Effect of NaOH Concentration Toward the Characteristics of Activated Natural Zeolite from Blitar – East Java

Andi Nafis An Naafi [a], Rachmat Triandi Tjahjanto [a,*], Yuniar Ponco Prananto [a]

[a] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang, Indonesia

* Corresponding author: rachmat_t@ub.ac.id

Article Info

Abstract

This study discusses the activation of natural zeolite from Blitar City – East Java using NaOH solution (0.5 M and 1.0 M). Characteristics of unactivated and activated zeolites were also investigated, as well as the effect of the activator (NaOH solution) on functional groups, element composition, pore size, specific surface area, and total pore volume. FTIR spectroscopy, XRF, and gas physisorption were conducted to support the study. Experimental data showed that: (1) the major functional groups were observed at 1250-780 cm^{-1} in the infrared spectra, in which the unactivated and the activated zeolite were not significantly different; (2) the elemental composition of zeolite (Si and Al) tended to decrease after the activation process; (3) the pore size of the activated zeolite increased while the surface area and total pore volume decreased. Based on this study, activated zeolite (AZB-1.0) showed the optimum result: the pore size increased by 4.12847 nm, and the total pore volume did not decrease significantly by 0.04987 cc/g.

1. Introduction

Several Indonesian areas with a large number of zeolites are West Java (185.595.160 tons), South Sulawesi (169.880.000 tons), Lampung (43.800.000 tons), West Sulawesi (26.400.000 tons), West Sumatra (16.200.000 tons), and East Nusa Tenggara (6.115.000 tons) [1, 2, 3]. Generally, the types of natural zeolites in Indonesia are mordenite and clinoptilolite [4]. Zeolite is a crystalline arrangement of aluminosilicate TO_4 (T = Si, Al). It has a pore size of less than 2 nm or micropores. The arrangement has a tetrahedral structure as the main building unit, with each oxygen atom shared with another tetrahedron [5, 6]. In addition, zeolite is a framework composed of cavities and channels with size dimensions varying between 3 Å and 30 Å, in which the channel size determines the physical and chemical properties and some applications of this material [7].

The three main components of a zeolite are an alumina-silicate framework, exchangeable cations, and water content [7]. The amount of water content in the zeolite framework varies due to the crystallization conditions and the cations exchanges through the cavities and channels. The negative charge on the specific framework of the zeolite occurs when Al^{3+} cations replace Si^{4+} cations which bind to four oxygen atoms [5]. Therefore, cations of alkali or alkaline earth metals such as Na^+, K^+, Ca^{2+}, and Mg^{2+} are needed to balance the charge on the framework [5, 8].

Natural zeolite is one of the minerals with low production costs and abundant quantities with excellent thermal stability and high surface area [2, 9]. On the other hand, the structure that composes the framework contains several metal impurities that close the pores, cavities, and channels [10]. Therefore, it will inhibit the diffusion between molecules and reduce its ability as an adsorbent for liquid and gaseous wastes [9, 11, 12], catalysts [13, 14, 15], drug delivery [16], separator media [5], and ion exchange resin [15].

There are several ways to overcome these limitations, such as physical activation, chemical activation, and modifying the structure of the zeolite [17]. Physical activation is a process of reducing the particle size of zeolite or heating it at high temperatures to increase its ability, such as the surface will get bigger and water molecules will be removed from the zeolite framework. In addition, chemical activation involves

mixing zeolite with acid or base solution to remove impurities like metal-oxide and change pore size, acidity, and Si/Al ratio [18, 19, 20].

Several researchers have researched various kinds of natural zeolites in Indonesia. Some examples are the activation process of zeolite from Bayah using a hydrochloric acid solution with a concentration of 6 M increased the Si/Al ratio [21]. Then another example is the modification of natural zeolite from Blitar to be used as a biodiesel catalyst and the modification of natural zeolite from Ende to be used as a biodiesel catalyst from commercial cooking oil [22, 23], and another one, the activation of natural zeolite Blitar using NaOH with a concentration of 0.02 M, 0.05 M, and 0.1 M for water adsorption. However, studies show no significant changes to the characteristics (pore size, components, XRD pattern, and morphology) of the zeolite after the activation process [22, 24].

