

Characterization of Natural Zeolite Modified through High-Temperature Heating and KNO_3 Addition

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ABSTRACT

Zeolite is a hydrated aluminosilicate containing alkali and alkaline earth metal cations such as potassium, sodium, and calcium, with a general formula ($Lm.Alx.Sig.O2nH2O$), where L represents a metal. Zeolites typically form as homogeneously distributed, fine-grained crystals within volcanoclastic and sedimentary rocks and can appear in shades of blue, brown, or white, with a specific gravity of 2-2.4. Zeolite modification aims to adjust the pore size and structure to improve the performance of zeolites. The modification involved heating the clinoptilolite-type natural zeolite to 500°C and adding KNO_3 . The study has tested XRD, FT-IR, and XRD analysis to gain a thorough understanding of the structure, chemical composition, and functional characteristics of zeolites and a comprehensive review of the properties of zeolites, including their capabilities in industrial applications such as a potential molecular filter and selective absorbent. In addition, XRD analysis showed a decrease in crystal size unexpectedly, attributed to the narrowing of pores due to potassium absorption in the modified zeolite, with a measurement of 5.91931 \AA . Atomic Absorption Spectroscopy (AAS) analysis revealed the presence of potassium in the KNO_3 -modified zeolite, with a concentration of 102.713 mcg/g , indicating effective potassium absorption. This study utilized Fourier Transform Infrared (FT-IR) spectroscopy that indicated an -OH bending frequency at 1639.4 cm^{-1} , suggesting the presence of potassium in the modified zeolite. Observing the XRD performance test, the modified zeolite demonstrates that using KNO_3 combined with high-temperature combustion enhances the adsorptive capacity by reducing the zeolite crystal size and increasing the pore volume.

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1. Introduction

Zeolite is an abundant agricultural product in Indonesia, but its use is still less optimal. This is a great opportunity for Indonesia to maximize natural products. Currently, many natural zeolites have been discovered and grouped based on their structural similarities [1]. Until now, 40 types of natural zeolites and more than 140 synthetic zeolites have been found. The usage of natural zeolites in Indonesia has great potential because most of Indonesia's territory consists of volcanoes, which are a source of zeolite minerals [2].

In basalt soils, zeolite often serves as a sediment aid. The chemical composition of zeolite is influenced by local hydrothermal conditions, including temperature, local water vapor pressure, and groundwater composition [26]. Consequently, zeolites with similar color and texture can exhibit

varying chemical compositions depending on regional factors due to additional contaminants and finely ground minerals [27].

Zeolite is fundamentally a mineral comprised of hydrated aluminosilicate crystals, with alkali or alkaline earth cations arranged in a three-dimensional framework. The general formula for zeolite can be expressed as $M_c/n\{(AlO_2)_c(SiO_2)_d\}bH_2O$, or alternatively, as its chemical oxide formula [28].

Natural zeolite has a large surface area that can be used as a microporous adsorbent in the oil, agricultural, and catalyst industries [3]. Zeolite can also be a catalyst for the development of metals, which distributes them evenly on their surface so that the overall surface area of the zeolite can increase [4]. One of the advantages of zeolite is metal absorption. Zeolites are used as adsorbents in purification and separation processes [5]. Besides its natural shape, the modified zeolite surface can also be used to recover valuable metals from various types of waste.

Zeolite is divided into two types: synthetic and natural zeolite, which come from nature. Natural zeolites usually contain cations such as Manganese, Calcium, Sodium, and Potassium, whereas synthetic zeolites usually only contain Potassium or Sodium cations [6]. Water molecules in the pores and free oxides found in natural zeolites can reduce the catalysis properties and adsorption capacity [29].

Based on its composition, the structure of synthetic zeolite can be predicted depending on the conditions of its formation in nature, so an activation process is needed when using natural zeolite as an adsorbent [7]. Increasing the specific properties of zeolites and removing impurities is the goal of the natural zeolite activation process [8]. Forms of the activation process in zeolites include changing the Silica/Aluminum ratio, the ions, and the material absorbed [1].

