450}{V} \dots \dots \dots (2)$$

Calculation of NaCl content with the formula:

$$\text{NaCl (mg/L)} = \text{content of Cl}^- \text{ (mg/L)} \times 1.65 \dots \dots \dots (3)$$

With the understanding:

A = the volume of AgNO₃ standard solution for sample titration (mL)

B = the volume of AgNO₃ standard solution for blank titration (mL)

N = the normality of the standard solution of AgNO₃ (mgrek/mL)

V = the volume of sample (mL)

To determine efficiency can be used the following equation:

$$\text{Efficiency (\%)} = \frac{(S_0 - S)}{S_0} \times 100\% \dots\dots\dots (4)$$

S₀ = the level of parameters before processing

S = level of parameters after processing

Results and Discussion

Characteristic Of MNZ Zeolite

Results of Measurement Si and Al of dealumination of Natural zeolite Using X-Ray Fluorescence spectrometry (XRF)

For modification of natural zeolite into zeolite with Si/Al ratio = ±1, it is necessary to know Si and Al content in natural zeolite after dealumination. Natural zeolite is heterogeneous system which consists of silica tems and alumina silica systems as well as other impurities such as organic materials. The silica system and organic impurities are parts that are not active as absorbent or can also be referred to as absorbent impurities, so the contents that can inhibit the absorp process need to be removed. Interaction with 6M HCl solution can also react with metals contained in natural zeolite so that it causes the occurrence of dealumination and decationation, namely the release of Al and other cations such as Fe²⁺, Mn⁺ in the contents of natural zeolite. However, interaction with 6M HCl, in certain natural zeolite does not cause the natural zeolite to be decomposed into silica and alumina free which is the raw materials of zeolite synthesis. The results of measurements with XRF after dealumination of natural zeolite with 6M HCl obtained Si = 39.28%, dan Al = 3.27%. From this result, to make zeolite with Si/Al ratio of ± 1 (hydrophilic zeolite), it will need a lot of Al from Al(OH)₃ which was quite a lot.

Results of Analyze of MNZ zeolite Using Fourier Transform Infra Red (FTIR)

Fig.1a and 1b can be seen FTIR spectra of the NZ and MNZ with characteristics based on the wave number of the zeolite mineral^{20,21}.

