International Journal of Applied Engineering Research ISSN 0973-4562 Volume 15, Number 7 (2020) pp. 730-734

A Review of Natural Zeolites and Their Applications: Environmental and Industrial Perspectives

Gilar Wisnu Hardi, Muhammad Artha Jabatsudewa Maras, Yori Rachmia Riva, and Siti Fauziyah Rahman*

Program Study of Biomedical Engineering, Department of Electrical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia,.

Abstract

Unique and outstanding physical and chemical properties of zeolite materials make them extremely useful in a variety of applications, including agronomy, ecology, manufacturing, and industrial processes. Zeolites are crystalline hydrated aluminosilicates with physical and chemical properties, including loss and adsorb water and other molecules that act as molecular sieves and substitution of their constituent cations without any structural change. In this review, we summarize the main uses of zeolites in environmental and industrial perspectives, including zeolite as pollutant removal, construction, and catalyst.

1. INTRODUCTION

Cronstedt (1756) created the term "zeolite" from the Greek with means "to boil" and "stone", for minerals that remove water when heated [1]. Zeolites have alkali and alkaline earth cations with crystalline hydrated aluminosilicate, open, three-dimensional structure. This is also able to reversibly lose and gain water and exchange extraframework cations, even without altering the structure of crystal. The broad structural cavities and the inlet channels contain water molecules, which form spheres of hydration around exchangeable cations [2].

The general formula for natural zeolites is

$$(Li, Na, K)_a(Mg, Ca, Sr, Ba)_d[Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}]\cdot mH_2O$$

where the part of the square brackets reflects the framework atoms and the part of the extraframework atoms outside the square brackets is cations plus water molecules [1]. Once dehydrated (or "activated"), a zeolitic phase can readsorb not only water, but also gases, vapors, and fluids, particularly if their molecules are polar [1].

Many zeolites naturally occur in volcanic lava flux cavities as mineral and are mined extensively all over the world. Other zeolites are synthetic and for commercial uses or produced for researchers [3]. Zeolites are presented in the hardened lava either during diagenesis due to active geothermal systems in high heat flow areas, during the burial metamorphism of the lava pile, or hydrothermal alteration of the continental basalts [3].

Due to their unique properties, zeolites are used in a variety of applications worldwide. This paper aims to give review regarding the implementation of natural zeolites, especially in the environmental and industrial perspectives.

2. CLASSIFICATION OF NATURAL ZEOLITE

Based on the framework structure of the natural zeolites, Gottardi and Galli classified natural zeolites into seven groups [1, 4]. Figure 1 shows the classification and type of natural zeolites.

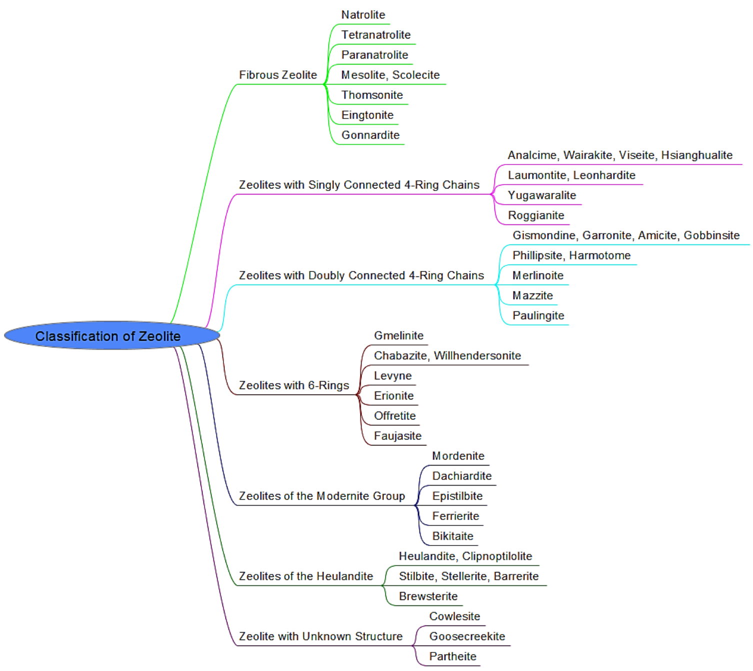

Figure 1: Classification of Zeolite

3. APPLICATION OF ZEOLITE

Figure 2 shows the applications of natural zeolite. Zeolite can be used to remove pollutants, both gas and wastewater, construction, catalyst, medical uses [5–7], and food and agriculture [2, 8]. In this paper, we will discuss more the application of zeolite for pollutants, construction, and catalyst.

