Activation of Natural Zeolite as Water Adsorbent for Mixed-Adsorption Drying

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Abstract: Mixed-adsorption drying with material using zeolite is an option to improve product quality and energy efficiency of drying seeds. In this case, zeolite and seeds are mixed and fluidized by warm air as drying medium. The air will desorb water from seed, and at the same time, zeolite will adsorb vapor from air. Thus, the driving force of drying can be kept high. However, in Indonesia, the zeolite with high adsorption capacity is hardly found in market. This research studied the activation of natural zeolite using two different methods: by heating at 200-400°C, and adding NaOH 0.5-2.0 N. Results showed that the adsorbing capacity of zeolite activated by 1.0 N NaOH is 0.170 gr water/gr dry zeolite. While, by heating at 300°C for 3 hours, is 0.140 gr water loaded/gr dry zeolite. With the performance, zeolite can be used for drying application.

Keywords: zeolite, fluidized, adsorption, drying, activation

1. INTRODUCTION

The drying is a process commonly used in post harvest treatment such as seeds. The process is aimed to purify the product, prolong storage life of the product, reduce microbial activity, and saving transportation cost. However, current drying process still deals with reducing product quality and high energy usage as well as low efficiency. In post harvest treatment, more than 70% of energy used in drying. This is quite big, thus the development of efficient drying with high product quality still the important issue [1].

Mixed adsorption drying using zeolite is a potential option to be developed. In this method, the seed and zeolite are mixed and fluidized by warm air. The air will evaporate water from product, and at same time, the zeolite will adsorb vapor from air. As consequence, the relative humidity of air can be kept low. In addition, adsorption process releases heat that can be used to increase sensible heat of drying air. Thus, the driving force of drying can be still high.

Zeolite is alumino-silicate compound with tetrahedral bound linked by oxygen. Atom Al is negative that can be neutralized by cation. The exchangeable cation affects the adsorption ability of zeolite. Beside that, the ability is also influenced by Si/Al ratio, surface area, and size of zeolite pore [2-4].

In Indonesia, the natural zeolite is available in market. Even, the potential of zeolite production is high [5]. However, adsorbing capacity of natural zeolite is too low rounding 0.7-0.9 gr water loaded/gr zeolite. In general, the natural zeolite contains organic and an-organic impurities, as well as having high Si/Al ratio. Additionally, the size of pore is not homogenous. For adsorbing water, it needs the size pore 3Å close to molecular diameter of water. Therefore, the activation process is required before using natural zeolite [6].

This research studies the activation of natural zeolite Indonesia by NaOH and heating. The aim is to find activated zeolite for water adsorbent that can be used as air dehumidifier in dryer. In this work, the effect of NaOH concentration, time, temperature on the adsorbed water capacity are studied at various air condition. In doing so, the physical properties of activated zeolite involving size and homogenous of pore are analyzed using scanning electron micrograph (SEM).

2. EXPERIMENTAL METHOD

Natural zeolite from local market Semarang was activated with two different methods: activation by heat, and NaOH 0.5-2.0 N. The aims are to remove the impurities, and form the homogenous pore size.

In activation by heat, natural zeolite was milled and screened to get the granule in the size of 1-2 mm. The granule was then weighed 25 grams and heated in autoclave at 200°C for 2 hours (see Fig. 1). The zeolite was then cooled in desicator. After that, the ability of zeolite for adsorbing water is evaluated in sorption-isotem tank.

In sorption-isotem tank at various air condition during 2-3 days. The water loaded in zeolite was measured by weighing the zeolite before and after put in sorption-isotem tank. While, the pore size of zeolite was
analyzed by SEM. The method was repeated for various activation time (2-5 hours) and temperature 300-500°C.

Fig. 1. Autoclave working at 200-500°C for zeolite activation

For activation by NaOH, natural zeolite was mixed with NaOH solution 0.5 and stirred under 60°C for 2 hours. The zeolite was then washed by water and dried at 110°C for 4 hours. The zeolite was cooled in desicator, and the water loaded capacity was tested in sorptio-isoterm tank. The activated zeolite was also analyzed by SEM in order to know homogenity and size of pore. The process was repeated for NaOH 1.0-2.0 N, and mixing temperature 70-90°C.

Fig. 2. Sorption-isoterm tank

3. RESULT AND DISCUSSION

3.1. Activation by Heat

Activation by heat aims to remove the organic impurities in zeolite pore. The thermal introduction can cause cation movement in which influences the pore size [4]. Table 1 presents the water loaded in the natural zeolite after activated by heat. In all cases, the capacity increases significantly. The best condition, can be reach at 300-400°C and heating time 3 hours, with capacity 0.137 gr water/gr zeolite. At temperature below 300°C, the organic impurities cannot be totally removed. While upper 300°C, perhaps, the formation of pores size is too big (bigger than molecular diameter of water), so the water is not optimally adsorbed. This result is also corresponding with Turkey’s zeolite where the process activation is 300-400°C [7].