On the other hand, activating zeolite using a high concentration of 2 M NaOH can change its composition significantly. The high concentration of NaOH causes dealumination and desilication. It has been reported that the Si−O−Si bond is relatively easier to break than the Si−O−Al bond in the presence of OH− due to the negative charge of the AlO_4^- tetrahedra [25]. Therefore, this study will examine natural zeolites from Blitar using higher concentrations of 0.5 M and 1.0 M to obtain better characteristics of zeolite in terms of elemental composition, pore size, specific surface area, and total pore volume from previous studies. This study aims to determine the effect of activation by NaOH solution on the characteristics of zeolite.

2. Methodology

2.1. Materials and Instrumentations

The materials prepared were 34 grams of mordenite type of natural zeolite from Blitar [22], NaOH (Merck) solution with concentrations of 0.5 M and 1.0 M, and distilled water. The equipment used in this research was a Universal pH indicator (Merck), analytical balance (OHAUS PIONEER series), Erlenmeyer flask 250 mL, beaker 250 mL, stirring rod, funnel, a set of mortar and pestle, sieve with a size of 100 mesh, electric shaker (WiseShake), oven (Fisher Scientific Isotemp 655F), furnace (Carbolite RHF 1500), FTIR spectroscopy (IR-Spirit-T, Shimadzu), XRF (PANalytical Minipal 4), and Gas Sorption Analyzer (Quantachrome Novatouch LX-4).

2.2. Experiments

2.2.1. Sample Preparation

Natural zeolite was ground by mortar and pestle and then sieved using a 100 mesh sieve. Zeolite was taken as much as 34 grams and put into a 250 mL Erlenmeyer flask. A 120 mL NaOH solution with 0.5 M and 1.0 M concentrations was prepared and mixed into the Erlenmeyer flask. After that, it was stirred using a shaker at 150 rpm for 4 hours and allowed to stand for 24 hours at room temperature. The mixture was washed and rinsed using distilled water until it reached a pH of 7 or neutral (tested using a universal pH indicator). Then it

was dried in an oven at 100°C for 3 hours and heated using a furnace at 500°C for 6 hours. The two samples were called AZB-0.5 and AZB-1.0. The initial letter A means activated, while the number represents the concentration of the alkaline solution employed.
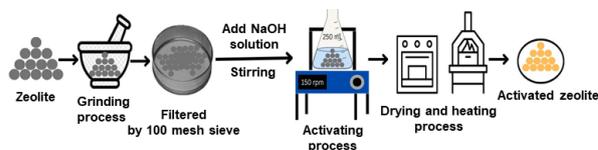

Figure 1. Schematic of the zeolite activation method

2.2.2. Sample Characterization

The functional groups of the samples were characterized using FT-IR (Fourier transform infrared) spectrometer type IR-Spirit-T in the range of 4000-400 cm⁻¹ under a vacuum state. The composition of elements in the sample was characterized using XRF PANalytical Minipal 4. The final characterization was done by gas physisorption using Quantachrome Novatouch LX-4 with a nitrogen adsorption-desorption process. The sample was heated to 300°C at 10.0°C/min and held for 60 minutes.

3. Results and Discussion

The unactivated and activated zeolites differ in their IR spectra, especially in the fingerprint area. Both groups of samples differ in the percentage of metal elements according to XRF measurement results. In addition, their surface area, total pore volumes, and pore size are also different base on gas physisorption measurement results.

3.1. The Yield of Unactivated and Activated Zeolite

The activation process using a NaOH solution with a concentration of 0.5 M and 1.0 M as much as 120 mL in 34 grams of natural zeolite caused the yield to decrease by up to 7%. The decrease in zeolite yield was due to the presence of some impurities that covered the pores, cavities, and channels of the zeolite dissolved in the NaOH solution. The solution could also cause the surface of the zeolite to erode, affecting the final mass to be smaller than the initial mass of the zeolite. The zeolite mass and yield data in this study are presented in Table 1.

Table 1. The yield of unactivated and activated zeolite

No	Materials	Mass of activated zeolite (g)	Yield (%)
1.	NZB	34.0333	–
2.	AZB-0.5	30.9217	91%
3.	AZB-1.0	30.4339	89%

The decrease in zeolite yield was due to the dissolution of some metal oxides contained in the pores or channels where base activation is one of the modification techniques that aim to reduce the percentage of silicon (Si) thus that the zeolite has larger pores and becomes more hydrophilic [18, 26].