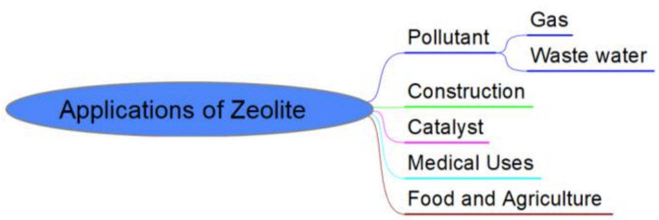

Figure 2: Applications of Zeolite

3.1 Pollutant

Removal pollutant from wastewater or gas process needs appropriately modified zeolite. Type of pollutants in wastewater consists of ammonium, phosphorus, heavy metal, inorganic anion, organics, and dye adsorption. Since natural zeolites have some physicochemical properties to adsorb or ion exchange some of compound, natural zeolites have the possibility to remove pollutant from water [9].

An et al. [10] conducted experiment and adsorption characteristics such as kinetics, isotherms, and mechanism of Mg^{2+} modified zeolite to adsorb NH_4^+-N and E-*coli*. The results showed that modified zeolite has higher activity due to the unique surface of the material. Langmuir model was used in the equilibrium adsorption model of NH_4^+-N and E *coli* with pseudo-second-order model as an adsorption kinetics model. Khosravi et al. [11] also investigated the removal of ammonium using modified natural zeolite with diluted acid and NaCl from Western Azerbaijan. They also studied adsorption kinetics using Langmuir and Freundlich isotherm models. They found that the kinetics studies followed pseudo-second-order model. Modification of zeolite showed improvement on ammonium removal process. Many researchers have reported the utilization of natural zeolite for removal of ammonium using modified natural zeolite [12–14]. Statistical analysis and optimization of ammonia removal were studied by Ding et al. [12]. They found that removal of ammonium depends on pH, ammonia concentration, and zeolite dose. They found that pH 6 was the best pH since ammonia under low pH conditions has NH_4^+ form. Higher composition of zeolite was also increasing removal efficiency. Based on their experiments, temperature was not significantly influence removal process.

Investigation of NaCl-modified zeolite on the removal of nitrogen and phosphorus by evaluating pH, reaction time, and zeolite dose was studied by Cheng et al. [15]. They used Langmuir and Freundlich adsorption isotherms models to analyze adsorbent kinetics and mechanisms of the zeolite. They compared characterization of natural and modified zeolite using XRD, XRF, SEM, and FTIR. They found that NaCl modified zeolite increased Si/Al ratio and content of exchangeable cations such as Na^+. Si/Al ratio influences their physicochemical properties of zeolite, while higher in Na^+ is a benefit for the removal of the other cations. Different from the studies by Ding et al., Cheng et al. found optimal pH for NH_4^+-N and PO_4^{3-} at pH 8. Different results influenced by type of zeolite and treatment. For phosphorous case, soluble inorganic can be present in chemical form: H_3PO_4 at pH < 2; $H_2PO_4^-$ at pH 3 - 6.5; HPO_4^{2-} at pH 7.5 - 12; PO_4^{3-} at pH > 12 [16]. Effect of reaction time and zeolite dosage was also investigated. They found that removal efficiency increased with the contact time. With dosage 1g zeolite/100mL, the removal reaction rate increased rapidly until it reached equilibrium at 360 mins. Increasing zeolite dosage increased surface area that can effectively decrease the unsaturation of the ion exchange sites of the zeolites. Lin et al. [16] conducted experiments for phosphorous removal rates by natural zeolites. They investigated the effect of pH, contact time, and removal mechanism between batch and column test. They found that optimum pH for recoveries of P and N was high at pH 9.3. They also proposed two-step mechanism for removal of P and N. First, ammonium was adsorbed to zeolite by releasing Ca^{2+} ion to solution, then Ca^{2+} ion formed precipitate with phosphate for removal.

