Thermal Behavior and Characteristic of Pangandaran Natural Zeolite

Wulandari, Dyah Arum
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Nasruddin
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Djubaedah, Euis
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Thermal Behavior and Characteristic of Pangandaran Natural Zeolite

Dyah Arum Wulandari[1,2,*], Nasruddin[1,*], Euis Djubaedah[1,3]

[1]Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI, Depok 16424, Indonesia

[2]Department of Mechanical Engineering Education, Faculty of Engineering, Universitas Negeri Jakarta, Jakarta 13220, Indonesia

[3]Agency for the Assessment and Application of Technology (BPPT), Serpong, Tangerang Selatan 15314, Banten, Indonesia

*Author to whom correspondence should be addressed,
E-mail: nasruddin@eng.ui.ac.id, dyah.arum51@ui.ac.id

Indonesia spread between many ocean and contain of so many islands which has lots of volcanoes that produce natural resources for example natural zeolite. It usually used for water treatment, catalyst and fertilizer but less in cooling application. The alternative use of cooling system which used solar energy is adsorption. This research intend to characterize natural zeolite from one area in Indonesia depend on their thermal behavior and other characteristic that useful for an adsorbent. The result show that it could be a great adsorbent according to its characteristic such as indicate from surface area, comparison of Silica and Alumina and other characteristic result.

1. Introduction

One of natural resources which abundantly available in Indonesia is natural zeolite from volcano rocks spread over 20 area with a huge amount of it parentheses[1]. Zeolite come from Greek term which means can take or adsorb water if it was heated and main component are Silica and Alumina[2].

In commercially sector, the electricity energy consumption needs some alternative system energy that uses the abandoned solar energy[3]. The wide use of natural zeolite was in catalysts and ion exchanger because of its microporosity and higher surface area[4]. The natural zeolite also has many limitations such as the properties could not optimized by nature and their structure has much more impurity[5]. Some methods of activation and modification could be done to solve that problem[6]. High energy consumption nowadays synonymous with the commercial buildings, almost 50% of energy consumption is use for HVAC[7], it could cause ozone depletion. More effort in renewable energy utilization[8] and activities in energy conservation need the worldwide energy policy where one is solar energy used for air-conditioning system[9,10]. It was a promising solution in alternative air-conditioning units that carry from renewable energies[11,12]. Adsorption is a chemical or physical reaction process between a solid (adsorbent) and a gas (refrigerant). Physically reaction between the adsorbent and refrigerant occurred through the connections of Van der Waals force were using in lots of use of adsorption chillers[13,14]. The Indonesian natural zeolites are common for agriculture, livestock, fisheries, drying agent and some industries uses[15] rarely for adsorbent in cooling application. The adsorbent and adsorbate should meet some requirements such as adsorb more adsorbate in a huge amount, could desorb when heated, low heat specific, good thermal conductivity (to shorten the cycle), do not getting worse after long period of using, do not poisonous and corrosion and suitable with refrigerant physically or chemically[11]. This research used one natural zeolites from Pangandaran areas where usually use for dehydration of bioethanol[16] and the others for CO_2 capture[17]. The problems are investigating the characteristic of natural zeolite that suite for adsorption cooling application, where they have to have a high pore to adsorb much refrigerant but they could not loss the performance of cooling system. This research aims to analyze the characteristic of the adsorbent which are natural zeolite from Indonesia as water adsorbent for cooling application.

2.   Materials and Methodology

2.1 Materials

The sample was taken from Pangandaran area, West Java province, Indonesia. It's grinded into small part about 1 or 2 mm then using a micro – size screen to get a uniform size. The liquid material is Aquadest from CV Dwinika.

2.2 Method of Activation

The natural zeolite activation according to[18] and was performed by washing the aquadest (1:3 w/v) under magnetic stirring for about 3 hours. The type of machine was IKA (R) C-MAG HS7 at rate of 2mot and room temperature and using 1000 ml breaker glass. After 3 hours, get some hours to precipitate the solid from the liquid. The second layer was clean natural zeolite which free from impurity while the first layer was quartz. Aeration need after that for pure layer and dried it enough that could take about several days.

The pure natural zeolite in solid phase was dried start from room temperature until 300°C for 3 hours using MEMMET UF 55 oven. Count and write down the weight of dried natural zeolite just after they were out from the drying process.

Physical activation' goal is to move away the molecule of water from the voids of natural zeolite and try to open the active site of natural zeolite.

