Effect of sonication process on natural zeolite at ferric chloride hexahydrate solution

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Abstract. Natural zeolite in FeCl₃·6H₂O solution which was exposed with high intensity ultrasonic for 40 min, 80 min and 120 min has been studied. X-Ray Diffraction (XRD) pattern revealed changed pattern and new peaks due to sonication process. Sonication contributed into element composition changes and it had been found also during quantitative chemical microanalysis analysis (EDX) and indicates an increment of 320.81 % (ZAM2) Fe element. Noninvasive back scatter (NIBS) analysis of various ultrasonic times affected to the particle size distribution, surface area and pore analysis. By using density functional theory (DFT), we revealed some improvements such as 44.03% surface area and 67.25% pore radius. We believe that controllable ultrasonic processing in the ferric chloride hexahydrate solution will produce uniform natural zeolite physical and chemical properties as a candidate of adsorbent materials.

1. Introduction
In an attempt to improve Indonesian natural zeolite chemical properties, the authors undertaken characterization and modification of natural zeolite produced in Bayah, Indonesia, which has appeared to consist mainly of mordenite type crystalline matter [1], and its modifications by treating with an addition of FeCl₃·6H₂O and sonification process for 40min, 80min and 120min and/or hydrothermal followed by microwave treatment. Bayah natural zeolites as various type adsorbates has been studied previously and this material has been standardized by Indonesian standardization body (SNI), as an adsorbent materials and is categorized as the material with the highest cation exchange capacity compared with other Indonesian natural zeolites from Sukabumi, Tasikmalaya and Cikalong [1,2].

High intensity ultrasonic processing is one of applied technology to produce Nano materials and chemical reaction process. High intensity ultrasonic liquid processor in operation produces micro bubbles in between of the primary and secondary flow, this sonification effect can increase 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 reactivity of both solid and liquid by the simulation of 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 a faster process and result [5].
2. **Experimental procedure**

Natural zeolite produced in Bayah, Indonesia was ground, homogenized and sieved below 150 µm (100 Mesh Tyler™) before characterization and experimentation [6]. Ferric Chloride Hexahydrate (FeCl$_3$.6H$_2$O) produced by Merck Millipore, Chemical Abstracts Service (CAS) #10025-77-1 as specified composition was diluted in 100 ml distillate water.

To remove impurities, sieved natural zeolite were washed and stirred with distillate water, washing process was conducted four times with two hours long for each sequence [7]. Natural drying was performed prior to initial characterization to find out zeolite properties and involved phase, a natural zeolite sample coding is ZA (natural zeolite).

Reflux zeolite which is prepare was added with FeCl$_3$.6H$_2$O as specified composition and dilute on 100 ml distillate water to become %wt composition of ZA$_{66.7}$FeCl$_3$.6H$_2$O$_{33.3}$. Synthesis of ZA$_{66.7}$FeCl$_3$.6H$_2$O$_{33.3}$ treated by high intensity ultrasonic liquid processor VCX750 at 20 kHz [8], 40 Amp for 40 min and sample code ZAM1, 80 min with sample code ZAM2 and 120 min with sample code ZAM3. Slurry product of sonification was precipitated and followed by Microwave heating of remain solid at temperature of 90°C for 30 min [7].

Particle size analysis was performed with dispersing 0.025 gr sample into aquades and evaluated with non invasive back scatter (NIBS) method.

X-ray powder diffraction analysis was performed using XRD analysis instruments (Philips PW3710). The samples of natural zeolites prior and after modification by adding FeCl$_3$.6H$_2$O were mounted on holders then introduced for analysis. The source consisted of CoKα radiation ($\lambda$=1.78896Å), monochromator on secondary optics, 40 kV power and 30 mA current. Each sample was scanned within the 2θ range of 20°-100°.

JEOL-6510 SEM-EDS equipment was utilized to carry out photomicrographs observation of natural zeolites prior and after modification by adding FeCl$_3$.6H$_2$O. The quantitative chemical microanalysis analysis (EDX) also observed to the samples for element composition characterization of the analyzed volume.

The natural zeolites prior and after modification by adding FeCl$_3$.6H$_2$O specific surface area was evaluated by the nitrogen gas adsorption method equipment (Quadrasorb-2 Quantachrome Instrument)

3. **Result and discussion**

Initial grinded and sieved zeolit (ZA) average particle size is 7154 d.nm. An addition of FeCl$_3$.6H$_2$O solution and sonification process into ZAM1, ZAM2 and ZAM3 found that significant particle size reduction to averages of 5031 d.nm, 4298 d.nm and 3387 d.nm respectively. figure 2 shows that particle sizes are distributed into smaller size and proportional with sonification duration.
The XRD analyses revealed a very complicated structure of the natural zeolite used, rietveld analysis by using GSAS software 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 8101.269, density 4.583 gm/cm$^3$, weight fraction 0.99949 and clinoptilolite phase unit cell formula weight 4247.800, density 5.027 gm/cm$^3$, weight fraction 0.51158 x 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 $\alpha=\beta=\gamma=90^\circ$ 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 $\alpha=\beta=\gamma=90^\circ$ and space group C1 2/m1.

