

Hydrogen Sulfide Adsorption improvement of Bayah Natural Zeolite

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ABSTRACT - Hydrogen sulfide adsorption performance of sonicated natural zeolite in the Ferric chloride hexahydrate solution has been studied. In this research natural zeolite exposed with high intensity ultrasonic waves for 40 minutes, 80 minutes and 120 minutes. Qualitative analysis and characterization of modified zeolite carry out with X-ray diffraction, Infrared spectroscopy, BET adsorption desorption, LAS particle size analysis and scanning electron microscopy prior and after H₂S adsorption. Natural zeolite phase are clinoptilolite and mordenite phase with 0.99%wt and 0.512×10^{-3} %wt respectively. By adding 5gr FeCl₃.6H₂O and ultrasonic exposure, zeolite chemical and physical properties such as chemical composition, particle size, surface area and pore radius are improved. Hydrogen sulfide %wt adsorption effectiveness showing that modified zeolite higher 70-117% comparing with unmodified zeolite.

Keywords - Natural zeolite, Ferric chloride Hexahydrate, Ultrasonic, Hydrogen sulfide

1. INTRODUCTION

In an attempt to improve the properties of Indonesian natural zeolite, we have undertaken modification and the characterization of natural zeolite produced in Bayah, Indonesia. Bayah natural zeolite mainly consists of mordenite type crystalline [1], Bayah natural zeolite has been used as adsorbents for various purposes it has been studied previously and standardized by Indonesian standardization body (SNI). As adsorbent material, Bayah natural zeolite categorized as material with the highest cation exchange capacity comparing with other Indonesian natural zeolites from Sukabumi, Tasikmalaya, Cikalong and Toraja [1,2,3].

Hydrogen sulfide (H₂S) gas very harmful to the human being and another living things, besides that hydrogen sulfide is one of substance that contribute to the steel corrosion process. Sour corrosion of hydrogen sulfide producing FeS as corrosion product between steel and H₂S will tend to cause local corrosion attack and produce pitting, in addition the reaction between H₂S and steel will produce H atoms that will diffuse into steel causing SCC sulfide [4].

Zeolite modification by treating with an addition of FeCl₃.6H₂O and sonification process for 40min, 80min and 120min and/or hydrothermal followed by microwave treatment. Expectation of FeCl₃.6H₂O addition are improving chemical properties and % weight of zeolite element especially Fe contain when 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 [5]. 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 [6]. 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 [7].

The research was conducted with the aim to prepare, perform adsorption H₂S test and characterize natural zeolite from Bayah by adding FeCl₃.6H₂O and introduce ultrasonic wave for 40 minutes, 80 minutes and 120 minutes, multiplication exposure duration to evaluate physical and chemical properties 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 [8].