3.2. Functional Group of Unactivated and Activated Zeolite

The band position and spectrum intensity produced by FT-IR spectroscopy (Figure 2) show the functional groups of unactivated and activated zeolite. The FT-IR spectra of zeolite show several bands at 3435.74 cm⁻¹, 3445.73 cm⁻¹, and 3445.73 cm⁻¹ associated with O-H or HOH stretching vibrations from silanol groups [5, 27]. Then, the bands at 1647.27 cm⁻¹ and 1648.70 cm⁻¹ are from the O-H bending vibration [27]. The spectra of unactivated and activated zeolite exhibit bands at 1222.26 cm⁻¹ and 1223.69 cm⁻¹, respectively. They are the asymmetric vibration band of the O-Si-O or O-Al-O bonds [1]. Asymmetric stretching vibration bands of Si-O or Al-O are also observed at 1052.54 cm⁻¹, 1045.41 cm⁻¹, and 1046.84 cm⁻¹ [18]. The shift of the peak to a lower wavenumber is caused by activation with alkaline solutions such that the Si-O-Si and Al-O-Al covalent bonds in the aluminate and silicate groups are affected [18]. Furthermore, the stretching vibrations of the O-Si-O or O-Al-O symmetrical stretching vibrations occur at 780.14 cm⁻¹ and 778.71 cm⁻¹, the bending vibrations of the Al-OH band at 694.57 cm⁻¹ [22], Si-O or Al-O symmetric stretching vibrations at 620.40 cm⁻¹ and 621.83 cm⁻¹ [21], and Si-O or Al-O bending vibration bands at 443.55 cm⁻¹, 452.11 cm⁻¹, and 453.54 cm⁻¹ [23] are characteristic for zeolites. Restructuring of quartz, siloxane, and silanol structures in the zeolite framework was caused by alkaline activation treatment and confirmed by a decrease in intensity and a shift in wave number from 780 cm⁻¹ to 778 cm⁻¹ [18].
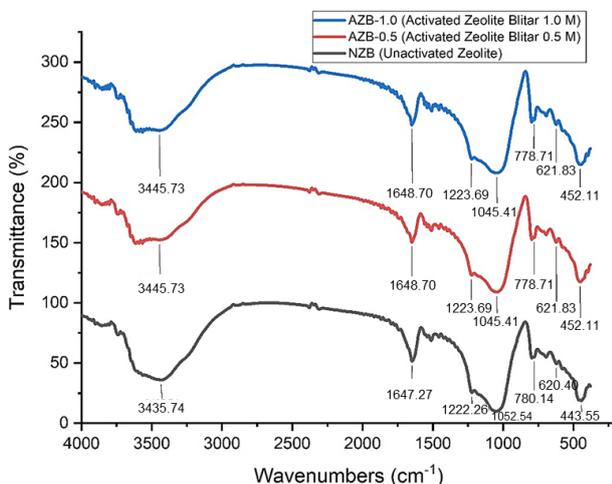

Figure 2. FT-IR spectra of unactivated and activated zeolite from Blitar

3.3. The Effect of the Addition of an Alkaline Solution on the Chemical Composition of Zeolite

The compositions of unactivated and zeolite activated by the concentration of 0.5 M and 1.0 M NaOH solution changed. The decrease in compound composition in activated zeolite was due to the dissolution of Si, Al atoms, and some impurities from the zeolite structure. The percentage of the chemical composition of the zeolite was analyzed using X-ray Fluorescence and listed in Table 2.

Some metal compositions are still present in the activated zeolite structure (such as iron and calcium) because of the strong interaction between the zeolite and these metals, so the removal of the metal becomes challenging [5, 28]. Afterward, base activation can affect the charge on the zeolite framework, where the Si-O-Si and Al-O-Al bonds break and form aluminates and silicates to make the charge negative. The higher concentration of NaOH used, the more negative the charge in the zeolite framework and the more silicate and aluminate groups formed due to the more silanol, aluminol, and siloxane groups used [18].