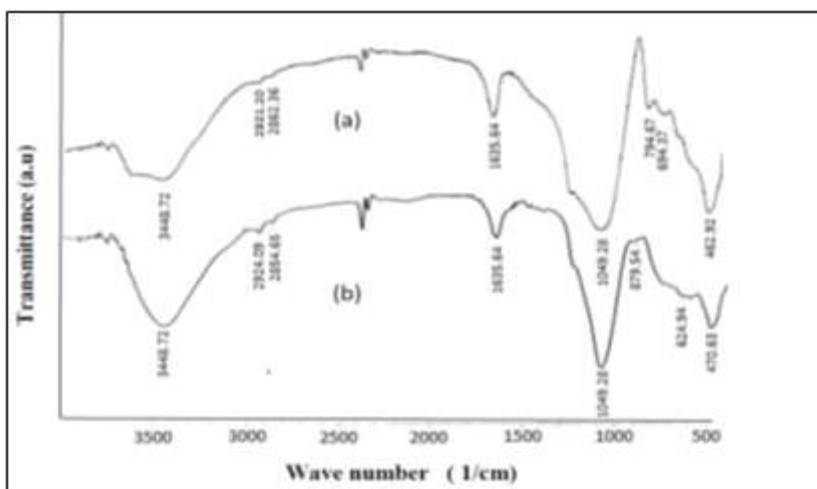


Fig.1. FTIR Spectra of (a) NZ (b) MNZ

Fig.1a for the NZ showed that wave number at 3448.72, 2931.80, 2862.36, 1635.64, 1049.28, 794.67, 694.37, and 462.92 cm^{-1} for Si-OH bonding (silanol), asymmetric stretching vibration of C-H, symmetric stretching vibration of C-H, O-H group bending vibration of the adsorbed water molecules, TO4 (Si-O and Al-O are finger print of zeolite), symmetric stretching vibration of Si-O and Al-O, symmetric stretching vibration of Si-O and Al-O, bending vibration of Si-O and Al-O respectively. Fig.1b showed some peaks of the MNZ that can be stated as follows: At wave number of 3448.72, 2924.09, 2854.65, 1635.64, 1049.28, 879.54, 624.94 and 470.63 cm^{-1} for Si-OH bonding (silanol), asymmetric stretching vibration of C-H, symmetric stretching vibration of C-H, an O-H group bending vibration of the adsorbed water molecules, TO4 (Si-O and Al-O are finger print of zeolite), symmetric stretching vibration of Si-O and Al-O, double ring, bending vibration of Si-O and Al-O respectively. In the modification of this natural zeolite, there was a shift in symmetric stretching vibration of Si-O and Al-O, symmetric stretching vibration of Si-O and Al-O, while TO4 (Si-O and Al-O finger print of zeolite) remained wave number. From this shift it is possible for new minerals or new types of zeolites not to be present in the composition of natural zeolites before being modified. Between the NZ and MNZ there were differences in sharpness. The NZ before modified seen the peak was widened. On the other hand after the NZ was modified has peaks sharper. This indicates that there has been increasing character of zeolite. The MNZ was more homogeneous compared with that of the NZ.

Results of Analyze of MNZ zeolite Using X-Ray Diffraction (XRD)

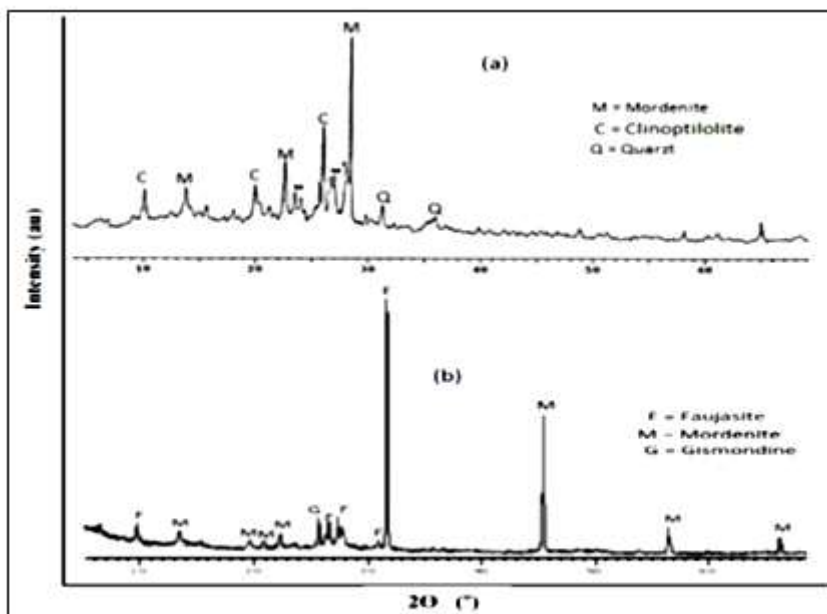


Fig.2. Diffractogram of a) NZ, b) MNZ

Natural zeolite is generally found in mixture with other type of zeolite and amorphous minerals such as feldspar, silica, clay, transition metal oxide, and organic contaminants²³. The XRD results in Fig. 2a showed that the natural zeolite (NZ) was composed of various minerals which showed heterogeneity implies. Impurities contained in the NZ higher. On Fig.2a showed that result of modified natural zeolite composed of crystalline peaks were sharper and higher and the highest peak at $2\theta = 27.99$, $d = 3.18$. The mineral content of NZ from Klaten based on 2θ include: mordenite, clinoptilolite and quartz, as well as other amorphous mineral. The dominant mineral content in the NZ based on strong peaks was mordenite based on its 2θ .