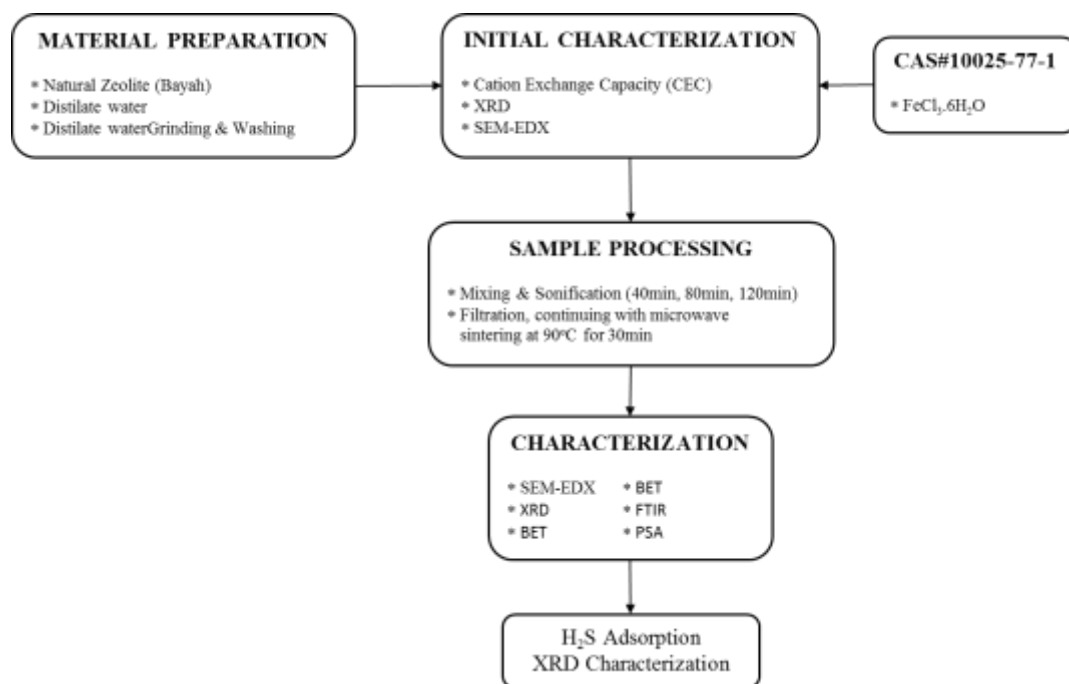


Figure 1. Research flow diagram

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Natural zeolite raw material from Bayah, Indonesia are split type with 3-4 cm size to get more homogeneous zeolite granules when the particle size is reduced, zeolite was grinded, homogenized and sieved below 150 μm (100 Mesh Tyler™) before characterization and mixing. Ferric Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) produced by Merck Millipore, Chemical Abstracts Service (CAS)#10025-77-1 as specified composition was diluted on 100 ml distillate water.

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

Reflux zeolite which is prepare was added with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as specified composition and dilute on 100 ml distillate water to become % wt composition of ZA(20gr)+ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5gr). Mixed of ZA/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ introduce with high intensity ultrasonic liquid processor VCX750 at 20 kHz, 40 Amp for 40 min for sample code ZAM4, 80 min for sample code ZAM5 and 120 min for sample code ZAM6. Slurry product of sonification are precipitated and followed by microwave heating of remain solid at temperature of 90°C for 30 min [9].

2.2 Characterization

JEOL-6510 SEM-EDS equipment utilized to carry out photomicrographs observation of natural zeolites prior and after modification by adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The quantitative chemical microanalysis analysis (EDX) also observed to the samples for element composition characterization of the analyzed volume. Particle size analysis was performed by dispersing 0.025gr sample into distillate water and evaluated with non-invasive back scatter (NIBS) method.

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 2θ range of 3–100 with step size 0.0170. The source consisted of Cu radiation ($\lambda=1.54060\text{\AA}$), monochromator on secondary optics, 40 kV power and 30 mA current with diffractometer type XPERT, each sample was scanned within the 2θ range of 3–100 degree.

Fourier transform infrared (FT-IR) spectroscopy was used to study zeolite and zeolite/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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. Specific surface area was evaluated by the nitrogen gas adsorption method equipment (Quadrasorb-2 Quantachrome Instrument).

3. RESULT AND DISCUSSION

Bayah zeolite sample calculation obtained a cation exchange capacity (CEC) value 116.04 meq/100gr, the value of this CEC is in the range of the previous research that was carried out between 115.77 meq/100gr to 119.01 meq/100gr [2]. XRF test results obtained Bayah zeolite material is dominated by the content of Si and Al, Comparison between Si/Al elements range 5 to 10 (75.12/7.21) so that zeolite samples can be classified in high silica zeolite [10].

Bayah natural zeolite sample (ZA) was characterized using X-ray diffraction (XRD) and set as the baseline prior to compare with another sample as shown on Figure 2. It can be observed that XRD analyses revealed a very complicated structure of the natural zeolite, according to the results of X-ray diffraction (XRD) studies and results of refinement with GSAS software, ZA sample mostly consist of clinoptilolite phase and a little mordenite phase as in previous studies [7], X-ray diffraction (XRD) and rietveld analysis of ZA samples showed clinoptilolite phase has a weight per mole of 8345,44gr/mole, density of 4,60gm/cm³, weight fraction of 0.99 and mordenite phase has a weight per mole of 6531.22gr/mole, density of 5.16gm/cm³ and weight fraction of 0.512 x 10⁻³ as shown on figure 2. Rietveld analysis are using ICSD reference code 99-100-6672 for mordenite phase, unit cell parameters a=18.358 Å, b=21.064 Å, c=7.590 Å and $\alpha=\beta=\gamma=90^\circ$ and space group Cmcm, and ICSD reference code 96-900-1275 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 C12/m1.

