Effect of ultrasonic processing on the $d$-spacing of natural zeolite

T A B Prasetyo and B Soegijono*
Department of Physics, Materials Science Program, Universitas Indonesia, Depok, Indonesia 16424

*E-mail: naufal@ui.ac.id

Abstract. The crystal geometry characteristics of sonicated Bayah natural zeolite using X-Ray diffraction (XRD) method has been studied. High intensity ultrasonic waves were exposed to the samples for 40 minutes, 80 minutes and 120 minutes. Rietveld analysis of X-Ray diffraction was conducted to evaluate effect of ultrasonic processing to the shifting of $d$-spacing each sample. Higher shifting $d$-spacing 0.01 up to 0.03 Å found at ZA40 sample and lowest shifting found at ZA80 sample 0.003 up to 0.007 Å. Relationship between sonification process with shifting of $d$-spacing are close relationship with duration of applied high intensity ultrasonic process resulted in crystallite morphology due to changes of O-H binding.

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 processing and result [5].

Rietveld analysis of X-Ray diffraction has been carried out to find out impact of ultrasonic duration into crystal geometry shifting at specific intensity of existing natural zeolite properties after introducing ultrasonic wave. Ultrasonic was carry out for 40, 80 and 120 min, multiplication exposure duration to evaluate shorten duration of effectiveness shifting and significant changes of $d$-spacing due to exposure duration and mechanical effect of ultrasound are responsible for mixing during the
homogenous liquid phase reaction of sonochemistry elapse time with saturation process [6, 7]. \(d\)-spacing observation perform on the higher percentage relative intensity in the range of 26 - 100% intensity, Shifted \(d\)-spacing very interesting related with crystal geometry [8].

2. Experimental Methods

Natural zeolite produced in Bayah-Indonesia was ground, homogenized and sieved below 150 µm (100 Mesh Tyler™) as part of sample preparation and characterization [9], 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 [10]. Air drying was performed prior to initial characterization to find out the baseline of zeolite. The natural zeolite sample is denoted as ZA (natural zeolite). Natural zeolite samples were exposed with high ultrasonic wave for 40, 80 and 120 minutes with the sample code of ZA40, ZA80 and ZA120 respectively. Another solution was exposed to high intensity ultrasonic liquid processor VCX750 at 20 kHz, 40 A for 40 minutes (sample code ZAM1) [11], 80 minutes (sample code ZAM2) and 120 minutes (sample code ZAM3). Slurry product of the sonication process were precipitated and subsequently heated by microwave furnace at temperature of 90°C for 30 minutes [11].

X-Ray Diffraction was used to study zeolite in various sonication processes using Philips Analytical PW 3050/60 X'Pert PRO instrument, sample was scanned within the 2\(\theta\) range of 3–100° with step size 0.0170. The source consisted of Cu radiation (\(\lambda=1.54060\)Å), monochromator on secondary optics, 40 kV power and 30 mA current with diffractometer type XPERT. Figure 1 shows the flow diagram of the experiment.

3. Results and Discussion

Bayah natural zeolite sample (ZA) was characterized using X-ray diffraction (XRD) and set as the baseline to be compared with another sample as shown on figure 2. It can be observed that XRD analyses revealed a very complicated structure of the natural zeolite used, rietveld analysis found that ZA sample majority consisting of mordenite and less clinoptilolite phase, according to the results of X-ray diffraction (XRD) studies and rietveld analysis of ZA sample found that mordenite phase unit cell formula weight of 8101.269, density of 4.583 g cm\(^{-3}\), weight fraction of 0.99949 and clinoptilolite phase unit cell formula weight of 4247.800, density of 5.027 g cm\(^{-3}\), weight fraction of \(0.51158 \times 10^{-3}\).

