Preliminary study of natural zeolite from Bayah for solar powered cooling application

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Abstract. This paper presents the first attempt to investigate of natural zeolite for cooling adsorption application. Representative samples were collected from Bayah-Banten, Indonesia. As known that zeolites can be used as an adsorbent. Unfortunately, natural zeolite has many limitation, among them contains a lot of impurities. To improve the characteristic of natural zeolite, activation and modification should be conducted beforehand. Activation was conducted by reducing grain size (1-2mm), washed by aqua dest and heated using microwave. While the chemical activation is done through acidification by adding HCl solution. Finally, the activated natural zeolite was calcined gradually initiated at room temperature to 150°C for 2 hours and then heating continued from 150°C to 300°C for 4 hours. The final zeolite activated product was characterized by X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) and Transmission Electron Microscopy (TEM). The result showed that the morphology of the natural zeolite was cubic shave as observed by TEM and the surface area of activated natural zeolite is greater than the raw material.

1. Introduction

The commercial buildings are synonymous with high energy consumption, about 40% - 50% of energy consumption is due to HVAC usage[1]. The usage of unfriendly refrigerant on HVAC systems also causes ozone depletion [2]. Currently, worldwide energy policy encourage an efforts of renewable energy utilization and energy conservation activities in all sectors [3, 4]. Nowadays, alternative air-conditioning units that are derived from renewable energies, present a promising solution [5, 6]. Solar energy is one of the renewable energy sources which suitable to be applied for air-conditioning system [5]. Adsorption cooling system which can be carried-on by low-grade heat sources, such as solar energy or waste heat. Adsorption is a physical or chemical reaction process between a solid (adsorbent) and a gas (refrigerant). Generally in the adsorption process of cooling machine, the physical reaction between the adsorbent and refrigerant occurred through the connections of Van der Waals force [7].

Figure 1 shows the ideal cycle of the cooling adsorption process that occurs: A-B is the preheating process (isoteric), B-C is the desorption process where the refrigerant contained in the adsorbent will be issued along with the increased in the temperature on the adsorbent, then after saturation occurs the
C-D process is precooling isoteric) and subsequently is the D-A evaporation process (adsorption). The adsorbent temperature continues to fall and the liquid refrigerant evaporates and extracts heat from the evaporator which creates a cooling effect [8].

![Figure 1. Ideal adsorption cooling cycle [8].](image)

On the cooling of the adsorption system, there are some of the main components that must be available i.e. heat source, adsorber, condenser and evaporator. The selection of pairs of adsorbents should consider the temperature of the heat source, the desired characteristics of the cooling system, the working properties of the adsorbent (the physical, chemical and thermodynamic properties of the substances), the price, the availability and the environmental impact [8].

Ammonia, methanol, and water are have relatively larger latent calorific values (1368, 1160, and 2258 kJ/kg respectively) and small specific volumes (in units of $10^{-3}$ m$^3$/kg) so they are the most commonly used as a refrigerants. Water is the most thermally stable refrigerant, followed by methanol, and ammonia. Water deficiency is not applicable for cooling requirements below 0°C [5]. A good adsorbent material should have a large pore (ranging between 600 m$^2$/g or more) to absorb a large amount of refrigerant, but this causes the thermal conductivity to be low, thus limiting the performance of the cooling system [9].

The most commonly used adsorbent pairs today are zeolite - water, silica gel - water, activated carbon - methanol and activated carbon with ammonia. The isothermal adsorption of Zeolite is highly dependent on non-linear pressure, and thus makes Zeolite a suitable choice for solar cooling application [5]. Silica gel almost meets all the criteria required in the selection of adsorbents, besides it often experience the phenomenon of decreasing adsorption and weathering capacity [10, 11].