Table 2. Major and minor components on the unactivated and activated zeolite

Element	NZB (%)	AZB-0.5 (%)	AZB-1.0 (%)
Al	8.4	8.2	8.2
Si	56.4	55.5	55.3
Fe	16.9	16.8	17.5
Ca	10.5	10.7	10.7
K	5.11	5.32	5.28
Ti	0.98	1.04	1.0
V	0.03	0.04	0.02
Mn	0.35	0.33	0.37
Cu	0.12	0.14	0.13
Zn	0.03	0.07	0.07
Sr	0.78	0.78	0.78
Si/Al	6.71	6.77	6.74

3.4. Gas Physisorption Analysis

The total pore surface area was determined by the BET (Brunauer-Emmett-Teller) method, and the pore size distribution was determined by the BJH (Barrett-Joyner-Halenda) method. The pore size distribution was classified into three parts according to the rules made by IUPAC. The first is microporous (d < 20 Å), the second is mesoporous (20 Å < d < 500 Å), and the last is macroporous (d > 500 Å) [29]. This classification is based on nitrogen gas adsorption at the boiling point of nitrogen gas by porous materials with a wide range of pore sizes.

The graphic pattern of the relationship between pore volume and pore diameter distribution shows that unactivated zeolite and activated zeolite with NaOH (0.5 M and 1.0 M) have different pore volumes and pore diameter sizes from the zeolite (Figure 3). Activated zeolite shows that the pore volume in the mesoporous and microporous ranges has decreased. The volume of the zeolite micropores decreases due to the breaking of the Si-O-Si and Al-O-Al covalent bonds, causing the mesoporous volume to become larger due to the change in pore size from micropores to mesopores [30].
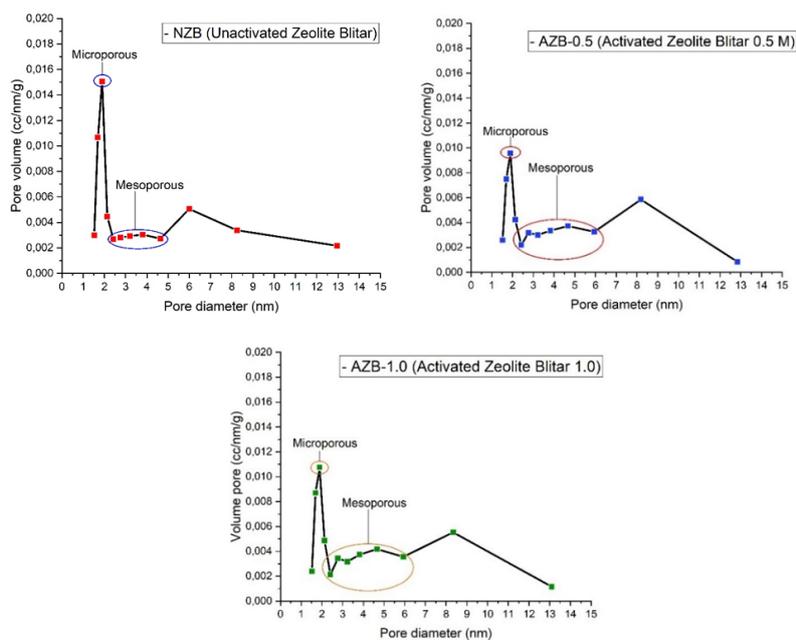
Figure 3. BJH desorption graph of unactivated and activated zeolites

The decreased capacity of the pore volume is caused by the alumina compound dissolving and precipitating on the surface when the zeolite is immersed in NaOH solution for four hours. The deposition of alumina compounds on the surface of the zeolite and drying of the zeolite at high temperatures will form alumina oxide compounds in the pores of the zeolite so that the volume capacity of the zeolite becomes smaller than the unactivated zeolite [26].

The relationship between alkaline solution activation, average pore size, and specific surface area shows that the activation process causes the pore size to increase. However, the surface area decreases due to the breaking the covalent bonds of Si-O-Si and Al-O-Al compounds in the zeolite framework. The difference in pore size and specific surface area in the sample is due to the characteristics of the NaOH solution, where the pores are eroded in the zeolite activation process, affecting the pore size to increase and the specific surface area to decrease as a result of several pores merging into one part [26, 31]. The decrease in the specific surface area of zeolite is also caused by large pores being more dominant than tiny pores and relatively large pores forming a hierarchical connection system between pores [32].