3.   Characterization of Natural Zeolite

This research held some technique to characterize the natural zeolite. They are Braunauer Emmet and Teller Surface Area (BET) analysis, Fourier Transform Infrared Spectroscopy or FTIR Spectroscopy, Scanning Electron Microscopy (SEM), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), and Thermogravimetric analysis or thermal gravimetric analysis (TGA). The aim of physical activation is to remove water molecules from the voids of zeolite and open the zeolite's active sites[18]. The data of BET, SEM and TGA show that the natural zeolite becomes ready to be an adsorbent.

4.   Results

4.1 Brauner, Emmet and Teller Surface Area (BET) Analysis

BET Analysis results some value such as BET surface area, pore volume, and pore size. These properties were very important to identify the porous of the natural zeolite especially in adsorption cooling application. More refrigerant like water was easy to adsorb by the adsorbent if there were much area of porosity. The sample of natural zeolite was measure by surface area and porosity analyzer from Micromeritics ASAP 2020 series in Chemistry Laboratory, Universitas Negeri Jakarta, Indonesia. The measurements of the adsorption isotherms of Nitrogen at 77°K became the base of the determination. The degassing sample take turn in 4 hours at 350°C. The BET equation in the relative pressure range of between 0.05 and 0.3, over 5 adsorption points to estimate the surface area. The t-plot Harkins and Jura equation is being calculated for micropore volume. Subtracting the micropore volume from the volume of liquid Nitrogen adsorbed at relative pressure of 0.990 being done to determine the corresponding mesopore volume. Non-local density functional theory for slit-like pore geometry was used to measure the pore size distribution.

The surface area of Pangandaran natural zeolite was 120.9648 m²/g and BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter is 16.807 m²/g. The surface area of Pangandaran natural zeolite before activation is 145.7866 m²/g and BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter is 24.900 m²/g. This value is higher for raw material of zeolite which has not activated before. As mention in table below:

Table 1. Surface area, pore volume and pore size of Pangandaran natural zeolite, before and after activation (H_0 and H_1)

	BET Surface area (m²/g)	t-Plot micropore volume (cm³/g)	BJH adsorption average pore diameter (nm)
Before activation (H_0)	145.7866	0.059796	14.2872
After activation (H_1)	120.9648	0.052085	17.6061

The reducing of BET surface area is normally as it goes in the previous paper with different type of Indonesia natural zeolite[18], but with another following treatment will be increase the BET data.

4.2 Fourier Transform Infrared Spectroscopy or FTIR Spectroscopy
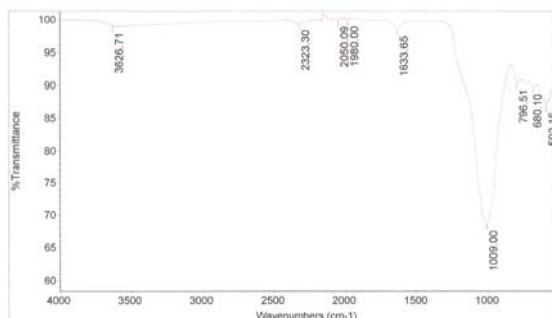
Fig. 1: The FTIR result for natural zeolite from Pangandaran using resolution of 4000.

As mention above, the result of natural zeolite from Pangandaran was tested using 128 number of scans, 64 background scans, and detector DTGS KBr., Beamsplitter: KBr and Source: IR in Laboratorium of Chemistry Engineering, Universitas Indonesia.

The peak from the left in wavenumbers of 3626.71 cm^{-1} indicate that Si-OH bond which reflect the surface of the natural zeolite have a strong bond of Silica. On the center in wavenumbers of 2323.3 cm^{-1} show the CO_2 bond and with 1633.65 cm^{-1} wavenumbers results the bond of H-O-H (H_2O) or water. This graph shown that this sample of natural zeolite could adsorb much water, which suitable the need of the objective of adsorber. On the right side with the tallest peak (about 1009 cm^{-1} wavenumbers) show the frame work of zeolite which still in the best form. The Si-Al frame work of zeolite was in a great condition that could adsorb and desorb water. Figure 1 also shows asymmetric stretching caused by the leaching of Al from zeolite framework and changes on the bond strength and Si-O-Si angle[19]. Since Si has higher electronegativity than Al and Si-O bond is shorter than the Al-O bond, the decrease of Al content causes the increase of Si-O bond strength.

