**International Journal of ChemTech Research**
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.11, pp 202-210, 2018

# Utilization of Modified Natural Zeolite using SomeTreatments For Reduction of $Na^+$, $K^+$, $Cl^-$And NaCl Contents in Brackish Water

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**Abstract :** Absorption of brackish water using modified natural zeolite has been done. There were 3 types of natural zeolit modification treatment. Firstly, the natural zeolite was only heated at temperature of 120 °C.Secondly,dealumination of natural zeolite with 6M HCl then dried at 120 ° C. Thirdly,dealumination of naturalzeolite with 6M HCl,then followed by treating with NaOH, $AlCl_3.6H_2O$, CTAB and distilled water (made hydrophilic zeolite).The mixture was regulated to pH of 12. Next, poured into a reactor for hydrothermal process at 140 °C for 24 h. The results of the dealumination of natural zeolite was characterized byX-ray Fluorescence and the modified natural zeolites were characterized using X-Ray Diffraction,and surface area analyzer.The Absorption ofbrackish water using modified natural zeolit was carried out in the variation of ratio of zeolite (g) to brackis water (mL) of 0.5 : 50; 1 : 50; 1.5 : 50; 2 : 50 and 2.5 : 50 respectively. The filtrate results of absorption were analyzed using Atomic Absorption Spectrophotometry ($Na^+$ and $K^+$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 content of 3.27 %. The results of measurements with XRD produced a different form of chromatogram and type of zeolite. The results of measurements with Surface area analyzer oobtained increase in surface area, pore volume and pore diameter from natural zeolite to modified natural zeolite with the addition of $AlCl_3.6H_2O$ and CTAB.Theabsorption results of brackish water were58.12(NZ ), 94.20(MNZ) and 90.45% (ZSNZ zeolite) respectivelyat ratio of 2.5 g zeolite to 50 mL of brackish water.

**Keywords :** natural zeolite, modification, absorption, brackish water.

**Alex A.Lepa *et al* /International Journal of ChemTech Research, 2018,11(11): 202-210.**

**DOI=** http://dx.doi.org/10.20902/IJCTR.2018.111120

## 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 grams[1].Brackish water can usually be found in river mouth areas.Salinity is generally caused by the presence of sodium (Na+), potassium ($K^+$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), chloride ($Cl^-$), sulfate ($SO_4^{2-}$) and bicarbonat ($HCO^{3-}$) in water[2].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 applications[3]. Substitution of silicon by aluminum atoms in the crystal framework leads to extra negative charge to be balanced by surrounding counter ions (such as $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$), and these counter ions are easily exchanged by other surrounding cations in a contact solution[4]. Zeolite materials allow an introduction of new functional groupsthrough several processes of modification, improving substantiallyits activity and selectivity on the removal several substances[5,6].Many authors show the use of modified natural zeolite on environmentalapplications, mainly anions uptake from effluents by adsorptionprocesses[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 properties[9].

Zeolites have in its internal structure channels and cavities interconnected of molecular dimensions where compensation cations allowing the ion exchange[10].Natural Zeolites are chargednegative by having an active groupcation exchange in the form of alkali cations oralkaline earth for example $Na^+$, $K^+$, or $Ca^{2+}$.This active group acts as load balancer that can be exchanged with other cations for example cationic surfactant[11]. 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 decades[12]. 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 adsorbent[13]. Natural zeolite has silica content ($SiO_2$) and alumina ($Al_2O_3$) that is still fused and chemically bonded in thenatural zeolite. Modification of natural zeolite from Wonosari Yogyakarta by using HCl solution was carried out and then used in paraffin hydrocracking[13]. Interaction of natural zeolite with brackish water can reduce the $Na^+$ contentof35,19%[14]. Activated zeolitewasable to absorb $Na^+$ content of 80% in brackish water[15]. Desalination of brackish water with surfactant-modified zeolite can reduce salinity up to 52% of its initial value[16].Modification of natural zeolites to adsorb $Fe^{2+}$ and $Mn^{2+}$ in water(Barloková and Ilavský[17]. Modification of natural zeolites for adsorption of heavy metals from drinking water[18].Modification of natural zeolites for adsorption of nitrates and ammonium ions from water.[19] Modification of natural zeolites for adsorption of nitrate from groundwater[20]. Removal of NaCl from aqueous solutions by using clinoptilolite zeolite[21].