Meanwhile, the XRD results in Fig. 2b) showed that the MNZ was composed of various minerals which showed more homogeneous implies. Based on JCPDS (Joint Committee on Powder Diffraction Standards), the XRD results in Fig. 2b) showed that the MNZ was composed of various minerals which showed heterogeneity implies but it was zeolite minerals. Based on 2θ the results of the diffractogram involved: $9.78^\circ =$ faujasite; $13.48^\circ =$ mordenite; $19.64^\circ =$ mordenite; $20.85^\circ =$ mordenite; $22.25^\circ =$ mordenite $25.67^\circ =$ gismondine; $26.26^\circ =$ faujasite; $27.35^\circ =$ faujasite; $30.92^\circ =$ faujasite; $31.69^\circ =$ faujasite; $45.43^\circ =$ mordenite; $45.56^\circ =$ mordenite; $56.48^\circ =$ mordenite; $75.26^\circ =$ mordenite; $83.98^\circ =$ mordenite respectively. The mineral content of MNZ results were faujasite, mordenite and gismondine. The dominant mineral content in the MNZ based on

strong peaks was faujasite zeolite. Synthesis of zeolite from raw material that its silica and alumina were still fused and chemically bonded such as natural zeolite, fly ash, volcanic ash generally produced a mixture zeolite²⁴⁻²⁷.

Results of measurement of surface area, pore volume and pore diameter

Table 1. Characteristics of NZ, and MNZ sample

Shape of zeolite	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (nm)
NZ	53.657	0.083	1.989
MNZ	285.538	0.303	7.892

In Table 1, the surface area, pore volume and diameter of the NZ were smaller than that of the MNZ. This condition may be because of the organic impurities and other non-zeolite material that covered the surface and pore of the NZ. The MNZ sample showed average pore diameter of 7.892 nm that was classified as mesopore. Likewise, MNZ has a surface area, pore volume and diameter larger than NZ. This could be caused by the addition of NaOH, or CTAB as a surfactant. Synthesis of mesoporous zeolite with the addition of NaOH solution had been conducted and reported that the addition of NaOH solution to produce zeolite mesoporous size is not too large, but a large pore size obtained after the addition of NaOH and followed by formation in hydrothermal reaction²⁸. Synthesis of mesoporous zeolite by adding NaOH solution whose concentration was varied and surfactant (CTAB) that concentration was kept as well as followed by formation in hydrothermal reaction, the result showed that NaOH, CTAB and hydrothermal process increase the surface area and pore size significantly²⁹.

Results of Absorption of Brackish Water Using Modified Natural Zeolite (MNZ)

The effect of Weight Change on Reduction of Na⁺, Cl⁻ and NaCl Content

Before the absorption of brackish water with MNZ zeolite, firstly the contents of Na⁺, Cl⁻, and NaCl were measured in the brackish water. Results of Na⁺, Cl⁻ and NaCl contents were 1568.06, 1352.15 and 5217.54 mg/L respectively.

Table 2 : Results of absorption of brackish water using NZ and MNZ

Zeolite weight (g)	Absorption using NZ (g/L)			Absorption using MNZ (g/L)		
	Na ⁺	Cl ⁻	NaCl	Na ⁺	Cl ⁻	NaCl
0.5	1.247	3.103	5.212	0.812	1.720	2.839
1.0	1.125	2.567	4.236	0.477	0.715	1.179
1.5	1.018	2.213	3.651	0.166	0.315	0.521
2.0	0.969	1.559	2.572	0.10	0.179	0.296
2.5	0.968	1.558	2.571	0.099	0.178	0.295

The data in Table 2 is the result of absorption carried out in the zeolite position in a container with variation in weight of zeolite and brackish water with a fixed volume. Stirring or contact between zeolite and brackish water was done for 1 h. The filtrate was analyzed for the content of Na⁺, Cl⁻ and NaCl. For NZ zeolite, there was reduction in Na⁺, Cl⁻ and NaCl contents, with an increasing in the ratio of zeolite to brackish water. However, this decline has not reached the maximum limit allowed in drinking water content. In the MNZ, there was also reduction in Na⁺, and Cl⁻ contents, along with the increasing ratio of zeolite to brackish water. The decrease by using MNZ at the ratio of zeolite to brackish water (2 g: 50 ml) had produced the maximum content and allowed for using as drinking water. The decrease with using NZ was lower than MNZ. On NZ, treatment was done only by heating at temperature of 120 °C for 4 h. By this treatment had surface area of 53.657 m²/g; pore volume of 0.083 cm³/g; and pore diameter of 1.989 nm respectively. Surface area, total pore volume and pore diameter of MNZ were 285.538 m²/g; 0.303 cm³/g; and 7.892 nm respectively. This measurement result was higher than NZ. The MNZ was obtained by In addition, organic impurities that cover the pores of the