Carbons Active - methanol are operate at low regeneration temperatures <120°C, has a large adsorption capacity, low adsorption heat and low freezing point. The activated carbon pairs - ammonia require a regeneration temperature above 150°C, but has lower adsorption capacity, has a very strong odor and corrosive [12, 13]. For zeolite - water pair, regeneration temperature above 200°C and adsorption evaporation temperature of up to 70°C or more, they are remains stable at high temperatures as well as latent heat from water higher than methanol, so zeolite - water pairing is more appropriate to apply to room air conditioning [5] because solidified water temperatures can resist clotting processes while the disadvantage that are not too high cooling capacity and low working pressure can inhibit mass transfer [13]. In a study conducted by Anyanwu and Ogueke [14] can be concluded that for the activated carbon pairs - ammonia and activated carbon - methanol is very congested for ice manufacture and Frozen food pickling applications. As for zeolite – water pair is more suitable for air conditioning application of adsorption system because the lowest water temperature is 1°C and its high latent heat is suitable for producing cold water [7].
Zeolite is a nonmetallic mineral material with a structure of alumina-silicate having pores and skeletons in molecular dimensions [15]. There are four processes as a description of the formation of zeolites, namely the process of sedimentation of volcanic dust on the lake environment that is alkaline, alteration process, diagenesis process and hydrothermal process [16]. One of the uniqueness of the zeolite is to have an area surface and acidity that is easy to be modified. To improve the character of natural zeolite such as impurity and its crystallinity that is not good, activation and modification is the common method to be conducted beforehand. Activation process is intended to modify the properties of zeolites, such as surface area and acidity. The increased surface area and acidity will caused the catalytic activity of the zeolite to increased [17]. The objective of this research is utilizing natural zeolite from Indonesia as an adsorbent for cooling application while the novelty is improving a low grade natural zeolite from Indonesia become an effective cooling adsorbent.

2. Material and Methods

2.1. Material
Natural Zeolite (ZA) was supplied by PT. Trasindo Citra Utama which is obtained from Bayah, Province of Banten-Indonesia. The zeolite was crushed into small size (1-2mm) and sifted using a micro-size screen to remove fine particle and then weighed the weight of the zeolite to be used. Other materials such as Aquadest and hydrochloric acid (HCl) used for activating of zeolite.

2.2. Treatment of zeolite
This treatment was started by washing of natural zeolite by Aquadest. Washing done 3 times to remove undesirable materials and then filtered it. The washed zeolite dried using microwave oven. the use of microwave oven is to shorten the drying time as did by A. Arafat when he prepared Zeolite Y and ZSM-5 in microwave oven [18]. Before heating, zeolite is weighed first to know the amount of water depreciation during the drying process. The washed zeolite is placed in a clean cup then heated in the microwave with full heating for 20 minutes. Every 1 minute the zeolite is removed and weighed. This warming is done continuously until the shrinkage of weight from zeolite does not happen again. This can be interpreted that the water content in the zeolite is almost nonexistent. This sample was coded as ZAH. After the zeolite is dried, the next step is the activation of zeolite. In general, The use of Acid in the activation process of zeolite is to remove impurities that block the pores [19] and to increased Si/Al ratio [20]. The acid used in this study is hydrochloric acid (HCl).

About 15g of natural zeolite sample in 40.5 ml HCl – 500 ml Aquadest solution. The suspension was stirred in 1000 ml beaker glass using a magnetic stirrer type IKA C-MAG at a rate of 2 Mot for 24 h and room temperature. Subsequently, the suspension was filtered and washed with distilled water. The wet modified material was dried gradually using Themolyne furnace starting from room temperature - 150°C for 2 hours. Then calcined at a temperature of 150 °C - 300 °C at a rate of 10C / min for 4 hours. This sample was coded as ZAAH.

2.3. Characterization
The raw natural zeolites (ZA), heater natural zeolite (ZAH) and activated natural zeolites (ZAAH) were characterized by a variety of techniques describe below:

2.3.1. BET
The surface area and porous properties are the most important characteristics of porous materials because it is strongly related to the performance in many applications. The surface parameters of the prepared zeolite samples were measured by Micromeritics ASAP 2020 series. The determination was based on the measurements of the adsorption isotherms of nitrogen at 77°K. All samples were outgassed for 4 h at 350°C. The surface area was estimated from the BET equation in the relative pressure range of between 0.05 and 0.3, over five adsorption points. The micropore volume was calculated from tplot Harkins and Jura equation. Corresponding mesopore volume was determined by
subtracting the micropore volume from the volume of liquid nitrogen adsorbed at relative pressure of
0.99. Pore size distributions were determined using non-local density functional theory for slit-like
pore geometry.