## Experimental

### Materials

Natural zeolite was obtained from Klaten, centre of Java, Indonesia. The chemicals used were HCl 37%, NaOH pellet, $AlCl_3.6H_2O$,NaCl,$AgNO_3$, $K_2CrO_4$, 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 Argapura , City of Jayapura,Papua, Indonesia.

## Instrumentation

X-Ray Fuorescence spectrometry(XRF): Bruker S2 Ranger ,X-Ray Diffraction (XRD): Shimadzu-6000 XRD, Atomic Absorption Spectrophotometry (AAS): Shimadzu 6650F, Surface area analyzer : NOVA1200 (QUANTACHROME).

## Procedure

### Modifiednatural zeolite (MNZ)and modification of natural zeolite to zeolite with rasio Si/Al of ±1(ZSNZ)

After being washed and separated with water then dried in oven at temperature of 120 $^oC$for 4 h, the natural zeolite was grinded and sieved (100 mesh). The natural zeolite (20 g) was destructed (dealumination) using 50 mL of 6MHCl at 100 $^oC$ 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$^oC$ for 4 h. Furthermore, synthesis treatment was carried out as follows:

Dealuminated natural zeolite (4.7 g) was mixed with NaOH (6.3 g), $AlCl_3.6H_2O$ (9.1 g) , CTAB (0.3 g) and distilled water was added to adjusted pH 12 while stirring for 48 h at room temperature. Then the samples done hydrothermally treated at 140 $^oC$ 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$^oC$ for 4 h and calcined at 350 $^oC$ for 3 h.

### Absorption process

Modified zeolite was interpreted with brackish water with variation of 0.5 g: 100 mL; 1 g : 50 mL ; 1.5 g: 100 mL ; 2 g :50 ml and 2.5 g : 50 mL. Each of variation was mixed and stirred using magnetic stirrer for 6 h, then separated (filtered) between the zeolite and the absorptionresults (filtering results) using whatman paper of 42. The filtering results (filtrate) was collected in container. The contents of $Na^+$ and $K^+$were determinedusing AAS, while the contens of $Cl^-$andNaClwere determined using the Mohr method[22].

### Determination of $Na^+$, $K^+$, $Cl^-$ and NaClcontents

The contents of $Na^+$ and $K^+$were determined using AAS, while the contents of $Cl^-$ and NaClwere determined using the Mohr method.The procedure for determining of $Cl^-$ as follows:

### Initial treatment

Standardization of the standard solution of $AgNO_3$ 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 mLof indicator solution of 5% $K_2CrO_4$ (w/v) and stirred. Then it was titrated with $AgNO_3$ solution until the color changes (brownish red color) and the volume of $AgNO_3$ solution used for the sample (A-mL) and blank (B-mL) was recorded. Calculation of the normality of the standard solution of $AgNO_3$ using formula :

$$\text{N of } AgNO_3 = \frac{V1.N1}{VA-VB} \qquad (1)$$

With the understanding:
N of $AgNO_3$ = the normality of standard solution of AgNO3 (mgrek / mL)
VA = the volume of $AgNO_3$ standard solution for titration of NaCl solution (mL)
VB = the volume of $AgNO_3$ 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 intothe Erlenmeyer flaskof 250 ml.. In the test sample, 2 mL of indicatorsolution of 5% $K_2CrO_4$ was added, then titrated with the standard solution of $AgNO_3$ until the end point of the titration was indicated by the formation of brownish red deposits from $Ag_2CrO_4$, then recorded the volume of $AgNO_3$ used. Blank titration of 100 ml of distilled water was carried out. The titration was repeated twice and averaged the volume of $AgNO_3$obtained. The desalination water was measured by chloride content using the formula equation:

Content of $Cl^-$ (mg / L) = $\frac{(A-B)xNx35450}{V}$ ...................................................................... (2)
Calculation of NaCl content with the formula:
NaCl (mg/L) = content of$Cl^{-1}$ (mg/L ) x 1.65 .................................................................(3)
With the understanding:
A = the volume of $AgNO_3$ standard solution for sample titration (mL)
B = the volume of $AgNO_3$ standard solution for blank titration (mL)
N = the normality of the standard solution of $AgNO_3$ (mgrek/mL)
V = the volume of sample (mL)

To determine efficiency can be used the following equation:

Efficiency(%) = $\frac{(So-S)}{So}$ x 100% ……………….................................................................. (4)

So = the level of parameters before processing
S = level of parameters after processing

## Results and Discussion

### Characteristic of NZ, MNZ And ZSNZ Zeolite

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

For modification ofnatural 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 systems 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 $Fe^{2+}$ , $Mn^+$ in the contents of natural zeolite. However, interaction with 6M HCl, in certain natural zeolite zeolites 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 $AlCl_3.6.H_2O$ which was quite a lot.