Natural zeolites can undergo three activation processes: physical activation by heating, chemical activation by mixing acids, and physicochemical activation by heating and mixing acid or base solutions [9]. The activation process by heating the zeolite has an operating temperature range of 200-4000°C for several hours. Meanwhile, base activation can be executed with a NaOH solution, where the Silica/Alumina ratio decreases when activated at a high pH [10]. The deluminescence process in zeolites is caused by the activation process of natural zeolites using HCl solutions at different concentrations and temperatures [11]. Chemical activation of natural zeolite using acid has been proven to make it more hydrophobic, reducing its adsorption capacity for water [12]. The higher acid concentration results in the zeolite adsorption capacity for water vapor reduction [11]; physical or chemical activation of the zeolite is required. Physical activation is done by heating treatment or hot air with a temperature range of 300°C to 400°C to release water molecules [10].

Characterization of zeolites aims to produce changes in the surface properties of natural zeolites. Zeolite characterization is generally carried out by coating organic polymers in the form of synthetic polymers or natural polymers [13]. The structure of zeolites can be modified using various methods, such as characterization via positive ion exchange (cation exchange), adsorption of polar molecules, and characterization of the framework in zeolites [14].

Zeolite activation is carried out to characterize the framework or non-skeleton structure in the zeolite so that the physicochemical properties of the zeolite are formed. In natural zeolite, activation occurs in the washing process to remove impurities in the natural zeolite framework structure [15]. Activation of zeolites affects certain types of metal cations and water molecules in the cavity and can expand the pore volume to increase the adsorption capacity [16]. Therefore, natural zeolite must be activated before use to increase its working capacity [17]. Activation of zeolite can generally be done in several ways, including [14]:

1. Calcination at a certain temperature and a certain time.
2. Exchange the positive ions contained.
3. Dealumination to change the Silica/Alumina ratio.

Reference [18] explained that modifying the natural zeolite by cleaning it using distilled water, decanting, and filtering, and then drying it at 120°C using an oven for 6 hours produced less significant changes in the zeolite structure.

In this research, physicochemical activation of zeolite was carried out by calcination treatment at a temperature of 500°C and mixing H₂SO₄ and characterization of the zeolite with KNO₃ to optimize the metal absorption capacity in terms of the size of the zeolite.

2. Research Methodology

2.1. Materials

Natural zeolite was obtained from Klaten, West Java Province, Indonesia. The solvents used included distilled water from CV. General Labora in Yogyakarta and sulfuric acid (H₂SO₄, 98% purity, Merck, Germany). Other reagents included barium hydroxide (Ba(OH)₂, 98% purity, Merck, Germany) and potassium nitrate (KNO₃, 99% purity, Merck, Germany).

2.2. Procedures

1) Preparation

This research used the main natural material, Klaten natural zeolite, obtained from the supplier Gangsar Jaya, Klaten. The natural zeolite was ground using a mortar and pestle and then sieved to obtain a fine powder with a particle size of 200 mesh. An 18 N H₂SO₄ solution was prepared by mixing 500 mL of H₂SO₄ with 1000 mL of distilled water.

2) Activation of natural zeolite

Dissolve 100 grams of 200 mesh natural zeolite in 100 mL of 0.5 M H₂SO₄ solution, then stir for 4 hours at room temperature with a ratio of 1:10. Allow the solution to cool for approximately 4 hours before filtering to separate the solid from the filtrate. Discard the filtrate and wash the solid with distilled water to neutralize its pH.

3) Neutralization of zeolite

The neutralization was monitored using Ba(OH)₂ solution, and the process was continued until the filtrate became clear, indicating neutral pH. The solid was then dried at 110°C for 720 minutes.

4) Modification of activated zeolite

Five grams of activated zeolite were modified by mixing 26.5 grams of solid KNO₃ with 100 mL of distilled water. The mixture was stirred at approximately 100°C until a paste formed. The paste was then dried in an oven at 130°C for 8 hours, followed by calcination at 500°C in a furnace for 4 hours. The calcined product was cooled to room temperature for 24 hours before being ground into a fine powder.