Si-O-Si and Al-O-Al covalent bonds are broken due to activation and washing processes, causing the percentage of Si and Al compounds in the zeolite structure to decrease. On the other hand, the activation process causes the formation of aluminates and silicates because of the silanol, aluminol, and siloxane groups used [18]. Then the chemical reaction in Si-OH compounds will be attacked by OH^- ions and form $Si-O^-$ and H_2O. Si-OR will react with H_2O and form Si-OH and ROH; this reaction is known as the hydrolysis process. $Si-O^-$ compounds will react with Si-OR to form new bonds, namely O-Si-O, known as the condensation process [33]. Table 3 shows the differences in the results of surface area, pore volume, and pore diameter between unactivated zeolite (NZB), activated zeolite NaOH 0.5 M (NZB-0.5), and activated zeolite NaOH 1.0M (NZB-1.0).

Table 3. BET characterization of unactivated and activated zeolites

Material	S_{ext}[a] $(m^2\,g^{-1})$	V_{micro}[b] $(cc\,g^{-1})$	V_{meso}[c] $(cc\,g^{-1})$	V_{total}[d] $(cc\,g^{-1})$	Pore size[e] (nm)
NZB	31.462	0.00578	0.04944	0.05522	3.51028
AZB-0.5	21.9152	0.00193	0.04291	0.04484	4.09164
AZB-1.0	24.1587	0.00155	0.04832	0.04987	4.12847

[a] Multipoint BET, [b] t-method, [c] $V_{total}-V_{micro}$, [d] at $P/Po = 0.93698$, [e] Average pore size

The shape of the adsorption and desorption isotherms is essential to indicate the presence or absence of mesopores in the material. The International Union of Pure and Applied Chemistry (IUPAC) has classified six types of isotherms for gas/solid adsorption–desorption based on the shape of the adsorbate–adsorbate pair. Then the curves for N_2 adsorption and desorption of unactivated zeolite (NZB), Activated zeolite 0.5 M (AZB-0.5), and Activated zeolite 1.0 M (AZB-1.0) are presented in Figure 4. These three samples have the fourth type of adsorption and desorption isotherm. This fourth type of isotherm describes the process of multilayer adsorption and capillary condensation in the mesopores. Then capillary condensation is known as a process that has a strong influence on the molecular transport process through the pores [5, 34, 35]. In addition, hysteresis loops are classified by IUPAC into four types. The shape of the three curves represents the third type of hysteresis loop. This type has a narrow loop hysteresis, where the adsorption and desorption curve gradient will increase gradually when the relative pressure gets higher, which means the adsorption volume increases rapidly. Adsorption saturation does not occur when the equilibrium pressure approaches the saturation vapor pressure, which usually exhibits a plate-like shape of pores leading to the formation of slit pores (squeezed pores with openings at both ends).
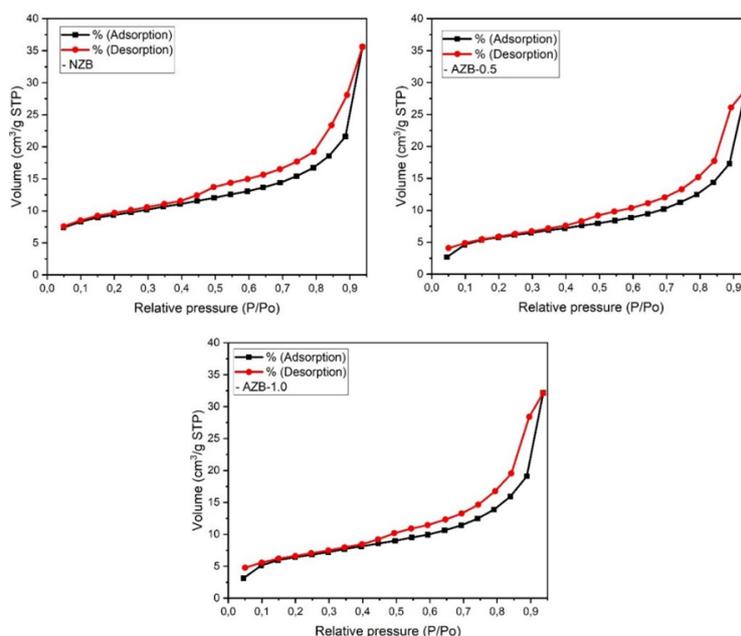
Figure 4. The N_2 adsorption-desorption of unactivated and activated zeolites