Table 1. Performance of zeolite activated by heating

<table>
<thead>
<tr>
<th>Temperature variation, °C, activation time 3 hour</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>gr water/gr zeolite</td>
<td>0.128</td>
<td>0.137</td>
<td>0.136</td>
<td>0.130</td>
</tr>
</tbody>
</table>

Activation time variation, hour; temperature, 300°C

<table>
<thead>
<tr>
<th>gr water/gr zeolite</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation time variation, hour, temperature, 300°C</td>
<td>0.130</td>
<td>0.137</td>
<td>0.136</td>
<td>0.135</td>
</tr>
</tbody>
</table>

Natural zeolite without activation 0.08-0.09 gram water/gram zeolite

3.2. Activation by NaOH

Using NaOH silica ion, a component forming the zeolite crystal is diluted. This process reduces the Si/Al ratio, then the affinity of zeolite to water increases [8]. In addition, other ion is also substituted by Na⁺, so the pore size of zeolite tends to be homogen in the form of homoionic [9]. With this condition, the pores of zeolite will have same size ranging 3-4 Å called micropore in which is suitable for water adsorption. The higher micropore, higher water capacity will be obtained.

Table 2 presents water loaded in zeolite activated by NaOH at different concentration and temperature. The water loaded in zeolite can reach 0.171 gr water/gr zeolite after activated for 2 hours under 70-80°C with NaOH 1.0 N. This improvement is quite significant, because natural zeolite can adsorb water 0.08-0.09 gram water/gr zeolite, only.

Table 2. Performance of zeolite activated by NaOH

<table>
<thead>
<tr>
<th>NaOH variation, N; temperature 80 °C</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>gr water/gr zeolite</td>
<td>0.155</td>
<td>0.171</td>
<td>0.167</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Temperature variation, °C; NaOH 1 N

<table>
<thead>
<tr>
<th>gr water/gr zeolite</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite without activation 0.08-0.09 gram water/gram zeolite</td>
<td>0.145</td>
<td>0.171</td>
<td>0.170</td>
<td>0.167</td>
</tr>
</tbody>
</table>
3.3. Scanning Electron Micrograph (SEM) Analysis

Fig. 3 presents the zeolite pore analyzed by SEM. After activation, the pore of zeolite is opened and the crystal structure changes. The crystal size becomes smaller as well as pore size enlarges. In addition, after activation, the pore size becomes more homogen in which increases water loaded capacity. In this case, activation by NaOH results the pore size more homogen than that of by heating.

![Zeolite before activation](image1)

![Zeolite activated by NaOH](image2)

![Zeolite activated by heating](image3)

Fig. 3. Zeolite before (a) and after activated by NaOH (b) and heat (c))

3.3. Adsorbing capacity

Table 3 depicts the water loaded in zeolite at different air condition. Results shows that the higher relative humidity, higher water loaded can be obtained. Conversely, higher temperature, lower water loaded. For synthetic zeolite, this behaviour is also similar [2,10-11].

High affinity casuses water loaded in zeolite is still higher. The affinity is affected by Si/Al ratio. Compare to another vapor adsorbent, the usage of zeolite is more beneficial, since it can adsorbs water at low relative humidity.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Relative humidity, %</th>
<th>20</th>
<th>60</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature 80 °C, activated by heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gr water/gr zeolite</td>
<td>0.040</td>
<td>0.087</td>
<td>0.101</td>
<td></td>
</tr>
<tr>
<td>Temperature 80 °C, activated by NaOH 1 N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gr water/gr zeolite</td>
<td>0.056</td>
<td>0.106</td>
<td>0.131</td>
<td></td>
</tr>
<tr>
<td>Relative humidity, 100%, activated by heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>40</td>
<td>60</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>gr water/gr zeolite</td>
<td>0.130</td>
<td>0.109</td>
<td>0.101</td>
<td></td>
</tr>
<tr>
<td>Relative humidity, 100%, activated by NaOH 1 N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>40</td>
<td>60</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>gr water/gr zeolite</td>
<td>0.161</td>
<td>0.142</td>
<td>0.131</td>
<td></td>
</tr>
</tbody>
</table>

4. CONCLUSION

Activation of natural zeolite can be done by both heating and NaOH. Results showed that the porosity of zeolite activated by NaOH is higher and more uniform than that of by heat activation. The adsorbing capacity also corresponds to the result where after activation with 1.0 N of NaOH under 70°C, the capacity of zeolite is 0.17 gr water/gr dry zeolite. While, the capacity of activated zeolite by heating at 300°C for 3 hours, is 0.14 gr water loaded/gr dry zeolite. The performance improvement is significant. Therefore, both methods can be an option to find zeolite with high water capacity for mixed-adsorption drying.

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