Synthesis of natural zeolite adsorbent for CO$_2$ adsorption FREE

Retno Ambarwati Sigit Lestari ✉ ; Supriono; Chandra Wahyu Purnomo

Check for updates

View Online   Export Citation   CrossMark

Articles You May Be Interested In

Novel soliton solutions of Sasa–Satsuma model with local derivative via an analytical technique

Journal of Laser Applications (May 2022)

Structural and optical modification of ZnO:Al thin films by molybdenum co-doping and the origin of green emission

AIP Conference Proceedings (May 2018)

Symmetry, full symmetry groups, and some exact solutions to a generalized Davey–Stewartson system

J. Math. Phys. (October 2008)

Synthesis of Natural Zeolite Adsorbent for CO$_2$ Adsorption

Retno Ambarwati Sigit Lestari[1,a)], Supriono[2,b)] and Chandra Wahyu Purnomo[3,c)]

[1]*Chemical Engineering Department of Universitas 17 Agustus 1945 Semarang, Indonesia*
[2]*Chemical Engineering Department of Universitas Setia Budi, Surakarta, Indonesia*
[3]*Chemical Engineering Department of Universitas Gadjah Mada, Yogyakarta, Indonesia*

[a)] Corresponding author: retnotengaran@gmail.com
[b)] suprisuwito@gmail.com
[c)] chandra.purnomo@ugm.ac.id

Abstract. Zeolite is one of the adsorbent materials that reduce CO$_2$ in biogas, due to being a mineral with silica-alumina clusters, which cross-knits through the binding of oxygen atoms to the hydrated structure (Al-Si)O$_4$ of alkali metals and alkaline soils. Natural zeolites generally have less crystallinity, different pore size, and many metal oxides. Therefore, this study aims to improve the quality of natural zeolite through activation and modification. Using FTIR spectroscopy, the activation of this mineral utilized NaOH and calcination at 500°C, where the analysis of specific chemical bonds and functional groups indicated a reduction in silica and the ratio of Si /Al. This activation technique also caused a greater adsorption capacity value by using bases (NaOH), with the zeolite structure becoming more negative. Subsequently, activation did not form new compounds, as it only removed impurities for pore optimization. The ZA1M activation decreased and increased the CO$_2$ and CH$_4$ concentrations of the biogas. The percentages of CO$_2$ removal used ZA, ZA1M, and ZA5M were 14,90%, 25,48% and 46,95% using flowrate of biogas 2000 ml/min for 15 min and 50 cm high of zeolite packing

INTRODUCTION

The reliance of humans on fossil fuels is found to reduce energy reserves, subsequently adding to the issues of environmental impacts such as air pollution. This leads to public awareness that the dependence on fossil fuels should be immediately reduced. To overcome this problem, cheap and readily available alternative fuels are needed, such as biogas, which is produced through the fermentation process of organic wastes, including food, animal, and industrial pollutants, respectively. Furthermore, the elements contained in this fuel are CH$_4$ (methane), CO$_2$ (carbon dioxide), O$_2$ (oxygen), H$_2$S (hydrogen sulfide), H$_2$ (hydrogen), and CO (carbon monoxide). Based on these elements, the most important ones used in determining the quality of biogas are methane (CH$_4$) and carbon dioxide (CO$_2$). This indicates that biogas has high and low heat values with increased CH$_4$ and CO$_2$ levels, respectively. Therefore, the reduction of CO2 content is very necessary when increasing the calorific value of the biogas. Also, methane content is increased through the separation of carbon dioxide and corrosive hydrogen sulfide (H$_2$S) from the biogas.