5) Characterization of zeolite

The activated and modified zeolite were analyzed using FT-IR, XRD, and AAS instruments. FT-IR analysis was used to determine changes in functional groups and the characteristics of the resulting solids, such as bond structure and functional groups. The results of FT-IR analysis helped identify chemical functional groups in the molecules. X-ray diffraction (XRD) analysis was used to determine the structural form (crystalline or amorphous) by interpreting the X-ray scattering diffraction pattern, which provides information on the symmetry and size of molecular units. Additionally, zeolite characterization was carried out using Atomic Absorption Spectroscopy (AAS) to determine the characteristics of the catalyst, including the Si/Al ratio and acidity level, using free atomic absorption in the form of gas and optical light radiation for measurement.

3. Results and Discussion

3.1. FT-IR Analysis

An important method for characterizing the zeolite framework structure and identifying the effect of KNO₃ is infrared spectroscopy, particularly Fourier Transform Infrared (FTIR) analysis. Generally, the 300-1300 cm⁻¹ range corresponds to tetrahedral bonds, specifically Si-O-Si [19]. The band between 900-1250 cm⁻¹ represents asymmetric stretching, while symmetric stretching is observed in the band between 650-850 cm⁻¹. Internal Si-O and Al-O bending appears in the 410-500 cm⁻¹ region, whereas external bending is seen in the 700-780 cm⁻¹ range [28].

The effect of activated treatment on the zeolite framework was characterized by FTIR based on the wave number of the Si-O site in the range of 1250 to 950 cm^{-1} [32]. Figure 1 shows that both the FT-IR spectra of activated and modified zeolites exhibit activation treatment, with vibration bands at 1051.75 cm^{-1} and 1057.80 cm^{-1} , respectively. These results are consistent with findings in the literature [20], where most absorption peaks in zeolites with a salt range between 1050 cm^{-1} correspond to the Si-O-Al and Al-O groups. This indicates that the Si-O-Al bond changes due to the decomposition of the zeolite framework into Si-O-Si.

Figure 1(a) displays the FTIR results of activated zeolite, which shows a peak at 591.40 cm^{-1} corresponding to C-S stretching. This result differs from that reported in Reference [33], which identified a band at 324.04 cm^{-1} as Si-O-Si. This discrepancy may be due to sulfuric acid being a strong oxidizer that interacts with organic compounds or sulfur-containing components in the zeolite, leading to chemical changes and the formation of organosulfur compounds with C-S bonds.

In the activated zeolite spectra, a Si-C vibration is observed at 723.33 cm^{-1} , while the modified zeolite spectra show a band at 794.89 cm^{-1} for the asymmetric stretching of Si-O. A Si-C vibration band around 723.33 cm^{-1} suggests carbon has been incorporated into the zeolite framework or surface. This is unusual for typical zeolite structures primarily composed of Si-O and Al-O bonds. The presence of Si-C bonds could indicate the incorporation of carbon-containing species during the activation process with H_2SO_4 . The shift to a band at 794.89 cm^{-1} for the asymmetric stretching of Si-O suggests changes in the zeolite's framework due to treatment with KNO_3 and high-temperature combustion. This shift may indicate alterations in the bond angles or local environment of the Si-O bonds, as high-temperature treatment can lead to structural rearrangements or changes in bond properties [34].

The presence of H^+ ions in the zeolite framework can form hydroxyl groups [37]. The O-H stretch can observe changes in the Brønsted acidity level at 3465.48 cm^{-1} and the O-H bend at 1642.16 cm^{-1} , as shown in Fig. 1.(a). The peak width of around 3500 cm^{-1} is attributed to the Hydroxyl group's Si-OH group, which originates from delocalized hydrogen bonding [31].

Modified zeolite with adding KNO_3 treatment made potassium ions replace some of the cations in the zeolite framework, and nitrate ions may be incorporated into the structure. However, potassium nitrate does not contain phosphorus, so the appearance of a P-H stretch might suggest the presence of an additional phosphorus-containing reagent or impurity that showed by the FT-IR result of modified zeolite wave peaks of 2362.18 cm^{-1} .

