Characterization of sonicated natural zeolite/ferric chloride hexahydrate by infrared spectroscopy

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Abstract. The characteristics of sonicated Bayah natural zeolite with and without ferric chloride hexahydrate solution using infrared method has been studied. High intensity ultrasonic waves were exposed to the samples for 40 min, 80 min and 120 min. Infra red spectra analysis was conducted to evaluate zeolite vibrational spectrum contributions, namely, the vibrations from the framework of the zeolite, from the charge-balancing cations, and from the relatively isolated groups, such as the surface OH groups and their behavior after sonication process. An addition of FeCl₃·6H₂O and sonication process on natural zeolite improved secondary building units link by forming oxygen bridges and also close relationship with duration of applied high intensity ultrasonic process. Longer ultrasonic process resulted in more increment of O-H absorbance.

1. Introduction
In an attempt to improve the properties of Indonesian natural zeolite, we have undertaken the characterization and modification of natural zeolite produced in Bayah, Indonesia. This Zeolite consists mainly of crystalline mordenite type [1]. Bayah natural zeolite has been used as adsorbates for various purposes. It has been studied previously and standardized by Indonesian standardization body (SNI). As an adsorbent material, it is categorized as a material with the highest cation exchange capacity compared with other Indonesian natural zeolites from Sukabumi, Tasikmalaya and Cikalong [1, 2].

High intensity ultrasonic wave processing has been used to produce nanomaterials and chemical reaction. High intensity ultrasonic liquid processor produces microbubbles in the solution between of the primary and secondary flow. This sonication process may increase or change the physical and chemical properties of a material [3]. It has been studied and understood that high power ultrasonic irradiation is very effective in homogenizing the reactants in the suspension, leading to the improvement of the reactivity of both solid and liquid by simulating their active surface [4]. Purification of Natural Zeolite by using ultrasonic technique is also applied by researchers to remove and separate impurities materials; this technique is believed to deliver faster process and result [5].

Infra red spectra analysis has been carried out to find out specific improvement of existing natural zeolite properties after introducing ultrasonic wave and its modifications by adding FeCl₃·6H₂O and performing sonication process for 40 min, 80 min and 120 min. Spectra were recorded in the range of 4,000-600 cm⁻¹ and evaluated on most of three spectra region; O–H spectra region is very interesting to be observed as gas-absorbent candidate material [6].

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2. Experimental procedure

Natural zeolite produced in Bayah, Indonesia was ground, homogenized and sieved below 150 µm (100 Mesh Tyler™) as part of sample preparation and characterization [7]. Addition of Ferric chloride hexahydrate (FeCl$_3$.6H$_2$O) produced by Merck Millipore, Chemical Abstracts Service (CAS) #10025-77-1 with specified weight was diluted in 100 ml of distilled water. To remove impurities, sieved natural zeolite were washed and stirred with distilled water. Washing process was conducted four times with two hours long for each sequence [8]. Air drying was performed prior to initial characterization to find out the baseline of zeolite infrared spectroscopy. The natural zeolite sample is denoted as ZA (natural zeolite). Natural zeolite samples were exposed with high ultrasonic wave for 40 min, 80 min and 120 min with the sample code of ZA40, ZA80, and ZA120 respectively. Another zeolite samples were added with 10 gram FeCl$_3$.6H$_2$O and diluted in 100 ml distilled water. The solution was exposed to high intensity ultrasonic liquid processor VCX750 at 20 kHz, 40 Amp [9] for 40 min (sample code ZAM1), 80 min (sample code ZAM2) and 120 min (sample code ZAM3). Slurry product of the sonication process were precipitated and subsequently heated by microwave furnace at temperature of 90 °C for 30 min [8].

Fourier transform infrared (FT-IR) spectroscopy was used to study zeolite and zeolite/FeCl$_3$.6H$_2$O in various sonication processes. Pure KBr powder was added to the slightly solid sample and then blended. This mixture was placed in a mold and pressurized by a mechanical pressure apparatus for a few minutes. The FT-IR spectra were recorded in the range of 4,000-600 cm$^{-1}$ using a Perkin Elmer GX-FT-IR spectrophotometer. Standard practice of general techniques for obtaining Infrared Spectra for Qualitative Analysis was referred to ASTM E1257-13. Figure 1 shows the flow diagram of the experiment.

![Figure 1. Research flow diagram.](image)

3. Results and discussion

Bayah natural zeolite sample (ZA) was characterized using FT-IR spectroscopy and set as a baseline to be compared with another sample as shown on figure 2. It can be observed that the band associated with the symmetric and asymmetric stretching vibrations of the hydroxyl functional group is situated at 3,406 cm$^{-1}$. Additionally, the band located at 1,630 cm$^{-1}$ is due to the vibration of the Si-O bond. The generated vibrations by Al-O bonds are shown at 1,033 cm$^{-1}$. The allotropic phase of SiO$_2$ is identified by the wave number and observed in 795 cm$^{-1}$. It is important to mention that the wave
number associated with the Si-O and O-Al bonds, which is typical of tectosilicates and has high intensity suggesting that the zeolite has large surface area [10].