One of the adsorbent materials that reduce CO$_2$ in biogas is zeolite, which is highly available within Indonesia [1]. This is a mineral with silica-alumina clusters, which cross-knits through the binding of oxygen atoms to the hydrated structure (AlSi)O$_4$ of alkali metals and alkaline soils [2]. Also, it is a porous material with a three-dimensional skeletal structure containing crystalline aluminosilicate, which forms pores of similar sizes and is commonly referred to as molecular sieves [3]. Subsequently, zeolites are materials very useful as adsorbents, which have a very regular crystalline shape with voids interconnected in all directions [4]. These materials are unique adsorbents due to being very small with uniform pore sizes, compared to others such as activated carbon and silica gel. This indicates that zeolites only absorb molecules whose diameters are less than or equal to those of the cavity. Under normal circumstances, the vacuum of a zeolite crystal is filled with water molecules around the cations. This indicates that water is removed when the zeolite is heated. Furthermore, natural zeolites have less crystallinity, different pore sizes, and many metal oxides, as their composition is generally dissosoque from mordenite and clinoptilolite types. In

addition, clinoptilolite is one of the most abundant types of zeolite, due to thermal stability, as well as high selectivity and cation exchangeability [5].

Activation and modification are known as the methods of improving the quality of natural zeolites. Moreover, the activation process is reportedly carried out in two stages, namely physical and chemical. Using the heat treatment process, the physical stage aims to evaporate the water contained in the zeolite pores, through calcination at 600°C. Meanwhile, the chemical stage aims to clean the surface of the zeolite pore through an acidic or alkaline solution, as well as remove metal oxides and reorganize interchangeable atom locations. This process is subsequently carried out with acidic compounds (HCl) and bases (NaOH) at various concentrations [6]. Besides eliminating impurities, the activation process changes the ratio of Si/Al, indicating that the characteristics of the zeolite are in line with the material to be suspended [7]. Furthermore, the zeolite activation obtained by the addition of the base is found to be more polar than that of the acid application. Chemical activation cleaned the compound pores and removed impurities by using a KOH base solution. This increased the crystallinity of the zeolite without exceeding the maximum limit. However, the concentration of KOH in this study (2.5 M) exceeded the maximum limit.

The type of compounds used for the basic chemical activation process is potassium or natrium hydroxides (KOH or NaOH), respectively. This is because NaOH is one of the strongest alkaline compounds that are stable and easily soluble in water. Therefore, further investigation on physically and chemically activated adsorbents are considered in this study. The influence of variations in the levels of the NaOH compounds is also considered, based on being the activators on the characteristics of zeolite adsorbents produced. This leads to a greater adsorption capacity value caused by Na+ base ions, which plays an important role in dissolving Si to form sodium silicate. Also, it allows the zeolite structure to be more negative [8]. Natural zeolites have better resistivity and thermal stability in different environments. Their thermal stability and chemical resistance improve with increased silica-alumina ratio as well as in the presence of alkaline cations in the zeolite framework [9].

In addition, the effects of the alkali melting temperature, SiO_2/Al_2O_3 ratio, and material pre-treatment on the physical properties of zeolite are also systematically investigated [10]. Therefore, this study aims to improve the quality of natural zeolite through activation and modification processes, where 0.5 cm flakes are used in conducting the adsorption of CO_2, H_2O, H_2S, and other gases.

STUDY METHODS

Based on this study, the natural zeolites derived from Gunung Kidul Yogyakarta were used. These were physically and chemically activated fragments of 5 mm in size. Activation was subsequently carried out by soaking the minerals in NaOH solutions of 1 and 5 M (ZA1M and ZA5M) for 24 h, respectively. This was accompanied by the processing of the zeolite, which was then activated in the furnace at 500°C. Furthermore, the results are washed with distillation water until neutrality is achieved. Once the neutral pH zeolite was dried to a constant weight in the oven at 110°C, the process of characterization was conducted.
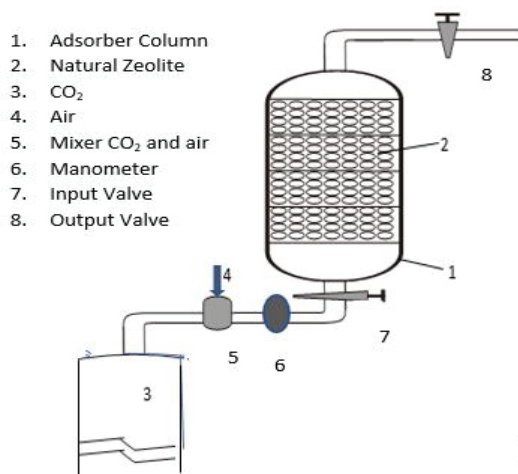