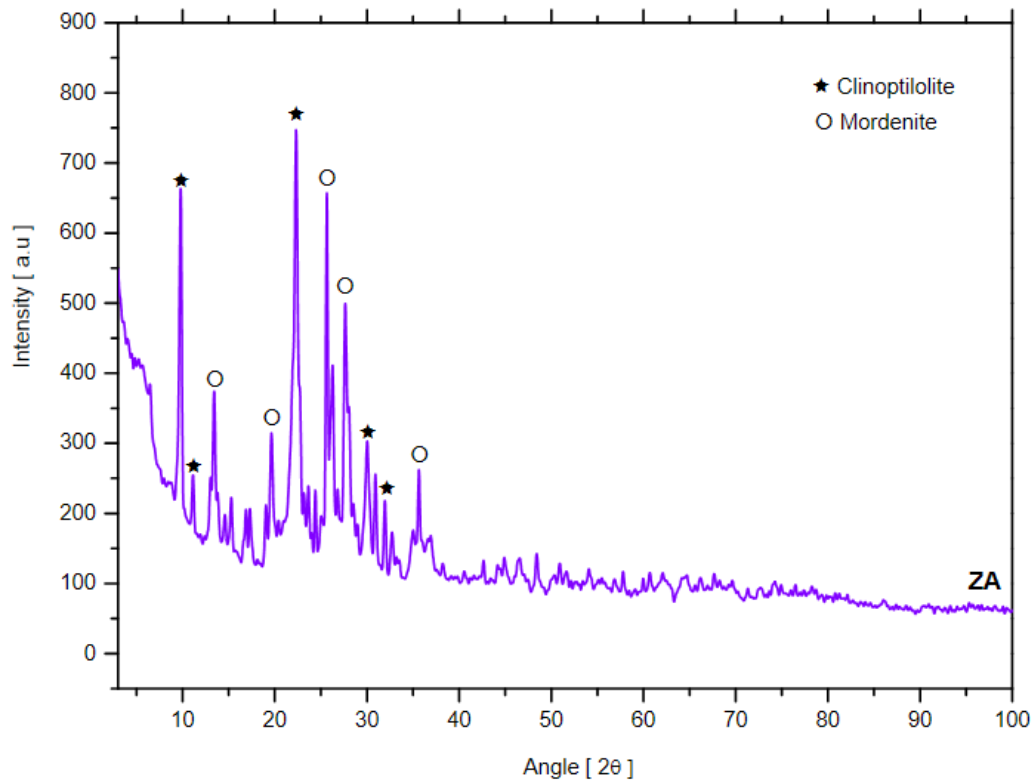


Figure 2. XRD Pattern of natural zeolite Bayah

An addition of 5gr FeCl₃.6H₂O solution and ultrasonic treatment for 40 minutes and 80 minutes into Bayah zeolite did not contribute to changing of particle size, but the ultrasonic treatment for 120 minutes would contribute to changes in particle size as shown on figure 3. The phenomenon of the correlation between the addition of FeCl₃.6H₂O and ultrasonic treatment duration showed that the weight addition of FeCl₃.6H₂O will accelerate the decay process and ultrasonic treatment time contribute to changes in particle size [11].