![Figure 2. FT-IR spectroscopy obtained from Bayah natural zeolite (ZA).](image)

Exposure of ultrasonic wave to the Bayah natural zeolite on sample ZA40, ZA80 and ZA120 are seen on figure 3. Second symmetric and asymmetric stretching vibrations of the hydroxyl functional group found at 3,630 cm\(^{-1}\). Second bridged hydroxyl associated with acidity and responsible for the catalytic activities of the acid sites of the samples and Si/Al ratio may suggest a correlation between the acidic strength of the OH groups and its band wavenumber [6].

Modified zeolite with an addition of FeCl\(_3\).6H\(_2\)O and sonification process for 40 min, 80 min and 120 min shown in figure 4. Infrared bands of silicon compounds O-Si-O asymmetric stretching on wavenumber ranges 1,130–1,000 cm\(^{-1}\) was detected [11]. Modified zeolite wavenumber shifted from 1,033 into 1,030, 1,031 and 1,032 cm\(^{-1}\) respectively. Halogen compound C–F stretching shifted from 795 into 790 and 795 cm\(^{-1}\) [4,5], C–H stretching were observed in the 1,600–1,800 cm\(^{-1}\) range, the second overtones at 1,150–1,210 cm\(^{-1}\) and the third overtones at 880–915 cm\(^{-1}\) [10,11], O–H stretching region was observed on 3,400–3,800 cm\(^{-1}\) range[12,13].

C–F stretching observation at 795 cm\(^{-1}\) wavenumber showing that ZAM3 absorbance was higher than ZAM2, ZAM1 and ZA. The O-Si-O asymmetric stretching observation at 1,033-1,030 cm\(^{-1}\) wavenumber showing ZAM1 absorbance was higher than ZAM3, ZA and ZAM2. O–H stretching observation at 3,800–3,400 cm\(^{-1}\) wavenumber showed that modified zeolite has higher absorbance compared to natural zeolites as well as multiple absorbance found at ZAM3, and it is often utilized as absorbent raw material [14].

Additional FeCl\(_3\).6H\(_2\)O and sonication process on ZA have influence on shifting of wavenumber for stretching of C–F, O-Si-O and O–H. The O–H absorbance increment on ZAM1, ZAM2 and ZAM3 may be due to high intensity ultrasonic exposure. Ultrasonic produces microbubblesin between the primary and secondary flow cracking of FeCl\(_3\).6H\(_2\)O [3]. Table 1 shows that ultrasonic process contributes to create second and third peaks overtones.
Figure 3. FT-IR spectroscopy obtained from (a) ZA, ZA40, ZA80 and ZA120. (b) Second symmetric and asymmetric stretching at 3,630 cm\(^{-1}\), and (c) O-Si-O asymmetric stretching.

Table 1. IR intensities adsorbent of ZA and its derivatives. The notations are as follows: w is weak, m is medium, s is strong.

| Sample | Ultrasonic (min) | Symmetric stretching O-Si-O and O-Al-O | Asymmetric stretching O-Si-O and O-Al-O | H-O-H Bending | OH Stretching Symmetric & Asymmetric |
|--------|------------------|----------------------------------------|------------------------------------------|---------------|--------------------------------------|
| ZA     | 0                | 795 s                                  | 1,033 s                                  | 1,630 s       | 3,406 s                              |
| ZA40   | 40               | 793 m                                  | 1,042 w                                  | 1,645 m       | 3,627 m; 3,455 m                     |
| ZA80   | 80               | 792 m                                  | 1,040 w                                  | 1,653 m       | 3,630 m; 3,449 m                     |
| ZA120  | 120              | 793 m                                  | 1,045 w                                  | 1,637 m       | 3,630 m; 3,451 m                     |
| ZAM1   | 40               | 795 s                                  | 1,030 s                                  | 1,629 s; 1,741 s | 2,970 s; 3,022 s; 3,408 s          |
| ZAM2   | 80               | 793 s                                  | 1,052 s                                  | 1,626 s; 1,740 s | 2,971 s; 3,023 s; 3,381 s         |
| ZAM3   | 120              | 790 s                                  | 1,031 s                                  | 1,630 s; 1,741 s | 2,971 s; 3,022 s; 3,434 s         |
Figure 4. FT-IR spectroscopy transformation of ZA, ZA40, ZA80, ZA120 and modified Zeolites with FeCl$_3$.6H$_2$O (ZAM1, ZAM2, ZAM3).
4. Conclusion
Natural and modified Zeolite from Bayah have been well characterized and the difference was distinctive. Ultrasonic exposure on Zeolite affect the absorbance properties. Modified ZA with ultrasonic process and Ferric Chloride Hexahydrate addition are improving secondary building units linked by forming oxygen bridges and strong intensities of infrared adsorption band. Ultrasonic process for natural zeolite develops second symmetric and asymmetric stretching vibrations of the hydroxyl functional group. Second bridged hydroxyl are associated with acidity and responsible for the catalytic activities of the acid sites of the materials and Si/Al ratio may suggest a correlation between the acidic strength of the OH groups and its band wavenumber. High ultrasonic exposure and addition of FeCl$_3$·6H$_2$O may enhance the properties of zeolite as absorbent material.

Acknowledgments
This research is supported financially by “Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa University of Indonesia” through letter of decree no. 630/UN2.R3.1/HKP.05.00/2017.

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