Characterization and ultrasound-assisted activation of Indonesian natural zeolite from Cikalong West Java Province

Regawa Bayu Pamungkas1,3,*, Mohamad Djaeni 2, Bakti Jos 2, Wancuh1
1 Department of Chemical Engineering, Faculty of Engineering and Science, University of Muhammadiyah Purwokerto, Jl. Dukuhwaluh Raya, Purwokerto, 53182, Indonesia
2 Department of Chemical Engineering, Faculty of Engineering, Diponegoro University Jl Prof H. Soedharto, SH, Tembalang, Semarang, Indonesia
3 Postgraduate Program of Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl Prof H. Soedharto, SH, Tembalang, Semarang, Indonesia

*e-mail: rbayup11@gmail.com

Abstract. Natural zeolite activation from Cikalong, Tasikmalaya Regency, West Java Province, Indonesia, has been investigated experimentally. The activation process is carried out with a solution of sodium chloride (NaCl), which is utilized by ultrasound cavitation. The purposes of this research are to determine the effect of variation of process variables on the physical-chemical characteristics of zeolites. There were two variables studied, namely; sonication time and NaCl concentration. The study was conducted with the one factor at a time (OFAT) method, which is observing responses to changes in one variable at other constant. The range of sonication time of 20 - 60 minutes, while the NaCl concentration is 0.25N - 4N. Natural zeolites and activated zeolites are then characterized using SEM, XRF, FTIR, iod number, and cation exchange capacity to test their physical-chemical characteristics. Characterization results showed that activated natural zeolite had better quality than natural zeolite. The results of the SEM analysis showed the crystal type of natural zeolite minerals in the form of elongated crystals and others, which indicate the shape of quartz and mordenite. XRF analysis results prove that the elements of Ferrum, calcium, magnesium, and potassium are cations that can be exchanged with other metal elements. The results of the volumetric analysis showed an increase in iodine number and cation exchange capacity, along with an increase in sonication time and decreased along with the increasing of NaCl concentration. Based on these properties, zeolites have excellent performance as an adsorbent.

1. Introduction
Zeolite is a natural mineral that can exchange cations, adsorb molecules, or filter molecules so that they are widely used as adsorbents [1],[2], catalysts, and soil remediation [3]. They occur naturally in the environment but can also be synthesized in a laboratory [4]. According to Ramesh et al. (2011), natural zeolites are some of the most commonly occurring sedimentary rocks [5]. Therefore, they are abundant quantity, available easily, and cheaply [6]. There are now over 50 species of natural zeolite recorded [5,7,8], but only nine zeolite minerals are often found, such as analcime, chabazite, clinoptilolite, heulandite, erionite, ferrierite, laumontite, mordenite, and phillipsite. Indonesia has
many types of natural zeolites that are spread across many islands. The Indonesian zeolite stockpile has estimated more than 400 million tons [8].

Zeolite is a hydrated porous mineral of alumina silicate crystal which has a three-dimensional skeletal structure, formed from tetrahedral [SiO4]4− and [AlO4]5− [9]. The structure of natural zeolite formed by alumina-silica atoms tetrahedral form three-dimensional structures that are connected through the sharing of oxygen atoms to form cavities and channels that contain water molecules and cations alkali and or alkaline [10]. In the zeolite, there is the partial substitution of Si4+ by Al3+, which results in excess of negative charge [4],[6]. The negative charge is neutralized by alkali and alkaline earth cations (Na+, K+, Ca2+, or Mg2+) [1],[11]. Zeolite structure, divided into three components, namely the framework of alumina silicates, empty space interconnected containing metal cations and water molecules. The water contained within the zeolite pores can be removed by heating to push the water in the zeolite pores [12].