4.3 Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)

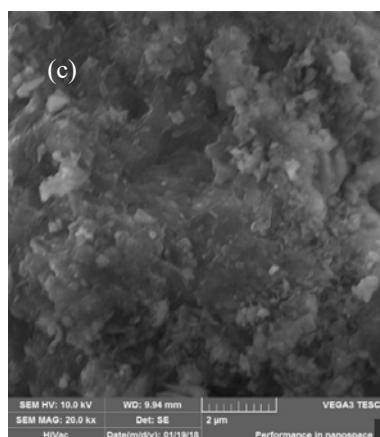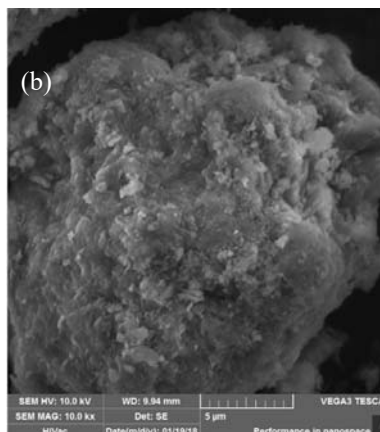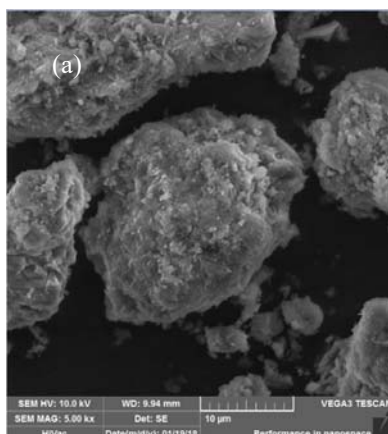The SEM result was taking by VEGA3 TESCAN of the Oxford Instrument in PT Gestrindo, Jakarta.

Fig. 2: The SEM result for natural zeolite from Pangandaran using resolution of 5000 (a) 10000 (b) and 20000 (c)

From the largest magnifying SEM result the form of natural zeolite with the form of cubical. By the picture below we could analyze the element inside the natural zeolite. The main elements are Silica which come from SiO_2 and Alumina which from Al_2O_3, from the number of both show that the comparison of Silica and Alumina was 35.3 / 8 = 4.4. It was indicate that this type of natural zeolite is more polar and they could adsorb more water. That is the goal of the natural adsorber which suitable for cooling application.
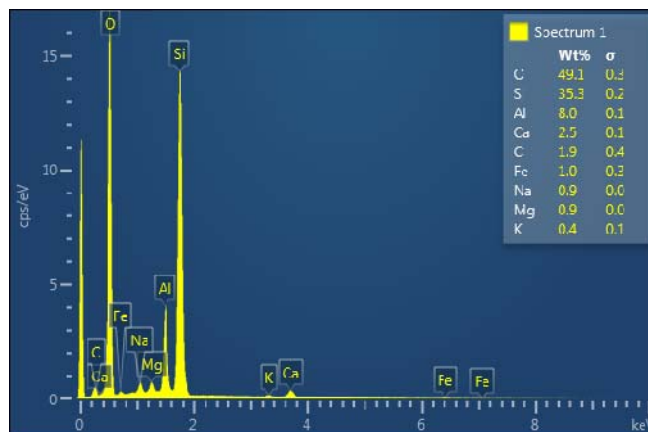
Fig. 3: Part inside that forming of the natural zeolite by SEM EDX test.

The Si/Al ratio can affect the mesopore formation in zeolite. The previous result[20] found that the optimal Si/Al ratio for introducing mesoporosity to zeolite framework is ~20-50. Below this ratio, only limited mesopore formation occured since the aluminium atoms prevent Si extraction from the zeolite framework.

4.3 Thermogravimetric analysis or thermal gravimetric analysis (TGA)

The result of TGA from the Pangandaran natural zeolite were provide from the laboratory of Centre for Material Processing and Failure Analysis (CMPFA), Metalurgi and Material Engineering Department, Universitas Indonesia with the serial number: 001061601, sample weight of 16.063 mg, validation by Calibration Information with program file Perkin Elmer, the initial conditions: temperature of 40.00 °C.
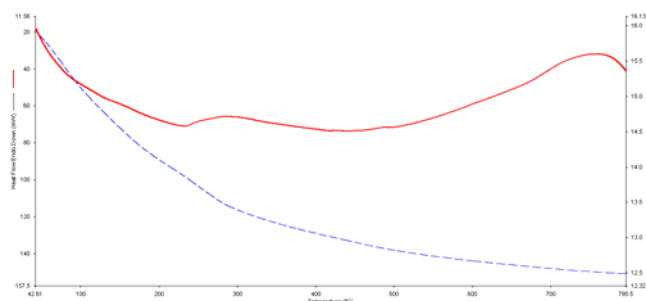

Fig. 4: Graph of Thermogravimetri test (TGA)

The water contain inside the natural zeolite will evaporate in the range of 100 until 200°C and it is in normally (endotherm). The amount of water that release is about 12.5% counted from initial weight of water reduced with the amount of water in evaporation time, then divided by the initial amount of water. There are some treatments if we want to increase this value (water release): cation exchange or desilication of surface using Natrium Clorida (NaCl) or both of them.