Heavy metals are classified as metallic elements with a relatively high density of over 5 g/cm^3 [17]. There have been growing local and global public health issues associated with the pollution of these metals by the environment. Removal of heavy metals by using natural and modified zeolite was also studied. Zamzow et al. determined the selectivity of removing heavy metals and other cations using clinoptilolites with sodium as exchangeable ion as follows: Pb>Cd>Cs>Cu(II)>Co(II)>Cr(III)>Zn>Ni(II)>Hg(II) [18]. Structural diversity of natural zeolites is essential for the adsorption of metal Pb in the wastewater, as reported by Curkovi et al. [19]. Borandegi and Ejhieh [20] had the finding that the modified zeolite by glutamic acid showed strong selectivity for cobalt in the presence of specific multivalent cations. Modification of zeolites using hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA) was also studied by Szala et al. [21] showed higher activity for removing of chromium (VI) using clinoptilolite.The adsorption process of cadmium and copper using modified natural zeolite was also investigated by Taamneh and Sharadqah [22]. The paper concludes that metal bulk concentration, adsorption time, and mass of adsorbent are factors affecting adsorption process.

3.2 Construction

The addition of natural zeolites to concrete is found to highly efficient in strengthening the stability of the final concrete product [23]. In China, as reported by Feng and Peng [24], in 2005, cement production is industry with the most significant zeolite consumption. In Germany, volcanic material from Keiserstuhl that contains 45% zeolite is used for concrete production [25]. The utilization of natural zeolite as a supplement in cement and concrete composites with 10-50% composition is also studied [26–30]. Furthermore, natural zeolite that is used for construction and building material has some unique characteristics, such as antibacterial agent, nonalkali antifreeze, and rapid mixing, carrier fluidizing agent (CFA) for concrete workability, and humidity-conditioning material [24, 31–33].

Natural zeolite can be used as pozzolanic materials since natural zeolite contains a large proportion of SiO_2 and Al_2O_3. The formation of calcium hydroxide in the hydration of cement can contribute to the formation of highly vulnerable concrete [23]. This problem can be reduced by mixing cement with natural zeolite. The mixing with natural zeolite can form dense microstructure of hardened cement and concrete since SiO_2 and Al_2O_3 in zeolite forming calcium silicate hydrate and aluminate hydrate gels [23, 32, 34–37]. Besides that, the effect on addition of natural zeolite also helps to reduce chloride ion penetration into concrete [35, 38]. The addition of natural zeolite as lightweight aggregates into concrete can reduce weight while improving the durability and thermal insulation ability of concrete [2, 23, 27, 29, 39]. All the results of construction research showed that cement or concrete with proper dosage of natural zeolite has high-performance ability.

Najimi et al. investigated mechanical and durability properties of concrete with addition of clinoptilolite [32]. The results showed satisfactory performance of concrete in acid environment. Durability of the concretes with the addition of 15% natural zeolite was found as an appropriate composition to enhance the effectiveness of water penetration, chloride ion penetration, corrosion rate, and drying shrinkage of concrete. However, the compressive strength of concrete containing natural zeolite was lower than without natural zeolite. Markiv et al. [27] also investigate the mechanical properties of concrete using natural zeolite. They found that the compressive strength using natural zeolite was higher than without zeolite after 180 days of hardening. They also found that natural zeolite is effective component to improve the durability of concrete that results in increasing the resistance of freezing and thawing damage and decreasing drying shrinkage, water penetration depth.