4. Conclusion

To some extent, the concentration of NaOH affects the character of the activated zeolite. The spectroscopic FTIR test showed a slight shift in wavenumber, which was not much different between unactivated and activated zeolite. XRF test showed differences in the percentage of compounds by 0.2% for Al, 0.9–1.1% for Si, 0.1–0.6% for Fe, and 0.2% for Ca. The results of the gas physisorption test using the BET/BJH method also have differences where the zeolite has an increase in pore diameter size from 3.51028 nm to 4.09164 nm and 4.12847 nm after activation with 0.5 M and 1.0 M NaOH solution. The specific surface area decreased from 31.462 m²/g to 21.9152 m²/g (NaOH 0.5 M) and 24.1587 m²/g (NaOH 1.0 M). The total pore volume decreased from 0.00578 cc/g to 0.00193 cc/g (0.5 M NaOH) and 0.00155 cc/g (1.0 M NaOH). The BJH graph of N_2 desorption from activated zeolite showed that mesopores were more dominant than micropores due to the change from micropores to mesopores, and the pattern of N_2 adsorption-desorption graphs showed that the sample obtained was hierarchical zeolite. Based on FTIR, XRF, and BET-BJH, it can be concluded that the activated zeolite (AZB-0.5 and AZB-1.0) showed damage to the zeolite Blitar structure after the activation process.

Acknowledgment

References

[1] Satriyo Krido Wahono, Hernawan, Anis Kristiani, Silvester Tursiloadi, Haznan Abimanyu, Characterization and Utilization of Gunungkidul Natural Zeolite for Bioethanol Dehydration, *Energy Procedia*, 47, (2014), 263-267 https://doi.org/10.1016/j.egypro.2014.01.223

[2] S. K. Wahono, D. J. Prasetyo, T. H. Jatmiko, A. Suwanto, D. Pratiwi, K. Vasilev, Transformation of mordenite-clinoptilolite natural zeolite at different calcination temperatures, *IOP Conference Series: Earth and Environmental Science*, 2019 https://doi.org/10.1088/1755-1315/251/1/012009

[3] Iwan Setiawan, Leny M. Estiaty, Dewi Fatimah, Sri Indarto, Lediyantje Lintjewas, Andri Alkausar, Aryo D. Handoko, Anita Yuliyanti, Jakah Jakah, Geologi dan Petrokimia Endapan Zeolit daerah Bayah dan Sukabumi, *RISET Geologi dan Pertambangan*, 30, 1, (2020), 39-54

[4] Dewi Yuanita Lestari, Kajian modifikasi dan karakterisasi zeolit alam dari berbagai negara, *Prosiding Seminar Nasional Kimia dan Pendidikan Kimia*, Yogyakarta, 2010

[5] Gustri Nurliati, Y. K. Krisnandi, R. Sihombing, Zainus Salimin, Studies of Modification of Zeolite by Tandem Acid-Base Treatments and its Adsorptions Performance Towards Thorium, *Atom Indonesia*, 41, 2, (2015), 87-95 https://doi.org/10.17146/aij.2015.382

[6] Grandprix T. M. Kadja, Moh Mualliful Ilmi, Noerma J. Azhari, Munawar Khalil, Adroit T. N. Fajar, I. G. B. N. Makertihartha, Melia L. Gunawan, Carolus B. Rasrendra, I. G. Wenten, Recent advances on the nanoporous catalysts for the generation of renewable fuels, *Journal of Materials Research and Technology*, 17, (2022), 3277-3336 https://doi.org/10.1016/j.jmrt.2022.02.033

[7] Natalia Sobuś, Izabela Czekaj, Volodymyr Diichuk, Igor M. Kobasa, Characteristics of the structure of natural zeolites and their potential application in catalysis and adsorption processes, *Technical Transactions*, 117, 1, (2020), 1-20 https://doi.org/10.37705/TechTrans/e2020043

[8] Mohamad Djaeni, Laeli Laeli Kurniasari, Setia Budi Sasongko, Preparation of natural zeolite for air dehumidification in food drying, *International Journal of Science and Engineering*, 8, 2, (2015),