Figure 1(b) shows O-H groups at wavenumbers 3459.12 cm^{-1} and 1639.40 cm^{-1} , respectively. Increasing O-H groups also show that modified zeolites have more H^+ ions. The detected O-H group is predicted to be located around non-aluminum species. This shows the formation of the Brønsted acid site. The O-H bend shows the formation of the Lewis acid site [35].

According to FT-IR theory from Reference [32], resilient vibrations indicate the bonding composition of the Si-Al zeolite framework, with a wavenumber range of 780-800 cm^{-1} . This study found vibrations in this range at 793.34 cm^{-1} and 794.89 cm^{-1} for both samples. Additionally, there is a similarity in the decrease of vibration ranges from 468.70 cm^{-1} to 461.72 cm^{-1} in activated and modified zeolites. Reference [36] shows that the area corresponding to Fe-O in modified zeolite is smaller than in natural zeolite. This reduction is attributed to decreased bending between Si-O and Al-O. The amount of bending energy for Si-O and Al-O is reduced, possibly due to Fe binding with -O of Si-O and Al-O. Further research is needed to explore the changes in bonding sites resulting from acid activation.

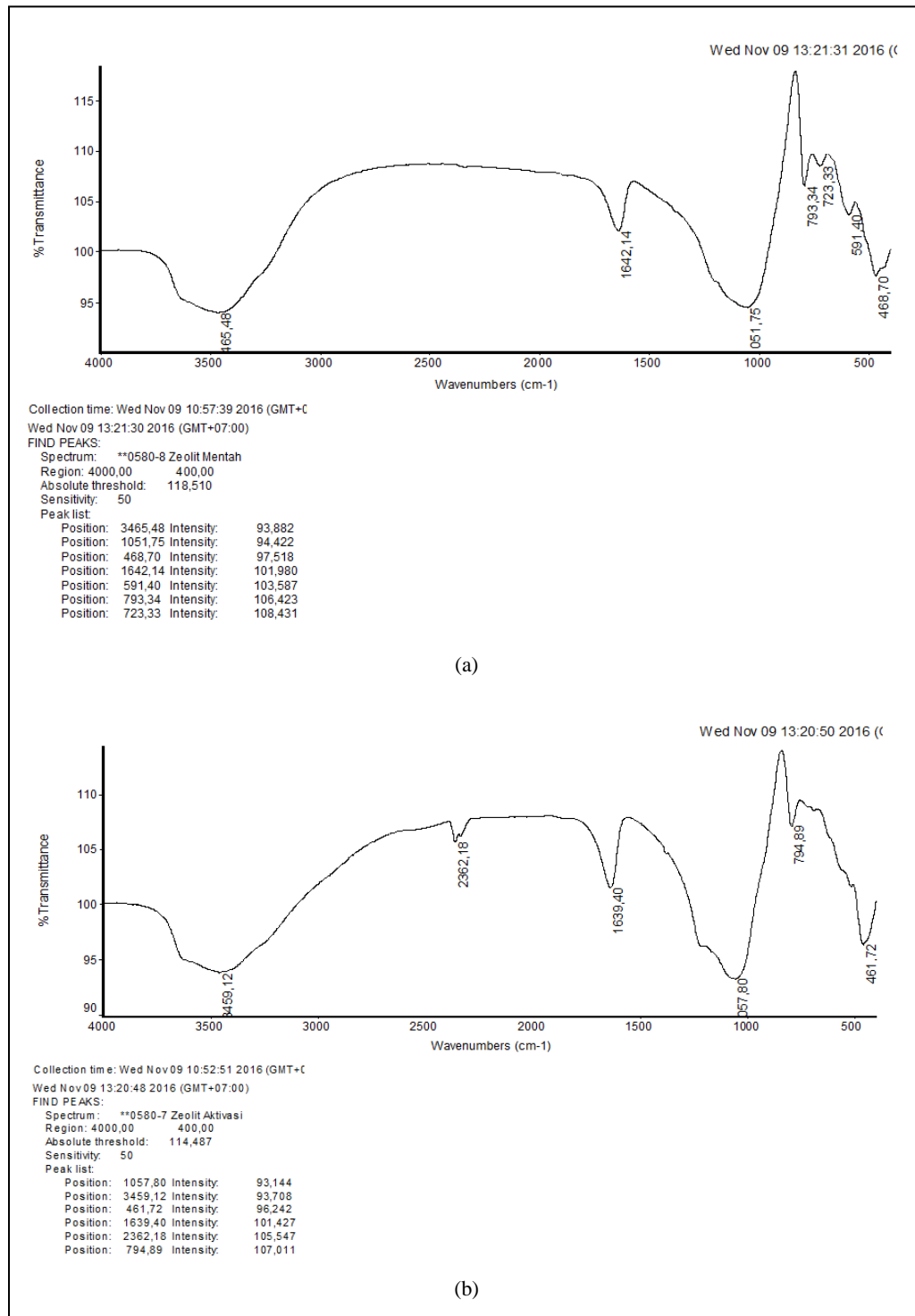


Fig. 1. The result of FT-IR spectra (a) activated; (b) modified zeolite.

3.2. XRD Analysis

The X-ray diffraction analysis provides information on the existence of compounds in the sample and the crystal characterization of the sample. The XRD pattern is depicted as a curve profile with various peaks; the 2-theta diffraction angle is the abscissa, while the calculated diffraction intensity completed is the ordinate [22]. Crystal lattice parameters, zeolite crystal size, and degree of crystallinity were obtained from the results of XRD analysis.