1. Adsorber Column
2. Natural Zeolite
3. CO_2
4. Air
5. Mixer CO_2 and air
6. Manometer
7. Input Valve
8. Output Valve

FIGURE 1. Experimental Equipment

This was an analysis of the crystallinity and morphology of zeolite, before and after activation. In addition, the morphological analysis was conducted by using JSM6510LA scanning electron microscope energy dispersion X-ray emission (SEMEDX), while chemical bond and functional group test was carried out through the Fourier transform infrared spectrometer (FTIR). The surface areas, analyzed by gas sorption analyzer BET method. Then the natural zeolite which has been activated (ZA1M and ZA5M) and no activated (ZA) tested for adsorb CO_2 in the mixture with air the adsorber column. Adsorber columns was made of acrylic material with dimention 50 cm of heigh and 5 cm of diameter, with a discharge hole every 10 cm of height. The adsorption process occurs by passing a mixture of CO_2 and air with a ratio of 55% CO2 and 45% air through the packing of zeolite. Next CO_2 will bond to the surface of the zeolite pore, and form a thin layer on the surface of the zeolite pore.

RESULTS AND DISCUSSIONS

Characterization of Natural Zeolite

FT-IR Analysis

The principle of FTIR spectroscopy stated that a molecule selectively absorbed the infrared light of a specific wavelength, indicating changes in the level of vibration and rotation. By analyzing the specific chemical bonds and functional groups derived from this spectroscopy number, molecular structure information was obtained. Based on FIGURE. 1, the FTIR spectroscopy of three zeolite types was observed, namely ZA (natural zeolite), ZA1M (natural zeolite activated with NaOH 1M) and ZA5M (natural zeolite activated with NaOH 5M). Moreover, three spectral charts were observed in FIGURE. 3, where absorption peaks were located at 3400 cm^{-1} (exactly 3407, 3419.45, and 3405.98 cm^{-1} for ZA1M, ZA5M, and ZA), 1600 cm^{-1} (exactly 1635.92, 1448.14, and 1632.93 cm^{-1} for ZA1M, ZA5M, and ZA), 1000 cm^{-1} (exactly 1020.35, 995.54, and 1020.71 cm^{-1} for ZA1M, ZA5M, and ZA) and 800 cm^{-1} (797.17, 777.13, and 796.71 cm^{-1} for ZA1M, ZA5M, and ZA) waves, respectively, as well as 2114.26 cm^{-1}, 627.35 cm^{-1} and 524.27 cm^{-1} for only ZA.

The peaks near 3400 and 1600 cm^{-1} occurred due to the stretching and bending vibrations of surface-absorbed water and HO bonds [11], respectively. Furthermore, the 1440 and 1000 cm^{-1} locations were assigned to the outer and inner asymmetric stretching vibrations of the (Si, Al) O bond [12]. The peaks at 670 and 466 cm^{-1} were also due to the internal vibrations of the (Si, Al) O-symmetrical expansion/contraction and bending, respectively. However, the peak of 545 cm^{-1} was caused by the external vibration of the double 4-membered ring of the Na molecular sieve. [13]. From the three spectral graphs, the adsorbents closely had similar group contents, although the natural zeolite without treatment (ZA) had an uptake at 1, 627.35, and 524.27 cm^{-1}, respectively. This indicated the presence of O-Si, showing that ZA had more Si content than ZA1M and ZA5M. The results also showed that when the dissolution process caused structural changes and reduced silica, the ratio of Si/Al decreased. Therefore, the NaOH activation with calcination at 500°C reduced silica in adsorbents, leading to a decrease in the ratio of Si/Al. Also, the use of bases (NaOH) in the activation process led to greater adsorption capacity value, due to playing an important role in dissolving Si to form sodium silicate, and subsequently making the zeolite structure more negative [8]. The infrared spectral patterns of the three adsorbent types also showed the number and location of relatively similar chart peaks, indicating that activation did not form new compounds, although removed impurities for pore optimizations.
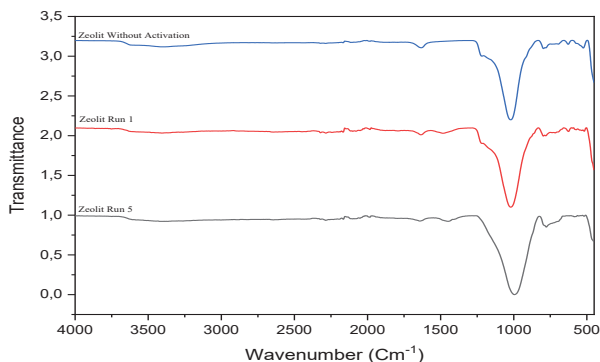