[9] Vanda Liliana Babalau Fuss, Gabriel Bruj, Lucian Dordai, Marius Roman, Oana Cadar, Anca Becze, Evaluation of the impact of different natural zeolite treatments on the capacity of eliminating/reducing

odors and toxic compounds, *Materials*, 14, 13, (2021), 3724 https://doi.org/10.3390/ma14133724

[10] Muhammad Al Muttaqii, David Candra Birawidha, Kusno Isnugroho, Muhammad Yamin, Yusup Hendronursito, Amila Dini Istiqomah, Diego Putra Dewangga, Pengaruh aktivasi secara kimia menggunakan larutan asam dan basa terhadap karakteristik zeolit alam, *Jurnal Riset Teknologi Industri*, 11, 2, (2019), 266–271 http://dx.doi.org/10.26578/jrti.v13i2.5577

[11] E. Davarpanah, M. Armandi, S. Hernández, D. Fino, R. Arletti, S. Bensaid, M. Piumetti, CO_2 capture on natural zeolite clinoptilolite: Effect of temperature and role of the adsorption sites, *Journal of Environmental Management*, 275, (2020), 111229 https://doi.org/10.1016/j.jenvman.2020.111229

[12] Chayun Pida Renni, F. Widhi Mahatmanti, Nuni Widiarti, Pemanfaatan Zeolit Alam Teraktivasi HNO_3 sebagai Ion Logam Fe (III) dan Cr (VI), *Indonesian Journal of Chemical Science*, 7, 1, (2018), 64–70

[13] Widayat Widayat, Roesyadi Achmad, Rachimoellah Muhammad, Diethyl Ether Production Process with Various Catalyst Type, *International Journal of Science and Engineering*, 4, 1, (2013), 6–10 https://doi.org/10.12777/ijse.4.1.6–10

[14] Anis Kristiani, Sudiyarmanto Sudiyarmanto, Fauzan Aulia, Luthfiana Nurul Hidayati, Haznan Abimanyu, Metal supported on natural zeolite as catalysts for conversion of ethanol to gasoline, *Sriwijaya International Conference on Engineering, Science and Technology (SICEST 2016)*, Palembang, 2017 https://doi.org/10.1051/matecconf/201710101001

[15] Ricky Indra Kusuma, Johan Prabowo Hadinoto, Aning Ayucitra, Felycia Edi Soetaredjo, Suryadi Ismadji, Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil, *Applied Clay Science*, 74, (2013), 121–126 https://doi.org/10.1016/j.clay.2012.04.021

[16] Ahmad Ainurofiq, Syaiful Choiri, Drug release mechanism of slightly soluble drug from nanocomposite matrix formulated with zeolite/hydrotalcite as drug carrier, *Tropical Journal of Pharmaceutical Research*, 14, 7, (2015), 1129–1135 https://doi.org/10.4314/tjpr.v14i7.2

[17] Karmen Margeta, N. Zabukovec Logar, Mario Šiljeg, Anamarija Farkaš, *Natural zeolites in water treatment–how effective is their use*, IntechOpen, 2013, https://doi.org/10.5772/50738

[18] R. F. I. Rahmayani, Y. Arryanto, I. Kartini, The effect of alkaline activation on the zeolite binding properties toward dissolved irons, *Journal of Physics: Conference Series*, Kota Banda Aceh, Indonesia, 2020 https://doi.org/10.1088/1742–6596/1460/1/012084

[19] Yulius Dala Ngapa, Study of the acid-base effect on zeolite activation and its characterization as adsorbent of methylene blue dye, *JKPK (Jurnal Kimia dan Pendidikan Kimia)*, 2, 2, (2017), 90–96 https://doi.org/10.20961/jkpk.v2i2.11904

[20] Cheng Wang, Shaozheng Leng, Huidong Guo, Liyun Cao, Jianfeng Huang, Acid and alkali treatments for regulation of hydrophilicity/hydrophobicity of natural zeolite, *Applied Surface Science*, 478, (2019), 319–326 https://doi.org/10.1016/j.apsusc.2019.01.263

[21] Suhartana Suhartana, Pardoyo Pardoyo, Activation of Natural Zeolite and Its Application for Adsorbents in Domestic Wastewater Treatment in Tembalang District, Semarang City, *Jurnal Kimia Sains dan Aplikasi*, 23, 1, (2020), 28–33 https://doi.org/10.14710/jksa.23.1.28–33