5. Conclusions

The characterization's data of the natural zeolite had been activated above result that it could be used as an adsorbent in cooling application. The following step of treatment of natural zeolite should needed to achieve the best result as being adsorbent. Acidification treatment followed by calcination will be require to increase if the BET surface area is low while Na-exchange treatment need to gain the optimal Si/Al ratio, strengthen by data from Fourier Transform Infra Red (FTIR), Thermal Gravimetric Analysis (TGA) and X-Ray Fluorescence (XRF) characterization.

References

1) Kusdarto K, "POTENCY OF ZEOLITE IN INDONESIA", *Jurnal Zeolit Indonesia,* **7**(2), 78-87 (2008).

2) Gottardi G, Galli E, *Natural Zeolites*, Springer Science & Business Media (2012).

3) Rouf RA, Khan M, Kabir K, Saha BB, "Energy Management and Heat Storage for Solar Adsorption Cooling", *Evergreen - Joint Journal of Novel Carbon Resource Sciences & Green Asia Strategy,* **3**(2), 1-10 (2016).

4) Bish DL, Ming DW, *Natural zeolites: occurrence, properties, applications*, Mineralogical Society of America (2001).

5) Weitkamp J, "Zeolites and catalysis", *Solid State Ionics*, **131**(1-2), 175-188 (2000).

6) Lestari DY, "Kajian modifikasi dan karakterisasi zeolit alam dari berbagai negara", *Proceeding of Seminar Nasional Kimia dan Pendidikan Kimia*, Yogyakarta (2010).

7) Pérez-Lombard L, Ortiz J, Pout C, "A review on buildings energy consumption information", *Energy and buildings*, **40**(3), 394-398 (2008).

8) Lubis H, "Renewable Energy of Rice Husk for Reducing Fossil Energy in Indonesia", *Akademia Baru. Journal of Advanced Research in Applied Sciences and Engineering Technology*, **11**(1), 17-22 (2018).

9) Ellabban O, Abu-Rub H, Blaabjerg F, "Renewable energy resources: Current status, future prospects and their enabling technology", *Renewable and Sustainable Energy Reviews*, **39**,

748-764 (2014).

10) Dincer I, "Renewable energy and sustainable development: a crucial review", *Renewable and sustainable energy reviews*, **4**(2), 157-175 (2000).

11) Fernandes M, Brites G, Costa J, Gaspar A, Costa V, "Review and future trends of solar adsorption refrigeration systems", *Renewable and Sustainable Energy Reviews*, **39**, 102-123, (2014).

12) Gugulothu R, Somanchi NS, Banoth HB, Banothu K, "A review on solar powered air conditioning system". *Procedia Earth and Planetary Science*, **11,** 361-367 (2015).

13) Choudhury B, Chatterjee P, Sarkar J, "Review paper on solar-powered air-conditioning through adsorption route", *Renewable and sustainable energy reviews*, **14**(8), 2189-2195 (2010).

14) Choudhury B, Saha BB, Chatterjee PK, Sarkar JP, "An overview of developments in adsorption refrigeration systems towards a sustainable way of cooling", *Applied Energy*, **104**, 554-567 (2013).

15) Thamzil L, Zamroni H, "Penggunaan Zeolit dalam Bidang Industri dan Lingkungan", *Jurnal Zeolit Indonesia*, **1**, 23-30 (2010).

16) Wahono SK, Maryana R, Pratiwi D, "Modification of Gunungkidul Natural Zeolite as Bioethanol Dehydrating Agents", *Energy Procedia*, **65**, 116-120 (2015).

17) Adriany R, "Pemanfaatan Zeolit Alam Termodifikasi Kation Na+ untuk Penangkapan CO2", *Lembaran Publikasi Minyak dan Gas Bumi*, **46**(3), 145-151 (2012).

18) Nurliati G, Krisnandi Y, Sihombing R, Salimin Z, "Studies of Modification of Zeolite by Tandem Acid-Base Treatments and its Adsorptions Performance Towards Thorium", *Atom Indonesia*, **41**(2), 87-95 (2015).

19) F.Cakicioglu-Ozkan, " Microporous and Mesoporous Materials", **77** (2005) 47.

20) M.C. Silaghi, C. Chizallet, P.Raybaud, "Microporous and Mesoporous Matter, **191** (2014) 82.