Natural zeolites have advantages, including cation exchange capacity, high surface area due to the structure of the porous, has structural stability, capable of neutralizing the acid solution through H+ ion exchange of cations in the solution with the cations zeolite. Behind its leading, natural zeolite also has a disadvantage since its content of impurities (alkali and alkaline earth metals), relatively low ion-exchange capacities, and the water content that can reduce the absorption capacity. Therefore, they are commonly activated by chemical or physical methods before used [13]. Ion-exchange with sodium chloride solution is widely employed because sodium ions can readily remove other cations and therefore enhancing the adsorption capacity [14]. Hydrochloric acid (HCl) is another reagent used to activate the natural zeolite. The ability of HCl-activated natural zeolite was higher than the natural zeolite without activation. Hence, the HCl substance might be able to exchange cation in the framework and to dissolve undesired components such as metal oxides contained within the zeolite [15].

In the view of environmental sustainability, the use of NaCl is more attractive than HCl, because it does not dispose of waste that damages the environment. Unfortunately, the activation process with NaCl still requires quality improvement. This process requires a long time consuming on the activation process, and the cation exchange capacity obtained is still relatively low. The aim of this research is to study the activation of natural zeolite using a solution of NaCl, which is treated by ultrasonic cavitation. Variations of two factors were examined, namely sonication time and NaCl concentration in response to cation exchange capacity and surface area indicated by iodine numbers.

2. Method of Experiment
This section consists of two subsections, namely, materials and equipment, and experimental and analytical.

2.1. Materials and equipment
Natural zeolite materials used in this study were obtained from Cikalong, Tasikmalaya Regency, West Java Province, Indonesia. Sodium hydroxide, oxalic acid, hydrochloric acid, iodine, potassium bromide, silver nitrate, sodium thiosulfate were from Sigma Aldrich. Meanwhile, equipment used in this study are crusher, sieve shaker, oven dryer, ultrasonic homogenizer (TU-250Y probe 6 mm, power 250 W), and instrument analysis X-Ray Florence (EDXRF, Nex CG Rigaku), FTIR (IRTracer-100 Shimadzu), SEM (TM 3000 Hitachi), spectrophotometer uv-vis single-beam 1280 (Shimadzu).

2.2. Experimental and analytical
2.2.1. Activation of zeolite. Natural zeolite was cleaned, crushed, and sieved to obtain -80+100 mesh size and dried. The dried natural zeolites 20 g were added to 100 mL of sodium chloride on a certain concentration. The mixture was sonicated for certain minutes at room temperature on ultrasound homogenizer TU-250Y probe 6 mm, power 250 W by operation of 5 seconds on and 1 second off, and percent power 50% and filtered. The activated zeolites were then air-dried prior to further use. There
were two factors of ultrasound-assisted activation have been investigated. Factor 1 is sonication time, and factor 2 is the concentration of NaCl. The study of factor 1 effects was carried out by activating of zeolite with 1N NaCl solution on the series of sonication time from 20, 30, 40, 50, 60 minutes. The study of factor 2 was carried out by treating of zeolite on the variation of NaCl concentration 0, 25N, 0,5N, 1N, 2N, 3N, 4N on the best sonication time.

2.2.2. Cation Exchange Capacity (CEC)

The method adopted in this study is the acid-base titration method. The dried sample 1 gram was added to a 10 mL solution of 5.5 N HCl and stirred for 2 hours with the speed of the stirring motor on a scale of 3. After the time stirring completed, the mixture separated by filtering and then washing the solid using distilled water to remove the remaining chlorine (white deposits) followed by washing with NaOH. The first washing was done by adding distilled water until the filtrate did not contain chloride. The test was done by putting AgNO₃ to the filtrate. The second washing was carried out by pouring carefully 250 ml of 1N NaOH, which has been standardized with oxalic acid. The cation exchange capacity was determined by acid-base titration of the last filtrate using 1 ml of 1N HCl with phenolphthalein (PP) indicator. The formula for testing the CEC value is to use the following equation:

\[
\text{CEC} \text{ meq/100 g} = \frac{(N_1 - N_2) \times 23 \times 100}{4 \times 40},
\]

where: \( N_1 \) = normality of NaOH for washing, \( N_2 \) = normality of NaOH after washing