Reference data from 99-100-6672 card to be used for mordenite phase unit cell parameters \(a = 18.3581\) Å, \(b = 21.0641\) Å, \(c = 7.5901\) Å and \(\alpha = \beta = \gamma = 90°\) and space group Cmcm. Reference data from 96-900-1275 card to be used for clinoptilolite phase unit cell parameters are \(a = 18.9119\) Å, \(b = 7.5915\) Å, \(c = 10.2398\) Å and \(\alpha = \beta = \gamma = 90°\) and space group C12/m1.

![Figure 1. Research flow diagram.](image-url)
Exposure of ultrasonic wave to the shifted $d$-spacing on Bayah natural zeolite on sample ZA40, ZA80 and ZA120 are seen on figure 3. Observation on highest intensity had conducted to the sample showing that ZA40 $d$-spacing increase and other sample ZA80 and ZA120 are decreased.

Highest intensity diffraction of lattice 020 and 200 shifted 0.03581 Å on sample ZA40 and shifted $-0.00766$ Å, $-0.08303$ Å on sample ZA80 and ZA120 respectively, relationship between lattice shifting with ultrasonic elapse time showing that ultrasonic energy microbubble between the primary and secondary flow cracking contribute to the lattice deformation [9].

Another lattice direction 111 and 220 of second and third highest intensity have the same profile shifted as highest intensity diffraction for ZA40, ZA80 and ZA120 respectively. Shifted of lattice direction have correlation with particle size and chemical bonding [12].

![Figure 3. Shifted $d$-spacing obtained from ZA, ZA40, ZA80 and ZA120 Rietveld analysis.](image_url)

| $2\theta$ [°] | Rel. Int. [%] | ZA | ZA40 | ZA80 | ZA120 |
|--------------|--------------|----|------|------|------|
| 9.71         | 53           | 9.0990 | 9.1298 (↑) | 9.0881 (↓) | 9.0041 (↓) |
| 9.74         | 26           | 9.0989 | 9.1296 (↑) | 9.0880 (↓) | 9.0041 (↓) |
| 9.81         | 100          | 9.0093 | 9.0451 (↑) | 9.0017 (↓) | 8.926 (↓) |
| 9.83         | 49           | 9.0092 | 9.0450 (↑) | 9.0016 (↓) | 8.9264 (↓) |
| 11.11        | 27           | 7.9579 | 7.9821 (↑) | 7.9545 (↓) | 7.8950 (↓) |
| 13.42        | 68           | 6.5926 | 6.6108 (↑) | 6.5887 (↓) | 6.5474 (↓) |
| 13.45        | 33           | 6.5925 | 6.6107 (↑) | 6.5886 (↓) | 6.5475 (↓) |
Figure 4. Image visualization of ZA, ZA40, ZA80 and ZA120.

Shifted $d$-spacing as describe on table 1 showed that highest diffraction intensity of ZA40 sample increased comparing with baseline sample ZA, while both of ZA80 and ZA120 $d$-spacing were decreased. 3D Image visualization by using program for structural models VESTA as describe on figure 4 are helping to identify shifting of $d$-spacing and lattice due to changes position of oxygen (red ball), changes and additional of oxygen on crystal structure are impact of ultrasonic process which are producing microbubble [13, 14].

4. Conclusions
Natural zeolite from Bayah have been well characterized and the difference was distinctive. Ultrasonic exposure on zeolite affect to the shifting of $d$-spacing. Ultrasonic process impact to the lattice direction
020 and 200 at the highest intensity shifted 0.03581 Å on sample ZA40 and shifted −0.00766 Å, −0.08303 Å on sample ZA80 and ZA120 respectively, lattice direction 111 and 220 are shifted too ant the second and third highest intensity. Lattice direction shifting are impact of ultrasonic process for natural zeolite due to energy microbubble between the primary and secondary flow cracking contribute to the lattice deformation with additional oxygen contain in the crystal structure. Shifting of d-spacing is one of parameter that interest for mesoporous zeolite as absorbent material.

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