FIGURE 2. Infrared adsorbent spectra of natural zeolite ZA, ZA1M and ZA5M

The activation process of natural zeolites was observed to increase the adsorption capacity, due to the impure consideration of the metal oxides and the clearance of the pore cavities from water molecules. Also, the empty voids formed on the zeolite surface increased the active area, leading to higher adsorption capacity [14]. The NaOH activation process further decreased the Si/Al ratio of the sample, leading to more openings on the active zeolite surface. This indicated that the addition of bases (NaOH) caused a greater adsorption capacity value, where the Na+ ions played an important role in dissolving Si to form sodium silicate, and also making the zeolite structure more negative. These properties were synergistically conducted in the biogas with CO_2, H_2O, and H_2S.

Surface Morphology

Based on FIGURE. 2, the SEM photographs of three zeolite types were observed, i.e., ZA, ZA1M, and ZA5M. This indicated immature zeolite particulates, where the ZA particles were irregular grains with a size of 10-20 μm. After the NaOH 1M activation treatment at 500°C (ZA1M), the surface of the zeolite was found to have an irregular spherical crystal shape, with a particle size less than 5 μm. However, similar SEM images from ZA were observed for the NaOH 5M activation treatment at 500°C (ZA5M).

| (a) | (b) | (c) |
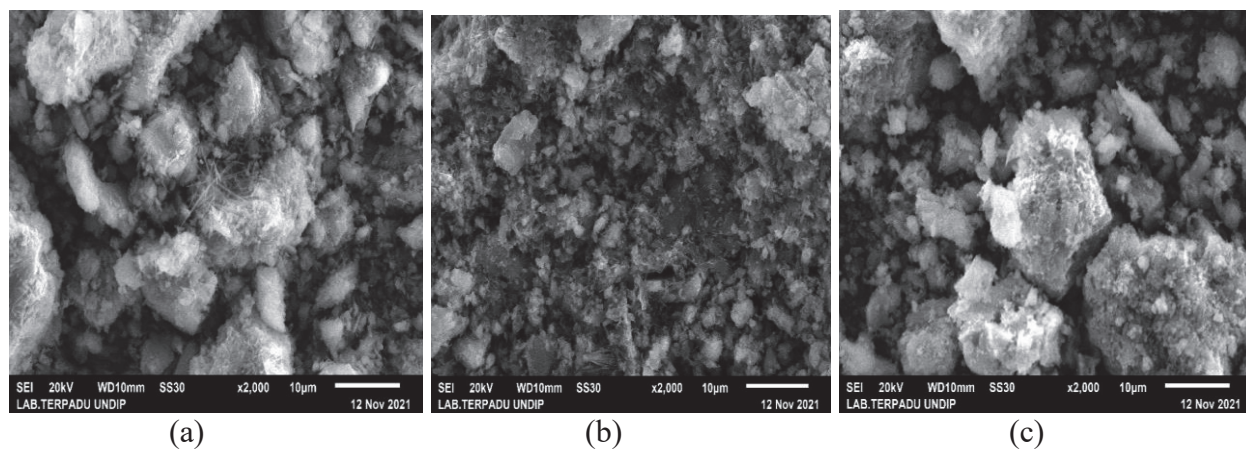
FIGURE 3. The adsorbents SEM image (a) ZA, (b) ZA1M, and (c) ZA5M

FIGURE 3(a) shows that an ZA surface morphology is heterogeneous with impurities covering pores. Figure 3(b) presents a more homogeneous morphology. While 3(c) indicates a heterogeneous surface with a tendency to clump. As written by Pa and Chik (2018)[15] that the micrograph SEM zeolite with 2 M NaOH has a tendency to be thick and rough.