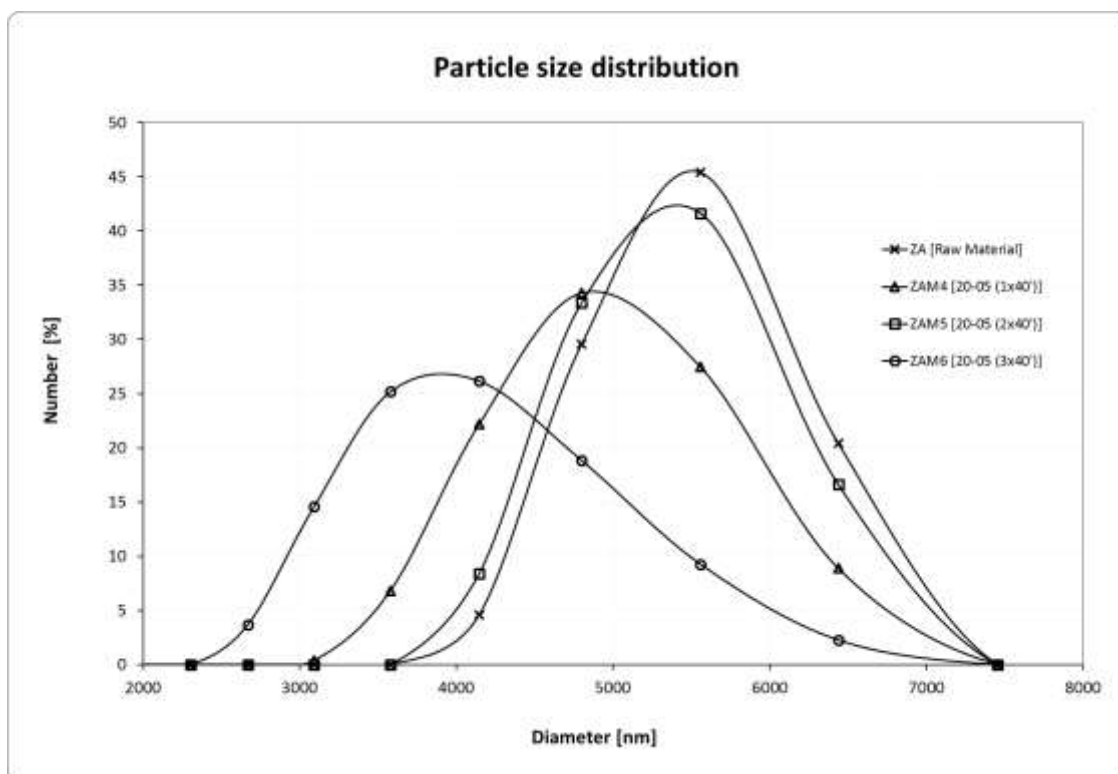


Figure 3. Particle size distribution

ZA samples that have been added with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and through the sonification process showing that wt% of Fe element increase in ZAM4, ZAM5 and ZAM6 as shown in table 1. Addition of elements in the sonification process is a reaction condition that occurs due to the process of compression and expansion resulting in an unusual chemical reaction [12]. Zeolite Bayah minerals are not a single mineral, but a group of minerals consisting of several types of elements $\text{M}_x\text{n}[(\text{SiO}_2)_y(\text{AlO}_2)_x] \cdot \text{MH}_2\text{O}$, where M is a constituent element consisting of C, Na, Mg, K, Ca and Fe, a decrease in the content of Na, Mg, Ca and K when added to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ allows an exothermic reaction and binds alkali and alkaline earth metals. NaCl, MgCl, CaCl and KCl dissolved in H_2O and carried away during the separation process between liquid and solid before drying process with the microwave as shown below reaction.

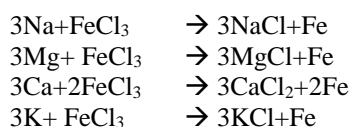


Table 1. SEM-EDX Quantitative analysis (% wt)

No	Element	Sample Code			
		ZA	ZAM4	ZAM5	ZAM6
1	C	7.80	11.33	6.70	3.86
2	O	40.80	40.56	42.12	44.94
3	Na	0.53	0.00	0.00	0.00
4	Mg	0.37	0.00	0.00	0.00
5	Al	5.96	6.30	6.11	5.82
6	Si	27.65	29.36	27.71	26.14
7	Cl	0.00	1.79	1.16	2.38
8	K	1.52	1.03	1.30	0.84
9	Ca	2.29	1.82	1.31	1.41
10	Fe	2.98	6.06	11.77	13.62

Changes in the surface area of ZAM4, ZAM5 and ZAM6 are proportional inversely to the increment radius of the pore according with the results of particle size distribution measurement. The surface area of ZAM4 samples is smaller than ZAM5 and ZAM6 because the particle size distribution of ZAM4 samples dominated by large particle size due to the low ultrasonic duration and small quantity $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as shown on figure 4, so that the decay process and duration of ultrasonic treatment do not contribute to changes in particle size [11].