2.3.2. XRD
The crystallinity phase of natural zeolite was analyzed by X-Ray Diffractometer (XRD) at PT.
Nanotech Hebal Indonesia, Balai Inkubator Teknologi BPPT- Serpong, Indonesia.

2.3.3. TEM
The technique of Transmission Electron Microscopy was conducted to observe the structural
characterization or morphologies of natural zeolite. TEM analysis was conducted at Universitas
Indonesia.

3. Result and Discussion
In previous study, Khaidir et al. [21] reported have modified natural zeolite from Bayah and use it as a
molecular sieves material on bioethanol dehydration. The result showed that the modified natural
zeolite by acidification can increased the properties of natural zeolite. Therefore, in the present paper,
effect of hydrochloric acid for the activation of natural zeolite from Bayah was investigated, and their
properties were characterized. The results described in the following section. From BET testing
conducted on the samples obtained the results of surface area, pore size and pore volume as shown in
the table 1.

| Sample of Zeolite | ZA     | ZAH    | ZAAH   |
|------------------|--------|--------|--------|
| BET Surface Area (m²/g) | 70.03  | 72.02  | 81.5   |
| t-Plot micropore volume (cm³/g) | 0.03   | 0.03   | 0.03   |
| Adsorption average pore width (4V/A by BET) (nm) | 5.7    | 5.8    | 5.8    |
| BJH Adsorption average pore diameter (4V/A) (nm) | 16.4   | 14.9   | 15.1   |
| BJH Desorption average pore diameter (4V/A) (nm) | 12.3   | 12.3   | 13.9   |

X-Ray Diffraction (XRD) pattern is shown by the figure 2. There are two strongest peaks available
i.e. peak at 2θ as describe in the table 2.

![Figure 2. XRD pattern of natural zeolite from Bayah](image-url)
Table 2. Strongest Peak List of XRD spectrum of natural zeolite from Bayah

| No. | 2-theta(deg) | d(ang.)     | Height(cps) | FWHM(deg) | Int. I(cps deg) | Int. W(deg) | Size(ang.) |
|-----|--------------|-------------|-------------|-----------|----------------|-------------|------------|
| 1   | 23.19(5)     | 3.832(8)    | 188(40)     | 1.41(9)   | 422(28)        | 2.2(6)      | 60(4)      |
| 2   | 26.92(6)     | 3.309(8)    | 94(28)      | 3.5(4)    | 574(94)        | 6(3)        | 24(3)      |

Razzak et al. have also conducted research on the characterization of zeolites from Bayah [22]. In their study which compared the XRD peaks with the ICDD 49-0924 and concludes that the natural zeolites from Bayah belong to a mineral mordenite group. It is different with that done by Supandi in his research [23] who reported that natural zeolite from Bayah belong to be a mineral clinoptilolite group and crystal structure of natural zeolite from Bayah may contains two crystal systems, there are crystal monoclinic with space group C2/m and crystal orthorhombic with space group of CmCm. This difference may occur due to the different mineral content of each mining site.

The technique of Transmission Electron Microscopy (TEM) was employed for the structural characterization of the natural zeolite. Figure 3 is illustrated a bright field TEM image corresponding to natural zeolite from Bayah, in which the presence of different phases can be observed. The result indicates the presence of the clinoptilolite phase and TEM image shows the cubic morphology of the material, which agrees with the XRD result to know more details about morphology and mineral content of natural zeolite, it is better to do SEM and EDX test.

Figure 3. The morphology of natural zeolite from Bayah using TEM examination.

4. Conclusion
Based on the results presented at above, it can be taken conclusions that through acidification treatment followed by calcination of natural zeolite from Bayah, it can be increased a surface area but the surface area obtained is still too small to be used as an adsorbent material to be applied for cooling. So another modifications are needed which can be improve the zeolite properties better.

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