[22] Arifin Arifin, Latifah Latifah, Sintesis Biodiesel Dari Minyak Goreng Bekas Dengan Menggunakan Katalis Zeolit Alam Termodifikasi, *Indonesian Journal of Chemical Science*, 4, 2, (2015),

[23] Dessy Dwi Septian, Sri Sugiarti, Modifikasi Zeolit Alam Ende dengan Garam Logam serta Potensinya Sebagai Katalis Transformasi Glukosa Menjadi 5-Hidroksimetilfurfural (HMF), *ALCHEMY Jurnal Penelitian Kimia*, 15, 2, (2019), 203–218 https://doi.org/10.20961/alchemy.15.2.28180.203–218

[24] D. A. Wulandari, E. Djubaedah, Nasruddin, Water adsorption behavior of Indonesian natural zeolite based on NaOH treatment: A preliminary study, *AIP Conference Proceedings*, Padang, Indonesia, 2020 https://doi.org/10.1063/5.0006710

[25] Ayten Ates, Gökçen Akgül, Modification of natural zeolite with NaOH for removal of manganese in drinking water, *Powder Technology*, 287, (2016), 285–291 https://doi.org/10.1016/j.powtec.2015.10.021

[26] Dorien Kerstens, Brent Smeyers, Jonathan Van Waeyenberg, Qiang Zhang, Jihong Yu, Bert F. Sels, State of the art and perspectives of hierarchical zeolites: practical overview of synthesis methods and use in catalysis, *Advanced Materials*, 32, 44, (2020), 2004690 https://doi.org/10.1002/adma.202004690

[27] Febi Yusniyanti, Wega Trisunaryanti, Triyono Triyono, Acid-Alkaline Treatment of Mordenite and Its Catalytic Activity in the Hydrotreatment of Bio-Oil, *Indonesian Journal of Chemistry*, 21, 1, (2020), 37–45 https://doi.org/10.22146/ijc.51496

[28] Rina Nurianingsih, Sriatun Sriatun, Adi Darmawan, Polyaniline Modified Natural Zeolite as Adsorbent for Chromium(III) Metal Ion, *Jurnal Kimia Sains dan Aplikasi*, 22, 6, (2019), 7 https://doi.org/10.14710/jksa.22.6.292–298

[29] Matthias Thommes, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol, Kenneth S. W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure and Applied Chemistry*, 87, 9-10, (2015), 1051–1069 https://doi.org/10.1515/pac-2014-1117

[30] Junwen Gu, Jiaqi Lin, Andrew J. Smith, Siriwat Soontaranon, Supagorn Rugmai, Chanapa Kongmark, Marc-Olivier Coppens, Gopinathan Sankar, Towards understanding mesopore formation in zeolite Y crystals using alkaline additives via *in situ* small-angle X-ray scattering, *Microporous and Mesoporous Materials*, 338, (2022), 111867 https://doi.org/10.1016/j.micromeso.2022.111867

[31] Nabiollah Mansouri, Navid Rikhtegar, H. Ahmad Panahi, Farideh Atabi, B. Karimi Shahraki, Porosity, characterization and structural properties of

natural   zeolite-clinoptilolite-as   a   sorbent, *Environment Protection Engineering*, 39, 1, (2013), 139–152

[32] G. U. Ryu, Hammad R. Khalid, Namkon Lee, Zhen Wang, Haeng-Ki Lee, The effects of NaOH concentration on the hydrothermal synthesis of a hydroxyapatite–zeolite composite using blast furnace slag, *Minerals*, 11, 1, (2020), 21 https://doi.org/10.3390/min11010021

[33] Ulrich S. Schubert, Nicola Hüsing, *Synthesis of inorganic materials*, 3rd completely rev. and enlarged ed., Wiley-VCH, Weinheim, Chichester, 2012

[34] Kateřina Hrachovcová, Zdeněk Tišler, Eliška Svobodová, Jan Šafář, Modified alkali activated zeolite foams with improved textural and mechanical properties, *Minerals*, 10, 5, (2020), 483 https://doi.org/10.3390/min10050483

[35] Mohammad A. Al-Ghouti, Dana A. Da'ana, Guidelines for the use and interpretation of adsorption isotherm models: A review, *Journal of Hazardous Materials*, 393, (2020), 122383 https://doi.org/10.1016/j.jhazmat.2020.122383