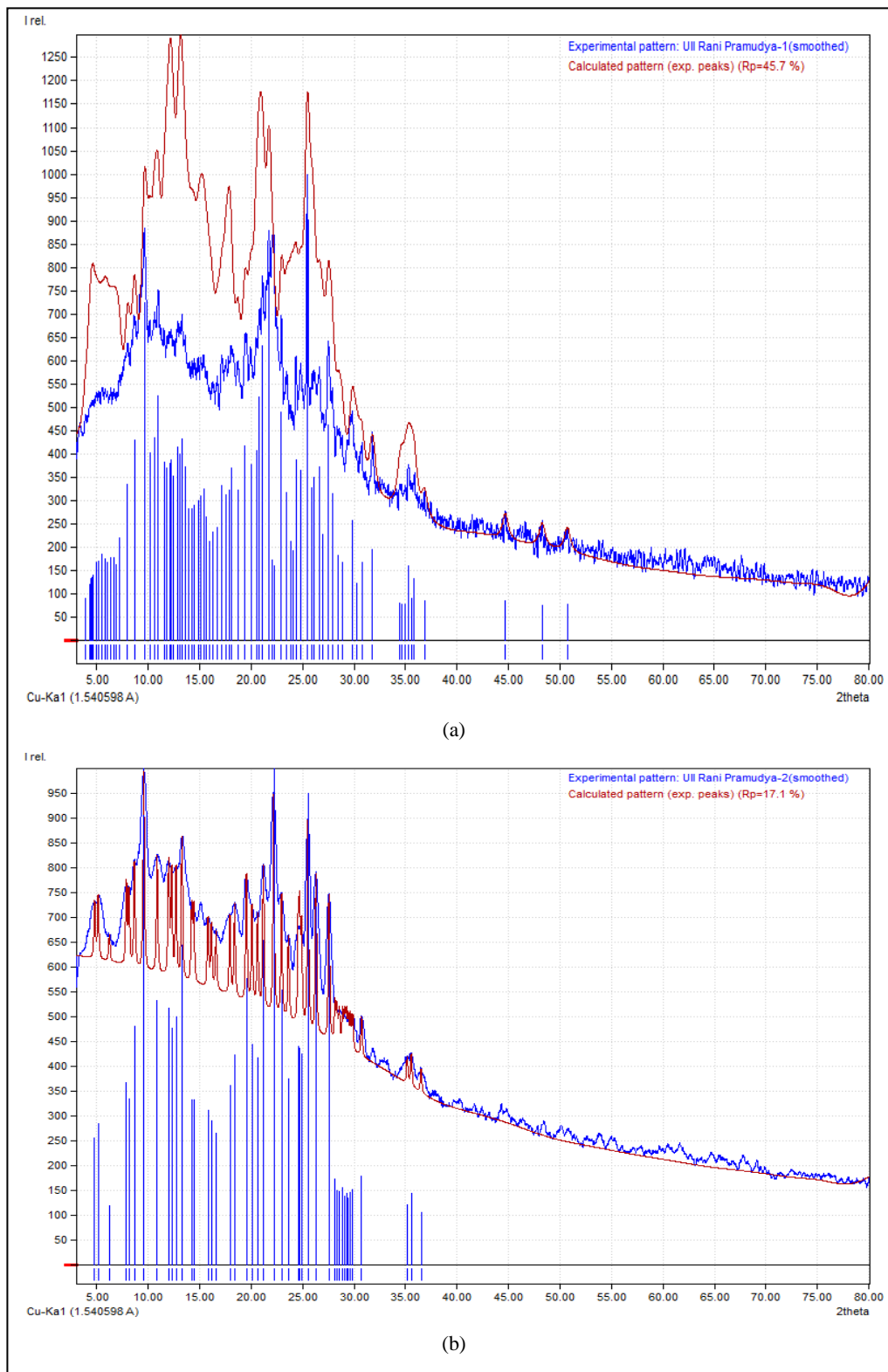


Fig. 2. The result of XRD analysis of (a) activated and (b) modified zeolite.

The acid treatment that transformed natural zeolite into activated zeolite appears to have caused a slight degradation of the crystal framework. When the concentration of Al^{3+} atoms in the original lattice is high, dealumination can lead to a loss of crystallinity, although the remaining framework may be strengthened [38].

Fig. 2. presents the X-ray diffractograms of activated and modified zeolites exhibiting crystalline structures. Acid pretreatment with H_2SO_4 sharpened the structure of each mineral type, as shown in Fig. 2.(a). Higher acid concentrations for zeolite activation resulted in sharper and smaller peak angles. Acid activation increased the peak height of the activated zeolite compared to the modified zeolite. This indicates that the concentration of activated zeolite increased after pretreatment, reflecting a higher Si/Al ratio. However, acid activation did not alter the fundamental structure of the zeolite itself [36].

Fig. 2.(b) shows a shift of peaks to higher angles (2θ) in the XRD pattern of the modified zeolite. This shift to larger angles typically indicates a decrease in d-spacing (the distance between crystal planes) or an increase in lattice density. Specifically, the pattern peaks at $25.505^\circ 2\theta$ for the modified zeolite (as listed in Table 2.). Overall, changes in peak intensities are attributed to alterations in atomic positions within the unit cell or changes in atomic density [4].

