The Characterization of Indonesian’s Natural Zeolite For Water Filtration System

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Abstract

The characterization of Indonesian’s natural zeolite for water purification has been done. The objective is to obtain a general guidance for development of natural zeolite in molecular sieves, ion exchange and catalyst applications. The zeolites originated from Lampung (ZL) was characterized by using XRD. It was found that the zeolites indicate belong to clinoptilolite and mordenite groups, respectively. The crystal system for ZL was monoclinic with end-centered lattice and space group of Cm/2 (12). The crystal system for ZB was orthorhombic with end-centered lattice and space group of CmC21 (36). The character of both zeolites were confirm by ICDD standard library. It was also found that the particle size of zeolites did not affect the XRD spectra where zeolite of 40-50 mesh was similar to that XRD spectra of zeolite of 170-200 mesh. The chemical analyses show that both zeolites contain almost similar chemical elements. The contents of Fe, Ca, and K were found higher in ZL as it is compared to ZB. Reciprocally, Na was found higher in ZB. The water filtration ability shows that ZB was better than ZL for filtering of Pb and Fe elements. These ability were improved by chemical activation of zeolites. These two zeolites, however, behave similar less ability for the filtering of Ca and Mg elements due to that elements probably were originally exist in the zeolite structure. These characterization is necessary to designing a further development of natural zeolite applications.

Keywords: natural zeolite, clinoptilolite, mordenite, x-ray diffraction, water filter

1. INTRODUCTION

Indonesia is carrying out different research work in order to improve the natural resources utilization. It was understood that the higher utilization of natural resources make higher contribution to natural development. In this work, natural zeolites which are abundance available in Indonesian wish to be developed to achieve a more added value materials such as water purification/filtration system.
In fact, the natural zeolites have been used in agriculture as soil conditioner, as component of fertilizer, animal feed as well as a neutralization agent for bad smell waste (Thamzil & Husen, 1999) (Supandi, 1999). The applications of zeolite in engineering are still very few. Some research were done to develop zeolites for its application as water filtration or as membrane system (Xiaochn, et al., 2004) (Worathanakul & Kongkachuchay, 2008) (Valentine, 2009) (Jie, et al., 2002).

According to various researches, zeolite mainly a synthetic ores may have a great potential as membrane system such as micro filtration (MF), ultra filtration (UF), ad reverse osmosis (RO) as well as a powerful catalyst, ion exchanger, and gas separation systems (Berrin, 2008) (Stankov, et al., 2003) (Drew Chemical Corporation, 1967) (Kaseno, 1999) (Hadiati, 1999) (Lanjar, 1999) (Takao,1999).

In fact, however the researches for the utilization of natural zeolites are still low due to some reasons. Among of that reasons were the variety of character of natural zeolites. Two sources of natural zeolite, i.e. originated from Lampung (ZL) and originated from Bayah, Banten (ZB) are used to be characterization in the present work. The characterizations of two zeolites were carried out using x-ray diffractometer (XRD) instrument.

The objectives of this work is to obtain a general orientation of zeolite’s crystal system, its properties as well as to determine a selective elements that probably affecting in the character of natural zeolite for its application as water filtration system.

2. MATERIALS AND METHOD

Materials
Natural zeolite were supplied by PT Minamata Mineral Perdana, i.e. originated from Lampung (ZL), and by volunteer zeolite mining agency, i.e. originated from Bayah, Banten (ZB). The zeolites were treated by ball milling and sieved to obtain a homogeneous powder size of 40-200 mesh, before used. Some necessary chemicals were used as a zeolite binder or as chemical activation agent.

Instruments
Shimadzu X-Ray Diffractometer instrument type 7000 made in Japan was used to characterization of crystal system. The instrument was first calibrating using silicon standard. Perkin Elmer Atomic Absorption Spectrometer (AAS) type AAAnalyst 700, made in USA was used to analyze chemical elements. Other equipments such Memmert Oven (Germany) and Vulcon Kiln type 550 (Germany) were used for drying and sintering work. Various tools, beaker glass and plastic equipments were used as necessary.