Brunauer-Emmett-Teller (BET) Analysis

Based on the results of BET analysis obtained that the surface area of natural zeolite ZA1M has a pore surface area of 14.2949 m^2 / g, while ZA5M has a pore surface area of 5.6213 m^2 / g. This suggests that natural zeolite activated with NaOH at high concentrations (5M) causes a decrease in the surface area of natural zeolite pores. It because the metal attached to the surface of the zeolite there are some that cover the pore cavity on the surface, so that the specific surface area can be reduced [16].

Effect of Activation Natural Zeolite to Adsorbed CO_2 of mixture of CO_2 and air

Based on FIGURE. 4, the influence of natural zeolite in decreasing the CO_2 concentration of mixture of CO_2 and air was observed for three mineral types, namely ZA, ZA1M, and ZA5M. This indicated that higher packing of adsorbents caused a decrease in the concentration of CO_2, due to being more adsorbed by the zeolite. Meanwhile, the ZA1M (natural zeolite that activated used NaOH 1 M) effect highly decreased the CO_2 concentration than ZA and ZA5M. This indicated that the ZA1M activation was likely to damage the zeolite.
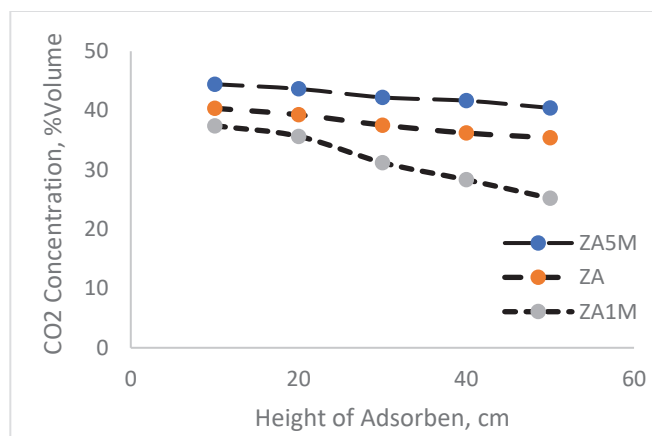
FIGURE 4. CO_2 concentration at various adsorbent high from natural zeolite

Effect activation of natural zeolite on percentage of CO₂ removal in mixture of CO₂ and air

The percentage CO_2 removal was measured using the same flowrate of mixture of CO_2 and air (2000 ml/min for 15 min) and 50 cm of hight of zeolite packing. FIGURE 5 shows that the percentages of CO_2 removal used ZA ZA5M, and ZA1M were 14,90%, 25,48% and 46,95%, respectively. Therefore, the activation natural zeolite used NaOH 1M increases the percentage of CO_2 removal in mixture of CO_2 and air the higher than used ZA and ZA5M. However, the activation used NaOH 5 M increases the percentage of CO_2 removal lower. This result is lower than a study conducted by Irvan et al. [17], that used natural zeolite (140 mesh, 400 °C for 4 hours) for CO_2 removal. The percentages of CO_2 removal at flow rates of 200, 400 and 600 ml/min were 92.5%, 82.5% and 60%. It is because in this study used mixture of CO_2 and air flowrate of 2000 ml / min, higher than the research by Irvan et al [17]. According to Kesnawaty [18], the low flow rate causes the contact time between gas and adsorbent in the column to be longer, so that the percentage of CO_2 removal increases.
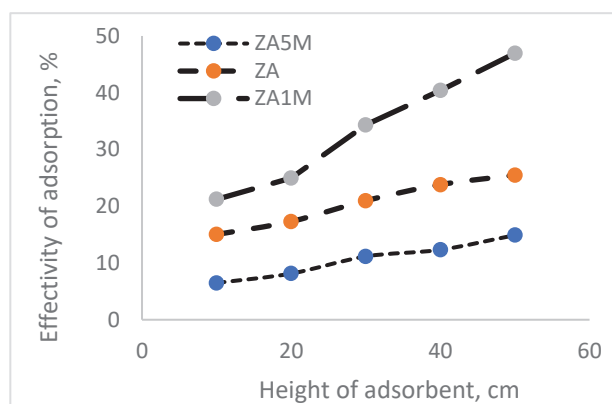