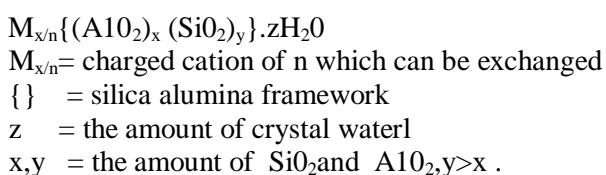
natural zeolite would also come out so that the surface area, pore volume and diameter of the pore would be more open and larger than before. Thus the absorption ability of MNZ was higher than NZ. Furthermore, on

MNZ also decreased of Na⁺, Cl⁻ and NaCl contents. This situation can be caused by the preparation of MNZ with the addition of Al(OH)₃ which was quite a lot to form Si/Al ratio = ± 1 (hydrophilic zeolite).

From the observations showed that zeolite could reduce the content of Na⁺, Cl⁻ and NaCl in brackish water by using MNZ. The efficiency of decreasing Na⁺, Cl⁻ and NaCl content with MNZ as adsorbents turns out to have good results. The efficiency of decreasing Na⁺, Cl⁻ and NaCl content would increase along with the increase in weight of the adsorbent because zeolite has a porous structure. This zeolite contains a lot of fine pores and a large surface area that allows Na⁺, Cl⁻ and NaCl particles to occupy empty space. This condition would adjust to the treatment variable which was the weight of the adsorbent and also affects the number of cells absorbed. The heavier zeolite adsorbents also produced good results and could be expressed that the more mass of adsorbent then Na⁺, Cl⁻ and NaCl was getting bigger. The dominant decrease occurred in the weight ratio of 2 g to 50 mL of brackish water. Furthermore, 2.5 g weight would still reduce Na⁺, Cl⁻ and NaCl but it would tend to be constant because the amount of brackish water was also fixed anyway.

The effect of Weight Change of zeolite and Long Time of Stirring on Reduction of Na⁺, Cl⁻ and NaCl Content

Zeolites belong to the alumina silica mineral group, so zeolites are defined as silica alumina which have hollow structure framework hollow and in it are filled with cations and water molecules that can move freely. To illustrate the relationship between chemical composition and structure, the zeolite empirical formula is as follows:



From the zeolite formula it is known that zeolite consists of three components namely, exchanged cations, alumina silica framework, and the water phase. By heating to a certain temperature, water can come out of the zeolite framework so that zeolites can function as absorbers of gases or liquids. With the release of water, resulting in zeolites have an open structure. The right size molecule can be trapped in these channels and pores. This is what allows zeolites to be used as selective adsorbents.

Table 3 : Results of absorption of brackish water using MNZ on variation of zeolite weight and long time of stirring

Zeolite weight (g)	The long time of stirring								
	1 h			2 h			3 h		
	Na ⁺ (g/L)	Cl ⁻ (g/L)	NaCl (g/L)	Na ⁺ (g/L)	Cl ⁻ (g/L)	NaCl (g/L)	Na ⁺ (g/L)	Cl ⁻ (g/L)	NaCl (g/L)
0.5	0.812	1.720	2.839	0.782	1.671	2.757	0.810	1.718	2.835
1	0.477	0.715	1.179	0.447	0.665	1.098	0.475	0.713	1.176
1.5	0.166	0.315	0.521	0.145	0.266	0.439	0.164	0.313	0.517
2	0.10	0.179	0.296	0.080	0.130	0.214	0.093	0.177	0.292
2.5	0.099	0.178	0.295	0.079	0.129	0.213	0.092	0.176	0.291

In Table 3, the results of the study showed that there was a decrease in the concentration of Na⁺, Cl⁻ and NaCl in brackish water treatment processes due to the influence of varying MNZ weight and at various contact or long time of stirring. The more MNZ zeolites, the more Na⁺, Cl⁻ and NaCl were absorbed so that moored species would increase in number. In this study, obtained at a weight of 2 g MNZ and stirring for 2 h resulted in the largest decrease of Na⁺, Cl⁻ and NaCl species. Furthermore, at a weight of 2.5 g MNZ, there was a condition where the adsorption that occurred tends to remain as shown in Fig. 3 and 4. The longer the stirring time, the

decrease in the concentration of Na^+ , Cl^- and NaCl would increasingly occur with a significant amount. Significant decrease occurred at the time of stirring 2 h in all adsorbent weights. This happens because at the time of stirring 2 h the longer the MNZ zeolite contact with Na^+ , Cl^- and NaCl so that the absorption capacity was greater. This was also supported by the surface area and pore of a large MZN so that it could adsorb Na^+ , Cl^- and NaCl bigger as well.