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

Natural zeolite is generally foundin mixturewithothertype ofzeoliteandamorphous mineralsuch asfeldspar, silica, clay, transition metal oxide, andorganiccontaminants[23]**.**The XRD results in Fig. 1a showed that the natural zeolite (NZ)was composed of various minerals which showed heterogeneity implies. Impurities contained in the NZ higher. The mineral content of NZ from Klaten based on 2Θ include: mordenite, clinoptilolite and quarzt, 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. 1b showed that the MNZ was composed of various minerals which showed more homogeneous implies. Impurities contained in the MNZhas decreased. The mineral content of MNZ after dealuminationbase on2Θ include: mordenite,clinoptilolite, as well as other amorphous mineral. The dominant mineral content in the MNZ based on strong peaks was still mordenite based on its 2Θ.

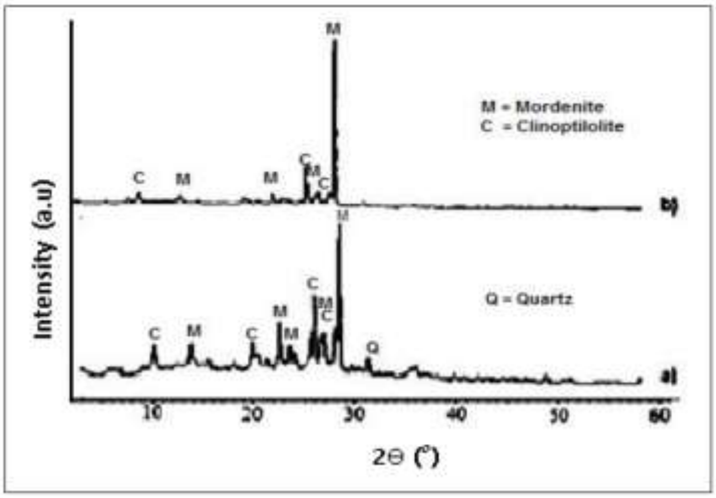

Fig.1. Diffractogram of a) NZ, b) MNZ

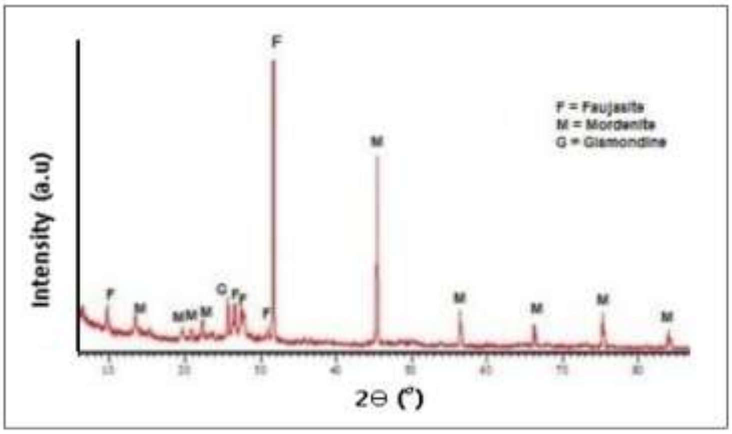

Fig.2. Diffractogram of ZSNZ

Base on JCPDS (2004) Joint Committee on Powder Diffraction Standards, the XRD results in Fig. 2 showed that the ZSNZ was composed of various minerals which showed heterogeneity implies but it was zeolite minerals. Base on 2Θ the results of the diffractogram involved: 9.78°= faujasite; 13.48° = mordenite; 19.64° = mordenite; 20.85° = mordenite; 22.25° = mordenite25.67°=gismondine; 26.26°=faujasite; 27.35°=faujasite; 30.92°= faujasite; 31.69° = faujasite; 45.43° = mordenite; 45.56° = mordenite; 56.48° = mordenite; 75.26° = mordenite; 83.98° = mordeniterespectively.The mineral content of ZSNZ results were faujasite,mordenite and gismondine. The dominant mineral content in the ZSNZ 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 zeolite[24-27].