3.3 Catalyst

Researchers are trying to explore the potential of zeolites in industrial applications as a catalyst due to its excellent absorbency. Zeolites have several advantages, such as it is abundant material, inexpensive, and environmental ecofriendly [40, 41]. The uses of natural zeolites as catalyst support include pyrolysis [40, 42], transesterification of palm oil [43], dimethyl ether from methanol synthesis [44], hydrogenation [45], and for isomerization process [46, 47].

The utilization of zeolites as catalyst support for transesterification of palm oil was studied by Kusuma et al. [43]. They prepared the zeolite catalyst by impregnation with KOH. Before preparation of catalyst, zeolite was treated with hydrogen peroxide solution. While preparing the catalyst, zeolites were calcined at 450℃. This process converted KOH into K_2O which become active site during the transesterification reaction. The catalyst was characterized and used as catalyst for biodiesel production. The results show that the performance of the catalyst was having high yield, good stability with three reaction cycles of reusability. Beside catalyst for biodiesel, zeolite was also used for dimethyl ether from methanol [44]. The results show that zeolites have properties to adsorb the water, so it has possibility to become inexpensive and efficient catalyst for DME production.

Zeolites, as pyrolysis catalyst, were also observed by Pütün et al. [42] and Lee et al. [40]. Lee et al. evaluated two-stage catalytic pyrolysis of lignin using fixed bed reactor system contain in-situ natural zeolite and ex-situ HZSM-5 as the additive and main catalyst. The results show natural zeolite was very helpful in improving alkylphenols and pyrocatechols. It was also decreasing guaiacols, eugenols, and heavy lignin pyrolyzates. It also shows that the two-stage pyrolysis using NZ and HZSM-5 made the process more economical. According to Pütün et al., the liquid obtained by pyrolysis using natural zeolite offers a strongly aliphatic substance with more olefinic and aromatic fractions compared to previous noncatalytic processes.

4. CONCLUSION

Natural zeolites have many advantages, such as abundant, inexpensive, and environmentally friendly materials. Zeolites have proved to be effective in various environmental and industrial applications. These applications are related to the adsorption properties of zeolites. Zeolites have been used for pollutant removal both gas and wastewater, construction as the addition of concrete materials to improve their stability properties, and catalyst for energy production.

Natural zeolites have some physicochemical properties to adsorb or ion exchange some of compound so that natural zeolites can remove pollutant from water. Besides for pollutant removal, the addition of natural zeolites in the application of constructions is found to have high-performance ability in strengthening the stability of the final cement or concrete with proper dosage of natural zeolite. Many researchers are also conducted to explore potential zeolites as catalysts. All the study showed that zeolites have high potential as catalysts, especially for dehydrogenation and dehydration.

ACKNOWLEDGMENT

We gratefully acknowledge the funding from Universitas Indonesia through Publikasi Terindeks Internasional (PUTI) Saintekes 2020 No. NKB-2450/UN2.RST/HKP.05.00/2020.

REFERENCES

[1] G. Gottardi and E. Galli, *Natural Zeolites*, 1st editio. Munich: Springer-Verlag Berlin Heidelberg, 1985.

[2] F. A. Mumpton, "La roca magica: Uses of natural zeolites in agriculture and industry," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 96, no. 7, pp. 3463–3470, 1999, doi: 10.1073/pnas.96.7.3463.

[3] M. Moshoeshoe, M. Silas Nadiye-Tabbiruka, and V. Obuseng, "A Review of the Chemistry, Structure, Properties and Applications of Zeolites," *American*

Journal of Materials Science, vol. 2017, no. 5, pp. 196–221, 2017, doi: 10.5923/j.materials.20170705.12.

[4] H. Ghobarkar, O. Schäf, Y. Massiani, and P. Knauth, *The Reconstruction of Natural Zeolites*. 2003.

[5] A. Mastinu *et al.*, "Zeolite clinoptilolite: Therapeutic virtues of an ancient mineral," *Molecules*, vol. 24, no. 8, 2019, doi: 10.3390/molecules24081517.