Zeolite Activation
The chemical activation of zeolite were done as follows:
50 gr of zeolites was kept in HCI 2M solution for one hour, washed and decanted by aquadest until neutral (pH=7.0). It was, they kept in NaNO$_3$ 2M solution for 1 hour, washed and decanted adequately by aquadest until neutral, and then dried in oven at 105°C until a constant weight.

XRD Characterization
Natural zeolite powder sample was put into a sample holder appropriately, kept homogeneous surface and placed it at measurement position. The measurement was done according to computer operating system and the obtained XRD spectrum was recorded. It took about 45 minute for each sample measurement. The obtained XRD spectrum was evaluated by standard diffraction data of x-ray from ICDD (International Centre for Diffraction Data).

AAS Measurement
0.5 gr of zeolite sample was destructed by aqua regia (HCl + HNO$_3$), diluted to 100 ml by distilled water and arrange the concentration to be appropriate for AAS measurement. The measurement was done by flame detector technique and the results were computerized recorded and print-out as necessary.

Filter Preparation
The zeolite sample was poured into a glass column (dia.3cm) for 5 cm thickness for media zeolite bed. The zeolite sample may be 40-200 mesh zeolite powder or a chemical activation zeolite. The media zeolite bed ability in filtering of different solution of Pb acetate (0.2 M), FeCl$_3$ (0.1 M), MgSO$_4$ (1.0 M), and CaCl$_2$ (0.2 M) were observed. The filtrate was measured by AAS after a necessary
dilution. The contents of Pb, Fe, Mg, and Ca either in filtrate and remain in media zeolite bed was evaluated. The filtering capability of natural zeolite that was prepared by a binder was also investigated.

3. RESULTS AND DISCUSSION

XRD of Lampung Zeolite (ZL)

Figure 1 shows the XRD Spectrum of Lampung zeolite. As can be seen in Fig.1, there are 3 strongest peaks, followed by another 3 weaker peaks. The position of the six peaks can be summarized in Fig. 2, and it details can be seen in Table 1. In Table 1, the strongest 3 peaks were found at 2θ of 27.9583°, 22.3963°, and 9.8631° where the ratio of I/I₀ were 100, 54, and 39 respectively. Another 3 peaks were found at 2θ of 42.6835°, 30.0600°, and 31.9600° where the ratio of I/I₀ were 38; 27; and 21, respectively.

According to ICDD 47-1870 data library, the existence of the strongest peaks may indicate that the mineral was appropriate with potassium sodium calcium aluminum silicate hydrate of clinoptilolite-Na.

Based on Bravais classification crystal system, it was found to be a base-centered monoclinic, with a lattice of end-centered and the space group of C2/m (12).

Accordingly, there are three unequal axes, one pair not at right angle, a ≠ b ≠ c, α = γ = 90° and β ≠ 90° [14]. The crystal system can be illustrated as the following figure (See Fig.3).

Fig.2. XRD Spectrum Line of Lampung Zeolit.

Fig.3. Bravais lattice for monoclinic crystal system.

Tabel 1. The Strongest Peaks of XRD Spectrum of Lampung Zeolite (Powder)

| # Strongest 3 peaks | 2Theta (deg) | (A) | I/I₀ | FWHM (deg) | Intensity (Counts) | Integrated Int (Counts) |
|---------------------|--------------|-----|------|------------|-------------------|------------------------|
| no. peak no.       |              |     |      |            |                   |                        |
| 1                   | 27.9583      | 3.18974 | 100  | 0.10640    | 715               | 4385                   |
| 2                   | 22.3963      | 3.96647 | 54   | 0.29940    | 308               | 6224                   |
| 3                   | 9.8631       | 8.96057 | 39   | 0.21860    | 282               | 3110                   |

Fig.1. XRD Spectrum of Lampung Zeolit.
The data indicate that the crystal structure should belong to a clinoptilolite, its density of 2.16 g/mol and a unit cell volume of 2100 Å. These agreed to description that was reported by Thamzil Las (Ph.D. Thesis) [15]. The unit cell may have a dimensions of a=7.41 Å, b=17.89 Å, and c=15.85 Å. If the data are compared to that ICDD library, then it seems to be the same. In other word, the ZL could be predicted behave a crystal structure belong clinoptilolite group. The chemical formula of clinoptilolite is assumed to be Na₆[(AlO₂)₆(SiO₂)₃O] 24 H₂O.