Long time of stirring time more than 2 h would tend to be constant, even for contact time of stirring of 3 h the content of Na^+ , Cl^- and NaCl tends to decrease as shown in Fig. 3 and 4. This happens could be possible because at the time of stirring more than 2 h and so on would experiencing a saturation point. By stirring 3 h in addition to saturation, it was also possible that the equilibrium shifts toward brackish water so that there were Na^+ , Cl^- and NaCl species coming out of the zeolite pore, thus they content in brackish water became greater than stirring 2 h.

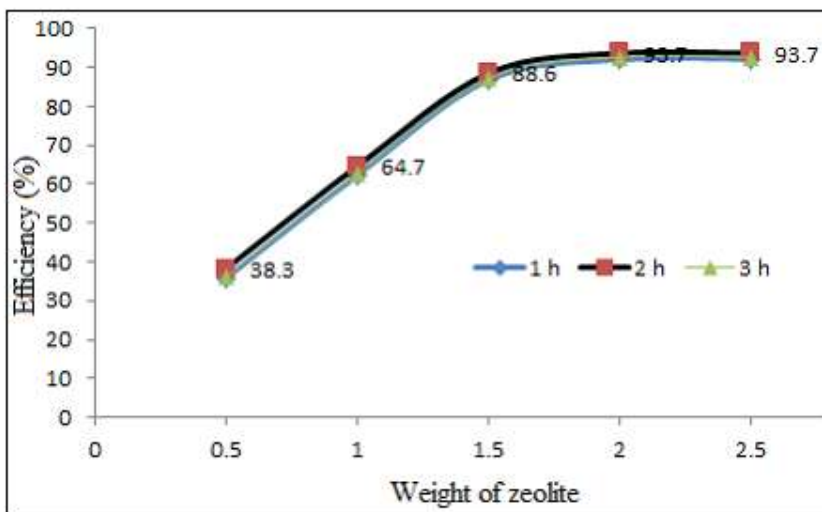


Fig. 3. Efficiency of reducing Na^+ content in brackish water using MNZ

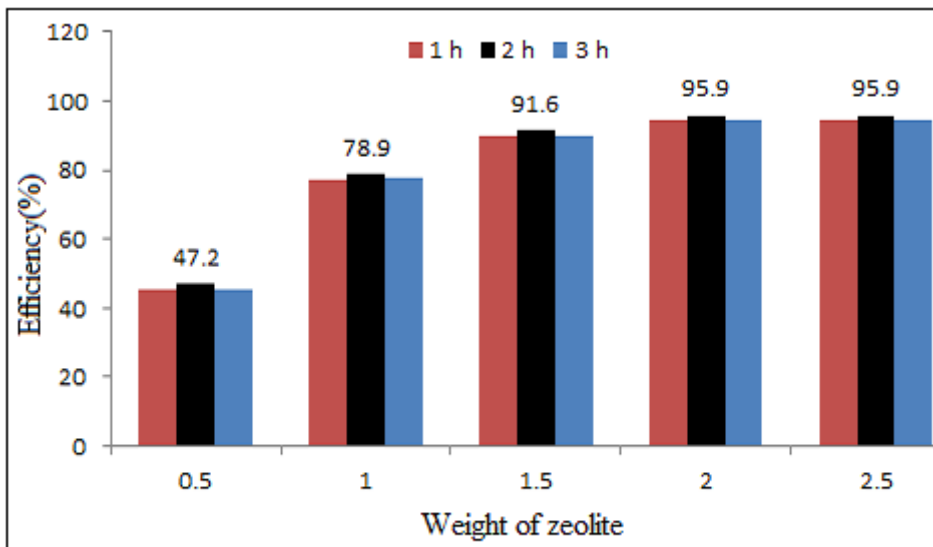


Fig. 4. Efficiency of reducing NaCl content in brackish water using MNZ

Fig. 3 and 4 showed that the efficiency of decreasing Na^+ content, and NaCl using MNZ zeolite as adsorbent turned out to have good results. The efficiency of decreasing the concentration of Na^+ , and NaCl species would increase with increasing MNZ weight and stirring time. Fig. 3 showed that the efficiency of decreasing Na^+ content in brackish water using MNZ zeolite by 93.7% which was obtained at 2 h of long time stirring and 2 g zeolite weight on brackish water volume by 50 mL. This value was the greatest efficiency compared with stirring for 1 h and 3 h and compared with zeolite weight 0.5; 1 and 1.5 g against 50 mL of