[6] L. Bacakova, M. Vandrovcova, I. Kopova, and I. Jirka, "Applications of zeolites in biotechnology and medicine-a review," *Biomaterials Science*, vol. 6, no. 5, pp. 974–989, 2018, doi: 10.1039/c8bm00028j.

[7] S. K. Pavelić, J. S. Medica, D. Gumbarević, A. Filošević, N. Pržulj, and K. Pavelić, "Critical review on zeolite clinoptilolite safety and medical applications in vivo," *Frontiers in Pharmacology*, vol. 9, no. NOV, pp. 1–15, 2018, doi: 10.3389/fphar.2018.01350.

[8] N. Eroglu, M. Emekci, and C. G. Athanassiou, "Applications of natural zeolites on agriculture and food production," *Journal of the Science of Food and Agriculture*, vol. 97, no. 11, pp. 3487–3499, 2017, doi: 10.1002/jsfa.8312.

[9] J. Shi *et al.*, "Preparation and application of modified zeolites as adsorbents in wastewater treatment," *Water Science and Technology*, vol. 2017, no. 3, pp. 621–635, 2017, doi: 10.2166/wst.2018.249.

[10] S. W. An, Y. C. Jeong, H. H. Cho, and J. W. Park, "Adsorption of NH4+-N and E. coli onto Mg2+-modified zeolites," *Environmental Earth Sciences*, vol. 75, no. 5, pp. 1–11, 2016, doi: 10.1007/s12665-016-5476-x.

[11] A. Khosravi, M. Esmhosseini, and S. Khezri, "Removal of ammonium ion from aqueous solutions using natural zeolite: Kinetic, equilibrium and thermodynamic studies," *Research on Chemical Intermediates*, vol. 40, no. 8, pp. 2905–2917, 2013, doi: 10.1007/s11164-013-1137-9.

[12] Y. Ding and M. Sartaj, "Statistical analysis and optimization of ammonia removal from aqueous solution by zeolite using factorial design and response surface methodology," *Journal of Environmental Chemical Engineering*, vol. 3, no. 2, pp. 807–814, 2015, doi: 10.1016/j.jece.2015.03.025.

[13] Y. bo Dong and H. Lin, "Ammonia nitrogen removal from aqueous solution using zeolite modified by microwave-sodium acetate," *Journal of Central South University*, vol. 23, no. 6, pp. 1345–1352, 2016, doi: 10.1007/s11771-016-3186-x.

[14] H. Guo, X. Zhang, and J. Liu, "Ion-exchange capability for ammonium removal using zeolite modified by potassium permanganate," *Chemical Engineering Transactions*, vol. 55, pp. 163–168, 2016, doi: 10.3303/CET1655028.

[15] Q. Cheng *et al.*, "Study on the adsorption of nitrogen and phosphorus from biogas slurry by NaCl-modified zeolite," *PLoS ONE*, vol. 12, no. 5, pp. 1–12, 2017, doi: 10.1371/journal.pone.0176109.

[16] L. Lin, C. Wan, D. J. Lee, Z. Lei, and X. Liu, "Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite," *Separation and Purification Technology*, vol. 133, pp. 351–356, 2014, doi: 10.1016/j.seppur.2014.07.010.

[17] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, "Heavy Metals Toxicity and the Environment," *Molecular, Clinical and Environmental Toxicology*, vol. 101, pp. 133–164, 2012, doi: 10.1007/978-3-7643-8340-4.

[18] M. J. Zamzow, B. R. Eichbaum, K. R. Sandgren, and D. E. Shanks, "Removal Of Heavy Metals And Other Cations From Wastewater Using Zeolites," *Separation Science and Technology*, vol. 25, pp. 1555–1569, 1990, doi: 10.1080/01496399008050409.

[19] L. Ćurković, Š. Cerjan-Stefanović, and T. Filipan, "Metal ion exchange by natural and modified zeolites," *Water Research*, vol. 31, no. 6, pp. 1379–1382, 1997, doi: 10.1016/S0043-1354(96)00411-3.