### Results of measurement of Surface area, pore volume and pore diameter

**Table 1. Characteristics of NZ, MNZ, and ZSNZ 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 | 193.023 | 0.167 | 2.771 |
| ZSNZ | 218.538 | 0.303 | 4.892 |

In Table 1, the surface area, pore volume and diameter of the NZ were smaller than that of the MNZ. This condition may be becaused by 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 2.77 nm that was classified as mesopore.Likewise, ZSNZ has a surface area, pore vole and diameter larger than NZ, or MNZ. This can 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 reaction[28]. Synthesis of mesoporous zeolite by adding NaOH solution whose concentration was vary 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 significantly[29].

**Result of absorption of brackish water using NZ, MNZ and ZSNZ zeolite**

Before the absorption of brackish water with NZ, MNZ and ZSNZ zeolite, firstly the contents of Na$^+$, Cl$^-$, K$^+$ and NaCl were measured in the brackish water. Results of Na$^+$, K$^+$,Cl$^-$ and NaCl contents were 1268.1; 63.5; 4120.2; and 6138.3mg/L respectively.

**Table 2 : Results of absorption of brachkis water using zeolite**

| Weight of zeolite in 50 mL of sample | Results of Absorption (mg/L) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Using NZ | | | Using MNZ | | | Using ZSNZ | | |
| | Na$^+$ | K$^+$ | Cl$^-$ | Na$^+$ | K$^+$ | Cl$^-$ | Na$^+$ | K$^+$ | Cl$^-$ |
| 0.5 g | 1157.2 | 58.4 | 3159.0 | 817.3 | 16.8 | 1776.4 | 2254.4 | 22.8 | 2420.1 |
| 1.0 g | 925.3 | 46.3 | 2567.3 | 482.2 | 12.4 | 1137.7 | 2872.4 | 16.7 | 1314.7 |
| 1.5 g | 718.7 | 37.7 | 2212.7 | 271.4 | 8.6 | 568.1 | 3417.7 | 14.2 | 724.5 |
| 2.0 g | 585.4 | 25.2 | 1607,3 | 105.6 | 6.4 | 243.2 | 4257.4 | 12.7 | 425.2 |
| 2.5 g | 463.1 | 23.1 | 1558.2 | 98.1 | 5.8 | 238.6 | 4351.3 | 11.8 | 393.6 |

The data in Table 2was the absorption results that were carried out in the zeolite position in fixed container with varying of zeolite and brackish water ratios. The filtratewas analyzed for the content of Na$^+$, K$^+$, Cl$^-$, and NaCl.For ZN zeolite, there were reduction in Na$^+$, K$^+$, and Cl$^-$ 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 zeolite, there were also reduction in Na$^+$, K$^+$, 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 zeolite.On NZ zeolite, treatment was done only by heating at temperature of 120 °C for 4 h. With this treatment had surfacearea of 53,657 m$^2$/g; pore volume of 0.083 cm$^3$/g; and pore diameter of 1,989 nm respectively. Surface area, total pore volume and pore diameter of MNZ zeolite were 193,023 m$^2$/g; 0.167 cm$^3$/g; 2,771 nmrespectively.This measurement result were higher than NZ zeolite.MNZ zeolite was obtained by dealumination treatment using 6M HCl so that it was possible for metals such as Mn$^+$, Fe$^{2+}$ and Al to come out of the zeolite framework.

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 zeoliteFurthermore, on ZSNZ zeolite also decreased of K$^+$ and Cl$^-$ contents. Decreasing using the weight ratio of zeolite to brackish water as seen above did not produce water that can be used for drinking water as required.For the Na$^+$ content there was an increase in its content along with the increasing ratio of zeolite to brackish water. This situation can be caused by the preparation of ZSNZ zeolite with the addition of $AlCl_3.6H_2O$ which was quite a lot to form Si/Al ratio = ± 1 (hydrophilic zeolite). As the result of this addition, to make pH = 12, then added significant of NaOH. Thus the modification would produce zeolite which was rich in Na$^+$ content. So that when absorption used ZSNZ zeolite,the Na$^+$ content in brackish water would grow even bigger along with the increasing ratio of zeolites to brackish water, although the surface area, pore volume and pore diameter of ZSNZ were greater than MNZ zeolite. The ion exchange process could bestill taken place but did not cause of Na$^+$ content from brackish water to decrease as result of trapping the metal in the ore of zeolite. As it is known that zeolites are microporousaluminosilicate minerals which could be used as ion exchanger in domestic and commercial water purification, softening and other applications[3].