brackish water. Furthermore in Fig 4, the efficiency of decreasing NaCl species was 95.9% that the greatest efficiency was obtained in the weight ratio of MNZ to brackish water with ratio of 2 g: 50 mL and long time of stirring for 2 h. The NaCl efficiency value was obtained by calculating the Cl⁻ content gravimetrically using the Mohr method. There was a slight difference between the Na⁺ content measured using AAS and the Na⁺ content incorporated in NaCl measured using the Mohr method. From the results of brackish water desalination research, it could be stated that the use of MNZ zeolite caused desalination of brackish water by 95.9% with the batch method. The efficiency of reducing Na content in brackish water by using MNZ was 93.7 % with stirring for 2 h.

Conclusion

Dealumination of natural zeolite using 6M HCl solution had Si content of 39.28%, and Al of 3.27%. The results of measurements with XRD produced a different form of chromatogram and type of zeolite. The dominant zeolite mineral in natural zeolite (NZ) was mordenite. The mineral contents of Modified natural zeolite (MNZ) were faujasite, mordenite and gismondine. The dominant mineral content in the MNZ based on strong peaks was faujasite zeolite. The MNZ had Surface area, total pore volume and pore diameter of MNZ zeolite were 285.538 m²/g; 0.303 cm³/g; and 7.892 nm respectively. The absorption results of Na⁺ and NaCl contents in brackish water were 93,7 %, and 95.9 % at ratio of 2.5 g zeolite to 50 mL of brackish water that was obtained at 2 h of long time of stirring.

Acknowledgement

The authors say thank to Higher Education (Kemenristekdikti) and Cenderawasih University for all support to this research so we can make paper.

References

1. Suprayogi I, Nadjindji A, Dijatnol, Muhammad I. Phenomenon of sea water intrusion in estrusi due to the high influence of installing seawater with river upper debit using physical model approach. *Parifikasi.*, 2006., 7, 2 : 133 – 138.
2. Farida NA, Latifah, Ella K. Utilization of natural zeolites activated by ammonium nitrate to reduce salinity brackish water well. *Indo.J.Chem.Sci.*, 2014,3,3: 233-238.
3. Singer PA, Salamanca-Buentello F, Daar AS. Harnessing nanotechnology to improve global equity, *Issues. Sci. Technol.* , 2005, 21: 57–64.
4. Tsitsishvili GV, Andronikashvili TG, Kirov GN, Filizova LD. *Natural zeolites*. Ellis Horwood., 1992, New York.
5. Curkovic L, Cerjan-Stefanovic S, Filipan T. Metal ion exchange by natural and modified zeolites. *Water Research.*, 1996, 31, 6 :1379-1382.
6. Dentel KS, Jamrah IA, Sparks LD. Sorption and cosorption of 1,2,3-trichlorobenzene and tannic acid by organo-clays. *Water Research.*, 1998, 32,12:3689-3697.
7. Faghihian H, Bowman SR. Adsorption of chromate by clinoptilolite exchanged with various metal cations. *Water Research.*, 2005; 39,6:1099-1104.
8. Haggerty MG., Bowman SR. Sorption of chromate and other inorganic anions by organo-zeolite. *Environmental Science and Technology.*, 1994, 28,3:452-458.
9. Lee KP, Arnot TC, Mattia D. A review of reverse osmosis membrane materials for desalination - Development to date and future potential, *Journal of Membrane Science.*, 2011, 370 : 1-22.
10. Kesraoui-Ouki S, Cheeseman RC, Perry R. Natural zeolite utilization in pollution controls: A review of applications to metals effluents. *Journal of Chemical Technology and Biotechnology.* , 1994, 59, 2:121-126.
11. Zhan Y, et al. Removal of Nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent, *J. Hazard. Mater.*, 2011, 186, 1972-1978.
12. Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.*, 2010, 156:11–24.