2.2.3. Iod number measurement. Iod number measurement was carried out to determine surface area based on the result of the Mianowski’s research [16]. Zeolite sample 0.5 g was added to 100 mL beaker glass, which contained 50 mL of 0.1 N iodine solution. The mixture was stirred at three scale magnetic stirrer for 10 minutes and filtered. Twenty mL filtrate was then titrated with 0.1 N sodium thiosulfate until pale yellow and added starch indicator, and titration continued until the blue color of solution disappeared. The volume of thiosulfate then recorded (Vs), and the titration is repeated for 20 ml of standard iodine solution (without the addition of zeolite) as blank. The volume of thiosulfate then recorded as Vb. The iodine number was calculated by the followed formula:

\[
\text{Iodine number} = \frac{V_{\text{fil}} - \left(\frac{V_{\text{tio}} \times N_{\text{tio}}}{N_{\text{iod}}} \right) \times W_{\text{iod}}}{Mz}
\]

Where \( V_{\text{fil}} \) = volume of filtrate, \( V_{\text{tio}} \) = volume of thiosulfate, \( N_{\text{tio}} \) = concentration of thiosulfate in normality, \( N_{\text{iod}} \) = iodine normality, \( Mz \) = zeolite mass, \( W_{\text{iod}} \) = molecular weight of iodine

2.2.4. Chemical analysis. Dry natural and activated zeolite samples were crushed by milling machine for 1-5 min to a fine powder. 8.0 g of the powder samples and 2 g of binder wax were homogenized by mixing, pressed in a small aluminum cup under pressure of about 200 KN for 30 seconds to get a disc of the sample with 40 mm diameter and 4 mm thickness. The XRF instrument EDXR, Nex CG Rigaku operated at 50 KV and 10 mA was used to analyze the major oxides in these samples.

3. Result and discussion

3.1. Zeolite Morphology

Zeolite morphology was obtained by instrument scanning electron microscopy (SEM) TM 3000 Hitachi. Figure 1 shows the SEM images of natural (a) and activated zeolites (b). SEM image shows the morphology of natural zeolite consists of amorphous and crystal materials with various shapes and sizes. The picture of natural zeolites shows various shapes of crystal, such as fiber-like, rod-like, prism-like, needle-like. That picture indicated that the zeolite mineral consists of mordenite and quartz, as stated by Widianti [17]. Sodium chloride (NaCl) activation induced by ultrasound
cavitation did not make any change on crystal forms. There were crystal in the prism formation still existed on both zeolite but activated zeolite illustrated cleaner crystal with bigger pore size. The bigger pore is about 6 µm for raw zeolite and 10 µm for activated zeolite, while the smaller pore is about 0.5 µm for raw zeolite and 1 µm for activated zeolite. Those images indicated that the amorphous structure materials had been dilu-

![Figure 1. SEM image natural zeolite (a) and activated zeolite with NaCl (b)](image)

3.2. Chemical compositions
The EDXRF Nex CG Rigaku instrument was used to analyze the chemical composition of natural zeolite and activated natural zeolite. Table 1 indicates the content of the two types of zeolite. The XRF characterization shows that the silica and alumina are the main compositions of zeolites. Other elements that are in zeolites include magnesium, calcium, potassium. Theoretically, these elements can be exchanged with other metals. While other elements, which are impurities present in the zeolite pore, can be reduced by heating and chemical activation in the zeolite by acid, base, or salt [18]. Based on Table 1, it can be seen that the activation with sodium chloride solution (NaCl), which was induced by ultrasound cavitation on natural zeolite, leads to an insignificant change of almost all cations except \( \text{Ca}^{2+} \) and \( \text{Fe}^{3+} \). The percentage of \( \text{Ca} \) element inactivated natural zeolite is smaller than the percentage in the raw natural zeolite, while the Fe element is the opposite. The percentage of \( \text{Fe}_2\text{O}_3 \) in activated zeolite increased by 7%, while the percentage of \( \text{Ca}_2\text{O}_3 \) decreased by 14% compared to raw natural zeolite. Natural zeolite pore cleansing has been carried out during activation.