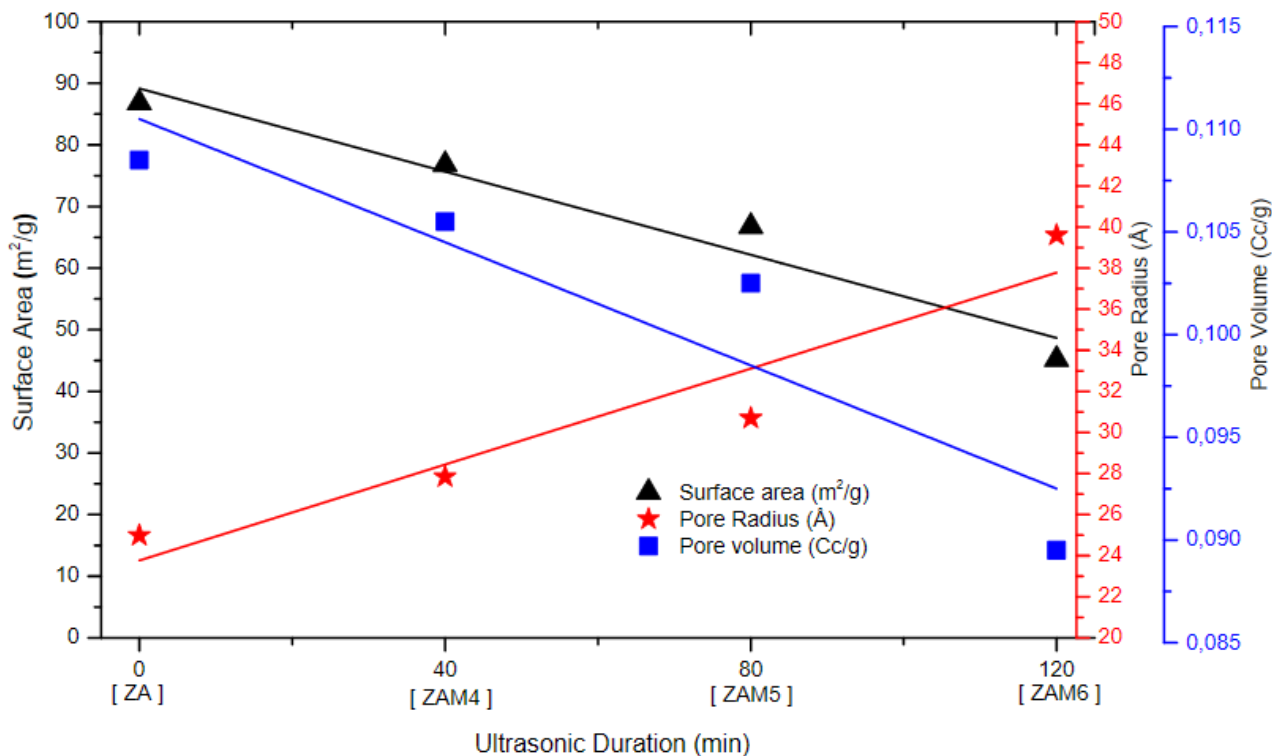


Figure 4. Surface area, Pore radius and volume of ZAM4, ZAM5 and ZAM6

Infrared spectroscopy of Bayah zeolite added with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sonification process for 40 minutes, 80 minutes and 120 minutes is shown in figure 5, showing an asymmetrical stretch of O-Si-O silicon compounds detected in the range $1130\text{-}1000\text{ cm}^{-1}$. Addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ resulted infrared waves shifting from 1033 to 1030 ; 1031 and 1032 cm^{-1} . Modified zeolite showing that infrared absorption are decreased when compared with infrared absorption of zeolite base material without ultrasonic. decreasing infrared absorption occurred at HOH bending in the wavelength range 1600 to 1800 cm^{-1} , symmetrical stretching and asymmetric OH in the wavelength range of 3300 to 3400 cm^{-1} , asymmetrical stretching OT (Si, Al)-O at wavelengths of 1040 to 1070 cm^{-1} and 800 cm^{-1} . Decreasing infrared absorption in modified zeolite showing that ultrasonic process and reactions that occur during the ultrasonic process will affect infrared absorption.

ZAM4, ZAM5 and ZAM6 samples after H_2S gas adsorption shows a shifting infrared waves and changes in transmitted infrared waves. In the ZAM4 sample the symmetric O-Si-O and O-Al-O stretches shifted from 800 to 791 cm^{-1} while the asymmetric O-Si-O and O-Al-O stretches shifted from 1032 to 1036 cm^{-1} , bending HOH shifted from 1622 to 1641 cm^{-1} , the second hydroxyl stretch appeared at 3626 cm^{-1} , in overall showing that infrared transmission was smaller than the sample which had not adsorbed H_2S , the condition showed that the adsorbent had been contaminated with sulfur which inhibited wave transmission infrared as shown on figure 6.