New peaks have been found and observed on ZAM1 and ZAM2 samples, those peaks indicated that sonification process contributed into Fe element composition changes indicated more aerinite phase on ZAM1 and ZAM2 but less aerinite phase on ZAM3 due to less Fe element as seen on figure 3, this peaks also found on quantitative chemical microanalysis analysis (EDX).

Photomicrographs observations of natural zeolites prior to and after modification by adding FeCl$_3$.6H$_2$O were conducted, ZA sample showed that elements are bonded each other’s and less porous [9]. Modified ZA samples with FeCl$_3$.6H$_2$O and sonicated at 40 min, 80 min and 120 min...
showed that elements spread out and increasing porous as shown on ZAM1, longer sonicated process will create higher porous on ZAM2 and ZAM3 as shown in figure 4.

Figure 4. Photomicrographs observation of ZA(a) ZAM1(b), ZAM2(c) and ZAM3(d)

The quantitative chemical microanalysis analysis (EDX) observed to the sampel major element composition of the analyzed volume. Modified ZA samples with FeCl$_3$.6H$_2$O with sonification process showed that significant increment of Fe element up to 160.07% (ZAM1) and 320.81% (ZAM2) as described on table 1, prolong sonicated duration did not influence %wt Fe element on ZAM3 due to saturated reaction of natural zeolite at ferric chloride hexahydrate solution, this process has been discussed on previous study on the relationship between ultrasonic sonochemistry elapse time with saturation process [10].

| Element (% wt) | ZA  | ZAM1 | ZAM2 | ZAM3 |
|----------------|-----|------|------|------|
| Ca             | 2.29| 1.41 | 1.10 | 0.92 |
| Fe             | 2.98| 7.75 | 12.54| 9.41 |
| Cl             | 0.00| 1.50 | 2.16 | 1.33 |
| Al             | 5.96| 6.20 | 5.60 | 4.97 |

Additional element at sonification procedures is one of reaction conditions was determined by its inherent reaction parameters, compared to traditional energy sources, ultrasonic irradiation provides rather unusual reaction conditions (a short duration of extremely high temperatures and pressures in liquids) that cannot be realized by other methods [11].
Surface area and pore analysis are conducted to ZA, ZAM1, ZAM2 and ZAM3 samples. Nitrogen gas utilized as analysis gas at bath temperature 77.3K and outgas temperature 300°C, thermal delay 30 second and outgas time 3 hours, reduction parameter are using Carbon adsorbent with Nitrogen adsorbate on temperature 77.35K and critical pressure 33.5 atm.

Table 2. Physical properties of ZA and ZA + FeCl$_3$.6H$_2$O

| Description             | ZA  | ZAM1 | ZAM2  | ZAM3  |
|-------------------------|-----|------|-------|-------|
| Surface area (m$^2$/g)  | 78.74| 58.04| 50.31 | 44.07 |
| Pore radius (Å)         | 24.98| 34.63| 36.19 | 41.78 |

By utilizing density functional theory (DFT) of Quantachrome’s data analysis software which contains a comprehensive library of DFT and M.C. methods allows a micro/mesoporous analysis of carbon, zeolites and siliceous materials [12]. Table 2 represents the sonication lead time proportional with surface area reduction up to 26.29% (ZAM1), 36.11% (ZAM2) and 44.03% (ZAM3).

Figure 5. Chemical microanalysis analysis (EDX) of ZA(a) ZAM2(b)

As seen in figure 6 the increment of sonification duration impacts the surface area reduction and simultaneously pore radius will increase up to 38.63% (ZAM1), 44.88% (ZAM2) and 67.25% (ZAM3) due to high intensity ultrasonic liquid processor in operation produced micro bules in between of primary and secondary flow, this sonification effect can increase the physical properties of
materials [3]. Isotherm adsorption/desorption of ZAM1 and ZAM2 are higher comparing with ZAM3, this condition is related with the physical properties of samples as shown in figure 7.

![Figure 7: Isotherm adsorption and desorption](image)

4. Conclusion
Natural zeolite (ZA) produced in Bayah mostly consists of mordenite and clinoptilolite phases. Ferric Chloride Hexahydrate addition on Natural zeolite with sonification processes increased Fe element 320.81%wt, besides that sonification effect could increase the physical properties of zeolite material to meet an adsorbent properties-requirements such as increasing 44.03% in surface area and 67.25% pore radius. This result demonstrated that ultrasonic processing on natural zeolite in the ferric chloride hexahydrate solution will produce uniform natural zeolite physical and chemical properties as a candidate of gas adsorbent materials.

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