Table 1 shows that the ratio of \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) natural zeolites is 6.2 (79.5/12.8), and increased slightly to 6.5(79.2/12.2) in the activated natural zeolite. The composition of silica and alumina in activated natural zeolites decreased compared with the results of XRF natural zeolite. The decrease in the percentage of \( \text{SiO}_2 \) is much smaller than \( \text{Al}_2\text{O}_3 \), which is 0, 377 percent compared to 4.687 percent. This has happened might because there had been an exchange of \( \text{Na}^+ \) cations from the NaCl activator solution to \( \text{Al}^{3+} \) on alumina structure. Dealumination of zeolites on sodium chloride salt treatment is more effective than their desilication.

|          | SiO$_2$ (%) | Al$_2$O$_3$ (%) | K$_2$O (%) | CaO (%) | Fe$_2$O$_3$ (%) | TiO$_2$ (%) | SrO (%) | MnO (%) | others (%) |
|----------|-------------|-----------------|-----------|---------|----------------|------------|---------|---------|-----------|
| Natural zeolite | 79.500 | 12.800 | 3.720 | 1.940 | 1.600 | 0.190 | 0.095 | 0.030 | 0.125 |
| Activated natural zeolite | 79.200 | 12.200 | 3.610 | 1.650 | 1.720 | 0.189 | 0.097 | 0.029 | 1.305 |
3.3. Effect of sonication time

Figure 2 indicates that the effect of sonication time on the response of cation exchange capacity (CEC) and an iodine number value (IN). The value of iodine number (IN) related to surface area ($S_{\text{BET}}$) [16], which is analyzed by BET methods [19]. The relation could be applied on the range 0 – 800 IN with formula $S_{\text{BET}}$ (m$^2$/gr) $\cong$ 0.986 IN (mg/ gr) $\cong$ 1 IN (mg/ gr). Based on Fig. 3, it can be understood that the longer sonication time will increase the value of the cation exchange capacity and the value of the iodine number to a certain value, then a further increase of sonication time causes a decrease in the value of both responses. The maximum response occurs at 50 minutes of sonication time.

The longer the sonication time, the more bubbles are formed, and the more bubble bursts occur. This bubble burst energy is capable of producing free radicals, which can accelerate the process of adsorption or reactions related to cation exchange. The longer the activation time, the bubble growth (bubble) due to the cavitation effect gained to optimal. Mass transfer occurs when the bubble that carries Na$^+$ ions broken into the natural zeolite tetrahedral framework and exchange Al$^{3+}$ ions. The optimal CEC value is obtained at the activation time of 50 minutes. While in the 60 minutes sonication, the CEC value has decreased, this is because the bubble growth phase (bubble) has passed the optimal growth time so that ion exchange does not occur and only generates heat.

![Graph of Cation exchange capacity and iodine number vs. Time of Sonication](image)

**Figure 2.** Effect of sonication’s time on cation exchange capacity and iodine number

3.4. Effect of concentration NaCl.

Figure 3 shows the cation exchange capacity and iodine number values at various activator concentrations (NaCl). Based on Fig. 3, it can be seen that an increase in NaCl concentration will increase the value of cation exchange capacity and the value of iodine number to a certain value, but increasing NaCl concentration after 0.5 N causes a sharp decrease in the value of both responses. The decrease of CEC is because the active site in the zeolite framework has been saturated, where the amount of Al$^{3+}$ ions was exchanged for Na$^+$ ions from NaCl activating solutions. The Na$^+$ ion, which cannot exchange Al$^{3+}$ ions in the tetrahedral structure, will attach to the outer surface of the zeolite. The decrease in the value of the iodine number with increasing NaCl concentration after the 0.5 N because of the increasing number of Na$^+$ ions, which are not exchanged with other ions in the tetrahedral zeolite structure. These ions accumulated together with other ions that might be formed in the sonication process and stick to the surface of zeolite so that it can cover the zeolite pores. Therefore, the amount of iodine entering the zeolite pore is only small.
Figure 3. Effect of concentration NaCl on cation exchange capacity and iodine number

4. Conclusion

An active zeolite could be prepared by activation using sodium chloride (NaCl) solution induced by ultrasonic cavitation. The effect of sonication time on the quality of active zeolite could be explained that the iodine number and cation exchange capacity increase along with the increase of sonication time before 50 minutes. On the other hand, the iodine number and cation exchange capacity decrease along with the increase of NaCl concentration for greater than 0.5 N. This condition stated that the highest quality was found on 50 minutes irradiation for the fixed NaCl concentration and 0.5 N concentration for the fixed sonication time.