13. Trisunaryanti W, Shiba R, Miura M, Nomura, Nishiyama M, Matsukata N. Characterisation and modification of Indonesian natural zeolites and their properties for hydrocracking of a Paraffin. *J. Jpn. Pet. Inst.*, 1996, 39, 1: 20–2.
14. Syahrul. Desalination using soyben waste and zeolite, *Marina Chimica Acta*, Department of Chemistry, FMIPA, Universitas of Hasanuddin., 2002, 2, 1: 6-8.
15. Gustian I., dan Totok E.S Study of decreasing water salinity using Bengkulu natural zeolites, *Gradient Journal.*, 2005, 1,1: 38-42.
16. Astuti W., Jamali A., and Amin M., Desalination of brackish water using surfactant modified zeolite (SMZ), *Indonesian Zeolite Journal.*, 2007, 6, 1: 32-37
17. Barloková D., and Ilavský J. Removal of Iron and Manganese from water using filtration by natural materials, *Polish J. Of Environ. Stud.*, 2010, 19, 6: 1117-1122
18. Gholikandi GB, Baneshi MM, Dehghanifard E, Salehi S, Yari AR. Natural zeolites application as sustainable adsorbent for heavy metals removal from drinking water, *Iranian Journal of Toxicology.*, 2010 3, 3
19. Mažeikiene A, Valentukevičiene M, Rimeika M, Matuzevičius AB, Dauknyš R. Removal of nitrates and ammonium ions from water using natural sorbent zeolite (clinoptilolite), *Journal of Environmental Engineering and Landscape Management.*, 2008, ISSN: 1648-6897, 16,1: 38–44.
20. Gaikwad RW, Warade AR. Removal of Nitrate from Groundwater by using natural zeolite of Nizarneshwar Hills of Western India, *Journal of Water Resource and Hydraulic Engineering.*, 2014,3, 4: 74-80.
21. Shokrian F, Solaimani K, Nematzadeh GH, Biparva P. Removal of NaCl from aqueous solutions by using clinoptilolite. *Intl J Farm & Alli Sci.*, 2015,4,1 : 50-54.
22. Day RA Jr, Underwood AL. *Analysis of quantitative chemistry fourth edition.* Erlangga Publisher., 1989, Jakarta.
23. Lee H-J, Park YS, Kim TS, Lee Y-J, Yoon KB. Separation of mixtures of zeolites and amorphous materials and mixtures of zeolites with different pore sizes into pure phases with the aid of cationic surfactants., *Chem Mater.*, 2002, 14: 3260–3270.
24. Lee K-M, Jo Y-M. Synthesis of zeolite from waste fly ash for adsorption of CO₂. *J Mater Cycles Waste Manag.*, 2010, 12: 212–219.
25. Vadapalli VRK, Gitari WM, Ellendt A, Petrik LF, Balfour G. Synthesis of zeolite-P from coal fly ash derivative and its utilisation in mine-water remediation. *S Afr J Sci.*, 2010, 106, 5/6 : 2–7.
26. Nunez VMS, Torres LDB. Synthesis of zeolitic materials from volcanic ash in presence and absence of Cetyl Trimethyl Ammonium Bromide. *Rev Int Contam Ambie.*, 2015, 31, 2: 185–193.
27. Salim I, Trisunaryanti W, Triyono, Aryanto Y. Hydrocracking of Coconut oil into gasoline fraction using Ni/modified natural zeolite catalyst. *International Journal of ChemTech Research.*, 2016, 9, 04 :492-500.
28. Katada N, Kageyama Y, Takahara K, Kanai T, Begum HA, Niwa M. Acidic property of modified ultra stable Y zeolite: Increase in catalytic activity for Alkane cracking by Treatment with Ethyl Diamine – Tetra Acetic Acid salt. *J Mole CatalA Chem.*, 2004, 211 (1-2): 119–130.
29. Salim I, Trisunaryanti W, Triyono, Aryanto Y. Proceeding The 2nd International seminar on new paradigm and innovation on natural sciences and its application., 2012, ISBN 978-602-18940-0-2 :134–138.