In ICDD 47-1870 data, the clinoptilolite-Na may contains of [Na, K, Ca]₅Al₆Si₃₀O₇₂·18 H₂O as can be seen in Table 2.

| Crystal System | Monoclinic | Space Group | C2/m (12) | a | α | b | β | c | γ |
|----------------|------------|-------------|-----------|---|---|---|---|---|---|
| Lattice        | End-centered | Density    | 2.046     | 18.007 | 116.3 |
| Lambda         | 1.5406     | Pattern    | 7,396     | 90 |

It can be concluded therefore, that the observed zeolite (ZL) should be a clinoptilolite with a monoclinic crystal system.

Further XRD measurement of ZL with different mesh has shown the same pattern of XRD spectrum. The strongest peaks was given at 2θ of 28.0520° followed by the second strongest at 2θ of 22.3963°. (See Table 3) From Table 3, the peaks of XRD spectrum at 2θ of 28.0520° and 22.3963° may be estimated as peaks character for natural zeolite of ZL. In fact, the XRD spectrum of ZL do not affected by the particle size, since the two XRD spectrum of ZL show the similar pattern.

**XRD of Activated Lampung Zeolite (ZL)**

Fig. 4 shows the XRD spectrum of activated zeolite ZL. As can be seen in Fig. 4, there are three other strong peaks i.e. at 2θ of 42.2126°, 31.4545°, and 51.4774° beside of three peaks that were assumed to be characterization’s peaks of clinoptilolite. Actually, the three other strong peaks have also available in XRD spectrum pattern of previously ZL, but in the form of weaker peaks.

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**Fig. 4.** XRD spectrum of activated Lampung zeolit.

Perhaps a higher peak at 2θ of 42.2126° as its compared to that previously ZL was caused by sodium cation that coming from activation process. If it’s true, it can be predicted that activated ZL may containing a single cation of Na. Therefore, the activation of zeolite can be favorable for molecular siever as well as for cation exchanger.

**XRD of Bayah, Banten Zeolite**

Fig. 5 shows the XRD spectrum of Bayah, Banten Zeolit (40-50 mesh).
Fig. 5 shows the XRD spectrum of Bayah, Banten zeolite (ZB) of particle size of 40-50 mesh. As can be seen in Fig. 5, there are three strongest peaks available i.e. peak at 2θ of 25.6897° (100), 27.3619° (95), and 26.6704° (77). Other strong peaks were shown at 2θ of 27.7185° (68), 9.8023° (62), and 13.6000° (51). All the peaks may be assumed as a characteristic XRD spectrum of ZB. Detail data of XRD spectrum of ZB are presented in Table 4.

**Table 4. The Strongest Peaks of XRD Spectrum of Bayah, Banten Zeolite (40-50 mesh)***

| **Group** | Zeolite |
|-----------|---------|
| **Data**  | 40-50 Mesh |

| # Strongest 3 peaks no. peak 2θ (deg) d (Å) I/I1 FWHM (deg) Intensity (Counts) Integrated Int (Counts) |
|---------|-----------|-----|-------|--------|---------|----------------|
| 1 46    | 25.6897   | 3.46495 | 100  | 0.24540 | 598     | 9606           |
| 2 39    | 27.3619   | 3.97250 | 95   | 0.41990 | 567     | 10712          |
| 3 49    | 26.6784   | 3.32874 | 77   | 0.37920 | 462     | 9189           |