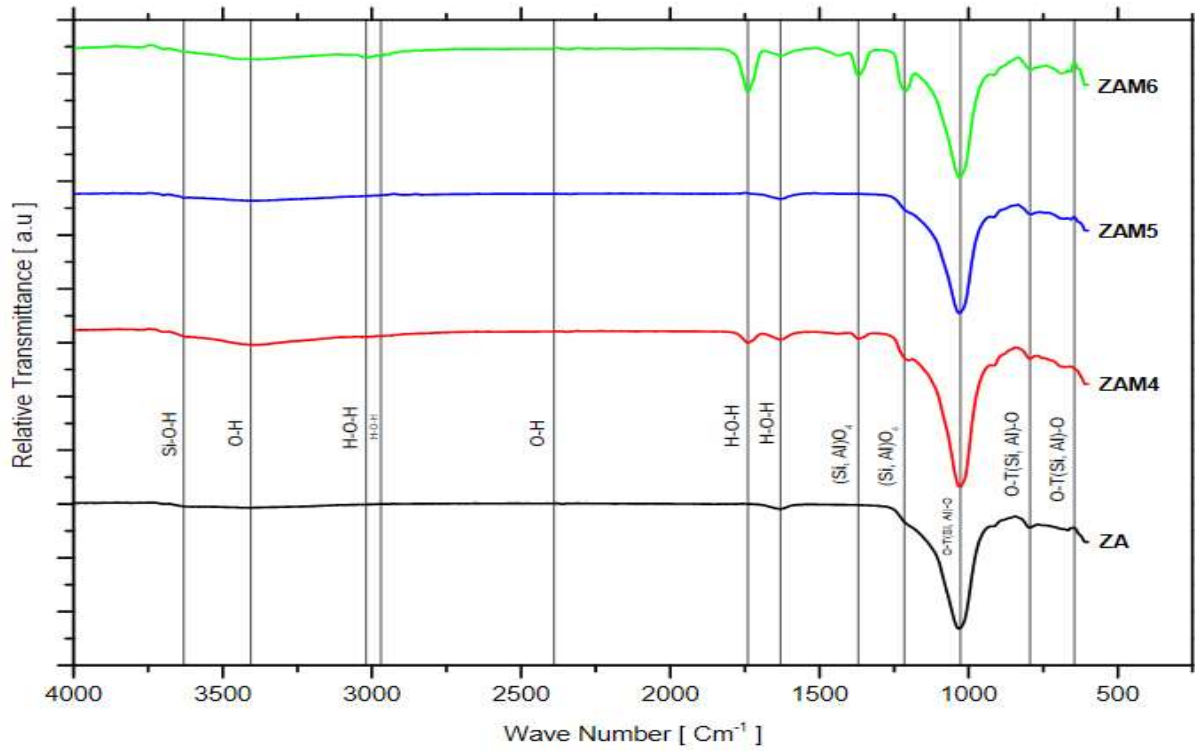


Figure 5. FTIR pattern of ZAM4, ZAM5 and ZAM6 before H_2S adsorption

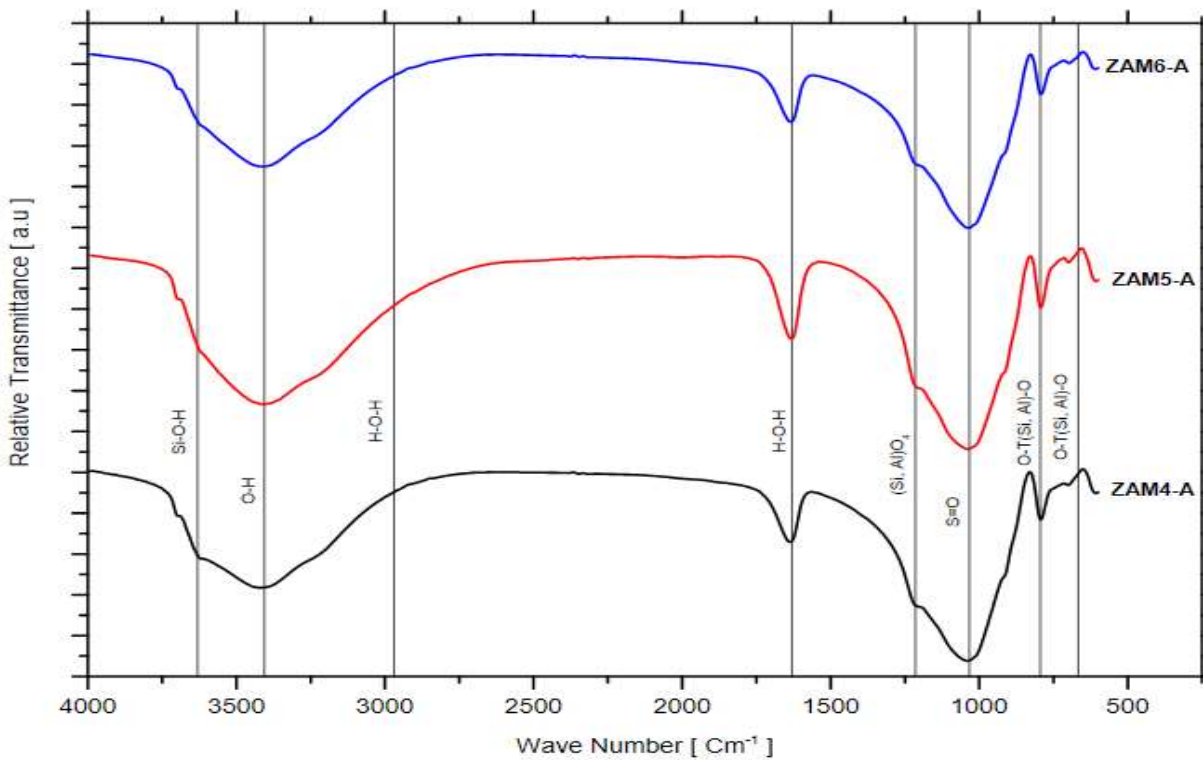


Figure 6. FTIR pattern of ZAM4, ZAM5 and ZAM6 after H_2S adsorption

Observations of modified Bayah natural zeolite by adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sonification process, showing that H_2S gas adsorption performance had improved comparing with non-modified zeolite as shown on table 2.

Table 2. Zeolite %wt composition after H_2S adsorption

No	Sample Code	Ultrasonic (Minute)	H_2S Adsorption (Hours)	Clinoptilolite (% wt)	Mordenite (% wt)	Sulfur (% wt)
1	ZA	0	24	66.32	10.08	23.60
2	ZAM4-A	40	24	29.40	30.20	40.40
3	ZAM5-A	80	24	31.90	22.60	45.40
4	ZAM6-A	120	24	34.40	15.20	50.50

Calculated Sulfur %wt based on refinement of XRD characterization after performing H_2S adsorption as shown on figure 7, addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ accompanied by an ultrasonic process to obtain the addition of % wt Fe has been indicate reactive to H_2S gas.