**Tabel 3 : NaCl contents results of absorption of brachkis water using zeolite**

| Weight of zeolite in 50 mL of sample (g) | Results of NaCl content (g/L) | | |
|---|---|---|---|
| | Absorption using NZ zeolite | Absorption using MNZ zeolite | Absorption using ZSNZ zeolite |
| 0.5 | 5.212 | 2.931 | 2.993 |
| 1.0 | 4.236 | 1.877 | 2.169 |
| 1.5 | 3.651 | 0.934 | 1.195 |
| 2.0 | 2.652 | 0.401 | 0.702 |
| 2.5 | 2.571 | 0.394 | 0.649 |

In Table 3, it can be seen that in NZ zeolite after absorption there was decrease in NaCl content along with increasing in the ratio of zeolite to brackish water similarly for MNZ and ZSNZ zeolite also decreased of NaCl content. For MNZ zeolite there was decrease in NaCl content,especiallyat ratio was 2 g zeolite to 50 mL brackish so that it met the requirementsfor using as drinking water.For MNZ there was decrease in NaCl content, especially at ratio of 2 g zeolite to 50 mL.So thatit was qualify for drinking water use.But for ZSNZ zeolite at this ratio, it was not enough to meet the requirements for using as drinking water.In Fig 3, efficiency using NZ zeolite also increased to 58.12% at ratio of 2.5 g zeolite to 50 mL of brackish water. Likewise absorption using MNZ and ZSNZ zeolite increased efficiency at the same ratio and obtained by 94.20 and 90.45% respectively.

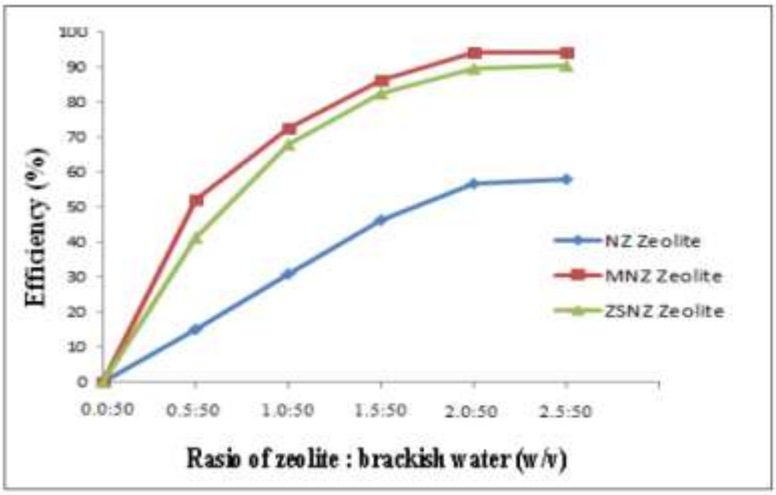

**Fig 3. Efficiency of reducing NaClcontent in brackish water usingNZ, MNZ, and ZSNZ zeolite**

## Conclusion

Dealumination of natural zeoliteusing 6M HCl solution had Si content of 39.28%, and Al content of 3.27 %.The results of measurements with XRD produced a different form of chromatogram and type of zeolite. The dominant zeolit mineral in NZ and MNZ zeolite were mordenite. The mineral content of ZSNZ results were faujasite, mordenite and gismondine. The dominant mineral content in the ZSNZ based on strong peaks was faujasite zeolite.The results of measurements with Surface area analyzer obtained increase in surface area, pore volume and pore diameter from natural zeolite to modified natural zeolite with the addition of $AlCl_3.6H_2O$ and CTAB.The reduction with using NZ was lower than MNZ zeolite.The reduction 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. Addition of $AlCl_3.6H_2O$ for zeolite synthesis produced zeolites which was rich in Na content in the its frame work so that it affects the adsorption of brackish water. Absorption of brackish water using ZSNZ does not reduce Na content but instead increases Na content in brackish water.The absorption results of brackish water were58.12(NZ ), 94.20 (MNZ) and 90.45% (ZSNZ zeolite) respectivelyat ratio of 2.5 g zeolite to 50 mL of brackish water.

## Acknowledgement

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

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