| # Peak Data List no. peak 2θ (deg) d (Å) I/I1 FWHM (deg) Intensity (Counts) Integrated Int (Counts) |
|---------|-----------|-----|-------|--------|---------|----------------|
| 1 5.4600 | 16.12776 | 5   | 0.24000 | 30     | 466     |
| 2 5.8200 | 15.11917 | 5   | 0.24000 | 30     | 475     |
| 3 6.0000 | 14.03815 | 5   | 0.11340 | 19     | 110     |
| 4 6.5213 | 13.54293 | 3   | 0.26990 | 32     | 443     |
| 5 8.3000 | 10.64423 | 3   | 0.28000 | 18     | 521     |
| 6 8.5800 | 10.29748 | 11  | 0.22400 | 65     | 606     |
| 7 8.9000 | 9.92794  | 25  | 0.44800 | 148    | 3129    |
| 8 9.5000 | 9.56388  | 17  | 0.00000 | 0      | 0       |
| 9 9.6092 | 9.01601  | 62  | 0.35890 | 373    | 7921    |
| 10 10.2000 | 8.66535 | 12  | 0.36000 | 72     | 2009    |
| 11 10.6000 | 8.39323 | 20  | 0.00000 | 44     | 0       |
| 12 11.1994 | 7.90126 | 20  | 0.37170 | 119    | 2844    |
| 13 11.5800 | 7.63560 | 8   | 0.00000 | 47     | 0       |
| 14 11.8000 | 7.43737 | 12  | 0.00000 | 73     | 0       |
| 15 12.0800 | 7.32066 | 15  | 0.00000 | 89     | 0       |
| 16 12.2600 | 7.21358 | 21  | 0.00000 | 124    | 0       |
| 17 12.7200 | 6.95373 | 13  | 0.00000 | 78     | 0       |
| 18 13.0000 | 6.80455 | 20  | 0.00000 | 120    | 0       |
| 19 13.3800 | 6.61217 | 36  | 0.00000 | 217    | 0       |
| 20 13.6000 | 6.50569 | 51  | 0.32540 | 304    | 4607    |
| 21 13.9400 | 6.34777 | 19  | 0.51000 | 112    | 3081    |
| 22 14.0000 | 6.14602 | 13  | 0.00000 | 77     | 0       |
| 23 14.7600 | 5.96911 | 13  | 0.00000 | 75     | 0       |
| 24 15.3000 | 5.78645 | 18  | 0.35560 | 108    | 2644    |
| 25 15.6200 | 5.66662 | 9   | 0.53600 | 53     | 1422    |
| 26 16.3790 | 5.40892 | 3   | 0.11000 | 19     | 128     |
| 27 16.7000 | 5.30438 | 5   | 0.21200 | 31     | 345     |
| 28 16.9305 | 5.23268 | 14  | 0.20760 | 81     | 759     |
| 29 17.3382 | 5.11054 | 15  | 0.30180 | 87     | 1290    |
| 30 17.7400 | 4.95668 | 8   | 0.18400 | 47     | 566     |
| 31 19.0447 | 4.65628 | 11  | 0.26550 | 65     | 848     |
| 32 19.6600 | 4.51192 | 29  | 0.20850 | 174    | 5403    |
| 33 20.1800 | 4.39682 | 32  | 0.00000 | 191    | 0       |
| 34 20.4800 | 4.33308 | 15  | 0.26660 | 92     | 2688    |
| 35 20.9272 | 4.24119 | 22  | 0.33750 | 134    | 2102    |
| 36 21.2600 | 4.17584 | 6   | 0.16800 | 34     | 372     |
| 37 21.5243 | 4.12516 | 4   | 0.27140 | 21     | 336     |
| 38 21.9400 | 4.04793 | 20  | 0.17180 | 121    | 1397    |
| 39 22.3619 | 3.97250 | 95  | 0.41990 | 567    | 10712   |
| 40 22.7400 | 3.90730 | 32  | 0.29340 | 192    | 3220    |
| 41 23.1772 | 3.83457 | 31  | 0.26210 | 186    | 2363    |
| 42 23.5805 | 3.76989 | 27  | 0.39540 | 162    | 2978    |
| 43 24.0283 | 3.70125 | 21  | 0.25870 | 127    | 1721    |
| 44 24.4333 | 3.62051 | 8   | 0.18330 | 45     | 449     |
| 45 25.0230 | 3.55574 | 23  | 0.30600 | 139    | 2589    |
| 46 25.6897 | 3.46495 | 100 | 0.24540 | 598    | 9606    |
| 47 26.6000 | 3.41398 | 33  | 0.00000 | 200    | 0       |
| 48 26.3820 | 3.38339 | 46  | 0.00000 | 277    | 0       |
| 49 26.6784 | 3.32874 | 77  | 0.37920 | 462    | 9189    |
The measurement of XRD spectrum of ZB for different particle size of 170-200 mesh results the same XRD spectrum pattern. The XRD spectrum of ZB which has particle size of 170-200 mesh shows three strongest peaks at 2θ of 25.78° (100), 22.38° (78), and 9.76° (54) and these similar to that XRD spectrum of other particle size of ZB. Therefore, the particle size of zeolite may conclude do not affect the pattern of XRD spectrum. Table 5 shows ICDD data for 49-0924
Tabel 5. ICDD Data for 49-0924