[20] M. Borandegi and A. Nezamzadeh-Ejhieh, "Enhanced removal efficiency of clinoptilolite nano-particles toward Co(II) from aqueous solution by modification with glutamic acid," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 479, pp. 35–45, 2015, doi: 10.1016/j.colsurfa.2015.03.040.

[21] B. Szala, T. Bajda, and A. Jeleń, "Removal of chromium(VI) from aqueous solutions using zeolites modified with HDTMA and ODTMA surfactants," *Clay Minerals*, vol. 50, no. 1, pp. 103–115, 2015, doi: 10.1180/claymin.2015.050.1.10.

[22] Y. Taamneh and S. Sharadqah, "The removal of heavy metals from aqueous solution using natural Jordanian zeolite," *Applied Water Science*, vol. 7, no. 4, pp. 2021–2028, 2017, doi: 10.1007/s13201-016-0382-7.

[23] Y. T. Tran, J. Lee, P. Kumar, K. H. Kim, and S. S. Lee, "Natural zeolite and its application in concrete composite production," *Composites Part B: Engineering*, vol. 165, pp. 354–364, 2019, doi: 10.1016/j.compositesb.2018.12.084.

[24] N. Q. Feng and G. F. Peng, "Applications of natural zeolite to construction and building materials in China," *Construction and Building Materials*, vol. 19, no. 8, pp. 579–584, 2005, doi: 10.1016/j.conbuildmat.2005.01.013.

[25] F. Hauri, "Natural zeolite from southern Germany applications in concrete," *Proceedings of 7th international conference on the occurrence, properties, and utilization of natural zeolites*, pp. 130–1, 2006.

[26] C. Karakurt and I. B. Topçu, "Effect of blended cements produced with natural zeolite and industrial by-products on alkali-silica reaction and sulfate resistance of concrete," *Construction and Building Materials*, vol. 25, no. 4, pp. 1789–1795, 2011, doi: 10.1016/j.conbuildmat.2010.11.087.

[27] T. Markiv, K. Sobol, M. Franus, and W. Franus, "Mechanical and durability properties of concretes incorporating natural zeolite," *Archives of Civil and Mechanical Engineering*, vol. 16, no. 4, pp. 554–562, 2016, doi: 10.1016/j.acme.2016.03.013.

[28] C. Bilim, "Properties of cement mortars containing

clinoptilolite as a supplementary cementitious material," *Construction and Building Materials*, vol. 25, no. 8, pp. 3175–3180, 2011, doi: 10.1016/j.conbuildmat.2011.02.006.

[29] B. D. Ikotun and S. Ekolu, "Strength and durability effect of modified zeolite additive on concrete properties," *Construction and Building Materials*, vol. 24, no. 5, pp. 749–757, 2010, doi: 10.1016/j.conbuildmat.2009.10.033.

[30] B. Ahmadi and M. Shekarchi, "Use of natural zeolite as a supplementary cementitious material," *Cement and Concrete Composites*, vol. 32, no. 2, pp. 134–141, 2010, doi: 10.1016/j.cemconcomp.2009.10.006.

[31] R. Figmig and M. Kováč, "Study on utilization of zeolite in concrete precast industry," *Selected Scientific Papers - Journal of Civil Engineering*, vol. 14, no. 1, pp. 93–102, 2019, doi: 10.1515/sspjce-2019-0010.

[32] M. Najimi, J. Sobhani, B. Ahmadi, and M. Shekarchi, "An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan," *Construction and Building Materials*, vol. 35, pp. 1023–1033, 2012, doi: 10.1016/j.conbuildmat.2012.04.038.

[33] F. A. Sabet, N. A. Libre, and M. Shekarchi, "Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash," *Construction and Building Materials*, vol. 44, pp. 175–184, 2013, doi: 10.1016/j.conbuildmat.2013.02.069.