FIGURE 5. The effectiveness decreasing of CO_2 concentration at various high packing of zeolite

CONCLUSIONS

Based on this study, the following conclusions were observed the NaOH activation with 500°C calcination reduced the silica contents in adsorbents, leading to a decrease in the ratio of Si /Al. Basic (NaOH) activation was found to provide higher adsorption capacity values, due to playing an important role in Si dissolution to produce sodium silicate, and also making the zeolite structure more negative. The activation did not form new connections, although removed impurities to optimize pores. The addition of a base (NaOH) increased the value of the adsorption capacity, due to

playing an important role in Si dissolution and subsequently making the zeolite structure more negative. ZA1M has a pore surface area of 14.2949 m^2 / g, while ZA5M has a pore surface area of 5.6213 m^2 / g. The ZA1M activation decreased the CO_2 concentrations of mixture of CO_2 and air, respectively.

ACKNOWLEDGMENTS

REFERENCES

1. M. Razzak, T. Las, and Priyambodo, Valensi. **3**, 2, 129-137 (2013).
2. M. Gougazeh and J.C. Buhl, J. Assoc. Arab Univ. Basic Appl. Sci. **15**, 35- 42 (2014).
3. M. Theo, "Chapter 1", The Zeolite Scene — An Overview. In: Jiří Čejka, H.v.B.A.C., Ferdi, S. (Eds.), 168, pp. 1–12 (2007).
4. G. J. Millar, A. Winnet, T. Thompson and S. J. Couperthwaite, J. Water Process. Eng. **9**, 47-57 (2016).
5. V. J. Inglezakis, M.A. Stylianou, M. Loizidou, A. A. Zorpas, Water Treat. **57**, 11610-11622 (2016).
6. M. Djaeni, L. Kurniasari A. Purbasari, and S. Sasongko, 2010, Proceeding of the 1st International Conference on Materials Engineering, 25- 26 (2010).
7. L. Kurniasari, M. Djaeni and A. Purbasari. Reaktor. **13**, 3, 178-184 (2011).
8. E. B. G. Johnson, E. Sazmal, Arshad, Applied Clay Science. **97-98**, 215-221 (2014).
9. A. Khaleque, M. M. Alam M. Hoque, S. Mondal, J. B. Haider, B. Xuc, M.A.H. Johir, A. K. Karmakar, J.L. Zhoud, M. B. Ahmed and M. A. Moni, Environmental Advances. **2**, 100019 (2020).
10. J. Chen, X. Lu, J. Mate. Cycles Waste. **20**, 489–495 (2017).
11. Y. Cui, Y. Zheng, W. Wang, Minerals. **8**, 338, 1-15 (2018).
12. E. A. Abdelrahman, J. Mol. Liq. **253**, 72–82 (2018).
13. Zhang, D. Tang, G. Jiang, Adv. Powder Technol. **24**, 689–696 (2013).
14. A. Alshameri, X. Wei, S.D. Ammar, X. Chen, Y. Chunjie and M. A. Amer. J. Ecol. Eng. **20**, 4, 157–166 (2019).
15. C.F. Pa and A. Chik, Effect of NaOH Concentration and Reaction Time on zeolite synthesized from treated Oil palm Ash, Journal AIP Conference Proceeding (2018).
16. L. B. Rianto, S. Amalia, S. N. Khalifah, ALCHEMY. **2**, 1, 58-67 (2012).
17. M. Irvan, B Trisakti, S. Maulina, R. Sidabutar, Iriany, M. S. Takriff, J. Eng. Sci. Technol. **13**, 10, 3058 – 3070 (2018).
18. D.A. Kesnawaty, Capacity testing from adsorption of gas carbon monoxide (CO) using metal oxide and activated carbon. Thesis. Department of Chemical Engineering, University of Indonesia, Depok, 2010.