References

[1] Erdem E, Karapinar N, and Donat R 2004 J. Coll. Interface Sci. 280 309
[2] Motsi T, Rowson N A, and Simmons M J H 2009 Int. J. Mineral Process. 92 42
[3] Wang S and Peng Y 2010 Chem. Eng. J. 156 11
[4] Colella, C., Mumpton, F.A. 2000 Natural Zeolites for the Third Millennium. ICNZ, International Committee on Natural Zeolites. A. De Frede.
[5] Ramesh, K., Damodar Reddy, D., Kumar Biswas, A., Subba Rao, A. 2011 Zeolites and their potential uses in agriculture Adv. Agron. 113, 219-241
[6] Bowman, R.S. 2003 Applications of surfactant-modified zeolites to environmental remediation. Microporous Mesoporous Mater. 61, 43-56
[7] Kowalczyk, P., Sprynskyy, M., Terzyk, A.P., Lebedynets, M., Namie_snik, J., Buszewski, B., 2006 Porous structure of natural and modified clinoptilolites J. Colloid Interface Sci. 297, 77-85.
[8] Kusdarto, 2008, Indonesian zeolite potential Indonesian Zeolite Journal Vol. 7 No. 2. November 2008 (in the Indonesian language)
[9] Setiawan Y., F. Widhi Mahatmanti, and Harjono 2018 Preparation and characterization of Nanozeolites from Gunungkidul Natural Zeolites with Top-Down Method Indo. J. Chem Sci 7 (1); 43-49 (in Indonesian language)
[10] Mirzaei N, Hadi M, Gholami M, Fard R.F., and Aminabad M.S. 2016 J. the Taiwan Inst. Chem.Eng. 59 186
[11] Doula, M.K.  2006 Removal of Mn$^{2+}$ ions from drinking water by using Clinoptilolite and a Clinoptilolite-Fe oxide system Water Research 40 (17) 3167–3176
[12] Lestari D Y 2010 Proceedings of the National Seminar on Chemistry and Chemistry Education Yogyakarta 1 (in Indonesian language)
[13] Inglezakis, V.J., Hadjiandreou, K.J., Loizidou, M.D., Grigoropoulou, H.P. 2001 Pretreatment of natural clinoptilolite in a laboratory-scale ion-exchange packed bed Water Research 35 (9), 161–2166.
[14] Günay, A., Arslankaya, E., Tosun, I. 2007 Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics Journal of Hazardous Materials 146 (1–2), 362–371.
[15] Ola, P.D., and Nesimnasi, A.M. 2012 Utilization of Natural Zeolites to Improve Quality of Used Cooking Oil Journal of Mathematics and Natural Sciences, Vol. 12, No. 1 59-68 (in Indonesian language)
[16] Mianowski, M. Owczarek & A. Mareck 2007 Surface Area of Activated Carbon Determined by the Iodine Adsorption Number Energy Sources, Part A, 29:839–850
[17] Widianti, T. 2006 Testing the zeolite cation exchange capacity as a natural cation exchange for industrial wastewater treatment, Annual meetings on testing and quality, Indonesian Institute of Sciences, Research Center for Quality Systems and Testing Technology (in Indonesian language)
[18] Margeta K, Logar N, iljeg and arkas A 2013 Natural zeolites in water treatment –how effective is their use (Water Treatment) ed W Elshorbagy and R K Chowdhury (Rijeka: InTech) chapter 5 pp 81-112
[19] Brunauer, S., Emmett, P. H., and Teller, E. J. 1938 Surface Area Measurements of Activated Carbons, Silica Gel, and Other Adsorbents. J. Am. Chem. Soc. 30:309–315.