[34] D. Caputo, B. Liguori, and C. Colella, "Some advances in understanding the pozzolanic activity of zeolites: The effect of zeolite structure," *Cement and Concrete Composites*, vol. 30, no. 5, pp. 455–462, 2008, doi: 10.1016/j.cemconcomp.2007.08.004.

[35] M. Rashetnia, Reza, Dousti Ali, Ahmadi Babak, Khatami, Dena, Shekarchi, "Effect of Natural Zeolite and Silica Fume As a Pozzolanic Materials on the Chloride Diffusion of Concrete," *International Congress on Durability of Concrete*, no. January, 2012.

[36] N. Burriesci, C. Arcoraci, N. Giordano, and P. L. Antonucci, "Zeolites from pumice and tuff as evaluation of pozzolanic cement constituents," *Zeolites*, vol. 5, no. 2, pp. 96–100, 1985, doi: 10.1016/0144-2449(85)90080-6.

[37] T. Perraki, G. Kakali, and E. Kontori, "Characterization and pozzolanic activity of thermally treated zeolite," *Journal of Thermal Analysis and Calorimetry*, vol. 82, no. 1, pp. 109–113, 2005, doi: 10.1007/s10973-005-0849-5.

[38] S. Y. N. Chan and X. Ji, "Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes," *Cement and Concrete Composites*, vol. 21, no. 4, pp. 293–300, 1999, doi: 10.1016/S0958-9465(99)00010-4.

[39] E. Vejmelková *et al.*, "Engineering properties of concrete containing natural zeolite as supplementary cementitious material: Strength, toughness, durability, and hygrothermal performance," *Cement and Concrete Composites*, vol. 55, pp. 259–267, 2015, doi: 10.1016/j.cemconcomp.2014.09.013.

[40] H. W. Lee *et al.*, "Catalytic pyrolysis of lignin using a two-stage fixed bed reactor comprised of in-situ natural zeolite and ex-situ HZSM-5," *Journal of Analytical and Applied Pyrolysis*, vol. 122, pp. 282–288, 2016, doi: 10.1016/j.jaap.2016.09.015.

[41] M. Alsawalha, "Overview of current and future perspectives of saudi arabian natural clinoptilolite zeolite: A case review," *Journal of Chemistry*, vol. 2019, 2019, doi: 10.1155/2019/3153471.

[42] E. Pütün, B. B. Uzun, and A. E. Pütün, "Fixed-bed catalytic pyrolysis of cotton-seed cake: Effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate," *Bioresource Technology*, vol. 97, no. 5, pp. 701–710, 2006, doi: 10.1016/j.biortech.2005.04.005.

[43] R. I. Kusuma, J. P. Hadinoto, A. Ayucitra, F. E. Soetaredjo, and S. Ismadji, "Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil," *Applied Clay Science*, vol. 74, pp. 121–126, 2013, doi: 10.1016/j.clay.2012.04.021.

[44] A. D. Kustovskaya and E. I. Kosenko, "Catalytic activity of natural zeolites in the conversion of methanol to dimethyl ether," *Petroleum Chemistry*, vol. 54, no. 2, pp. 137–141, 2014, doi: 10.1134/S0965544114020054.

[45] S. Yilmaz, S. Ucar, L. Artok, and H. Gulec, "The kinetics of citral hydrogenation over Pd supported on clinoptilolite rich natural zeolite," *Applied Catalysis A: General*, vol. 287, no. 2, pp. 261–266, 2005, doi: 10.1016/j.apcata.2005.04.002.

[46] B. Atalay and G. Gündüz, "Isomerizaton of α-pinene over H3PW12O40 catalysts supported on natural zeolite," *Chemical Engineering Journal*, vol. 168, no. 3, pp. 1311–1318, 2011, doi: 10.1016/j.cej.2011.02.037.

[47] H. C. Woo, K. H. Lee, and J. S. Lee, "Catalytic skeletal isomerization of n-butenes to isobutene over natural clinoptilolite zeolite," *Applied Catalysis A: General*, vol. 134, no. 1, pp. 147–158, 1996, doi: 10.1016/0926-860X(95)00216-2.