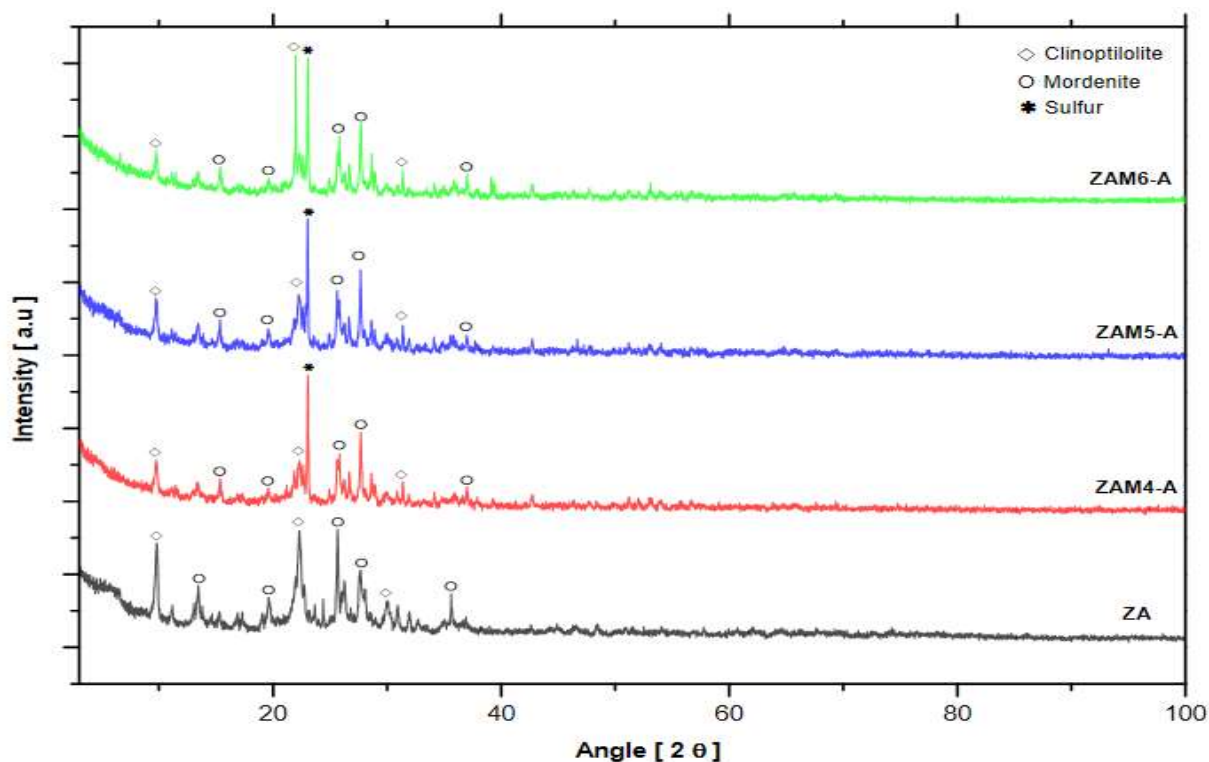


Figure 7. XRD Pattern after H_2S gas adsorption process

4. CONCLUSION

Studied Bayah natural zeolite can be used as an adsorbent because it has a cation exchange capacity (CEC) between 115.77 and 119.01 meq/100gr. Characterization of natural zeolite after adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ultrasonic processes undergoing physical and chemical properties confirmed that physical changes occur in particle size, porosity, surface area and volume; chemical changes occurs in % wt zeolites elements and their compound bonds. Performance of modified zeolite adsorption with the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ultrasonic treatment, proved be able to increase the performance of H_2S gas adsorption by 70% wt to 117% wt higher than without the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ultrasonic treatment.

5. ACKNOWLEDGEMENT

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