| ICDD 49-0924 | Mineral: Mordenite, syn Sodium Aluminum Silicate – Zeolite Al-modenite | Chemical: Na$_2$Al$_2$Si$_{13.3}$O$_{29.6}$ + x |

| Crystal System | Orthorhombic | Space Group | Cmc21 (36) | α | β | γ |
|----------------|--------------|-------------|------------|---|---|---|
| Lattice        | End-centered | Density     | -          | b | 20,284 | 90 |
| Lambda         | 1,5406       | Pattern     | 1          | c | 7,491  | 90 |

If the XRD peaks of ZB is compared to that ICDD 49-0924, then it can assumed that ZB belong to a mineral mordenite group. The crystal system should be orthorhombic, lattice of end-centered, and space group of Cmc21 (36). In this case, there are 4 possible Bravais lattice of orthorhombic crystal system i.e. simple or primitive (P), body centered (I), end centered (C), and face centered (F) as shown in Fig. 6 (Cullity, 1987). There are also exist three unequal axis at right angles, $a = β = γ = 90^°$. Supandi (1999) reports that crystal structure of Bayah zeolite may contains two crystal systems, there are crystal monoclinic with space group C2/m and crystal orthorhombic with space group of CmCm. Supandi conclusion based on a calculation by a refinement Rietan method. Perhaps, the conclusion was correct, because the XRD spectrum of our sample ZB didn’t merely follows the ICDD orthorhombic crystal system. Therefore, it can be assumed that our ZB sample may comprises a mixture of mineral mordenite and clinoptilolite.

4. Chemical Analysis

Table 6 show some metal oxide that containing in ZL and ZB as it was compared to others results.

| Metal Oxide | Percentage of Metal Oxide (%) |
|-------------|-------------------------------|
|             | Current Result | *PT Minamata | *Supandi |
|             | ZL  | ZB  | Clinoptilite | Mordenite |
| Fe$_2$O$_3$ | 0,94 | 0,80 | 1,29 | 1,46 |
| Na$_2$O     | 0,63 | 0,98 | 0,75 | 0,20 |
| K$_2$O      | 0,70 | 0,67 | 1,54 | 2,81 |
| CaO         | 0,52 | 0,42 | 1,31 | 2,36 |

*The comparison is assumed that the zeolite comes from the same area, but not exactly the same sample.*
As can be seen in Table 6, the metal oxides that containing in ZL were almost nearly similar that containing in ZB. But it was not in case of the results that reported by others. The different may caused by the different of analysis method or different sample itself.

The result of Croatian zeolite of clinoptilolite was also different (Cerjan, et al., 2004). Therefore, the different origin of zeolite may provide different characteristics and chemical containment. For the reason, the characterization of natural zeolite became very important, before it’s planned to be utilized for specific purpose.

**Zeolite Filter Performance**

Table 7 shows the zeolite filter performance. It can be seen in Table 7, that activated ZL was found to be the best for filtering heavy metal of Pb. In this case, original solutions that contain 19.07 gr could be reduced to be 8.86 (almost 50%). On the other hand, ZL and ZB could be able to reduce only smaller i.e. it is reduces to be 15.33 and 10.33, respectively. In case of Fe, ZB shows the best as compared to that ZL and activated ZL i.e. it can reducing Fe from 0.49 gr to 0.18 gr, whereas ZL and activated ZL could reduce only 0.43 gr and 0.26 gr, respectively. All kind of zeolite (ZL, ZB, and activated ZL) was found to be worse to reduce Mg and Ca. Even more Ca became higher in case of ZL and ZB performance. The results indicate that activated zeolite became very important to design an appropriate application of natural zeolite.

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