The XRD results reveal the diversity of crystals formed in natural zeolite at a temperature of $500^\circ C$, including $Si_{32}O_{72}$, $K_4O_{46} \cdot 8SiW_{12}$, $C_{64}Si_{32}$, and SiO_2 . The analyzed samples show the formation of SiO_2 crystals. The XRD patterns, the x-axis represent 2θ , and the y-axis represents intensity. The three highest peaks indicating SiO_2 crystals are as follows:

Table 1. Interpretation of activated zeolite (XRD)

2θ ($^\circ$)	FWHM ($^\circ$)	Intensity (Counts)
25.425	0.187	275
22.100	0.480	180
21.700	0.000	178

The crystal size is determined from the highest peak in the XRD data. Scherrer's formula can be used to determine crystal size [23].

$$t = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where:

t = crystal size, \AA

λ = the X-Ray wavelength, \AA (commonly 1.54\AA)

K = Scherrer factor (range 0.9 to 1.0)

β = FWHM (Full Width at Half Maximum), $^\circ$

θ = the diffraction angle, $^\circ$

The FWHM and the diffraction angle should be converted to Radians if those are measured in degrees using the conversion factor [37]:

$$\beta = \frac{\beta (\text{degrees}) \pi}{180} \quad (2)$$

Table 1 shows that the XRD analysis interpreted the FWHM (β) as 0.187° ; 2θ as 25.425° ; λ as 1.54° ; K as 0.9 which should be converted to:

$$\theta = \frac{25.425^\circ \pi}{2} = 39.952^\circ$$

$$\theta = \frac{39.952 \pi}{180} = 0.697 \text{ radian}$$

$$\beta = \frac{0.187 \pi}{180} = 0.003 \text{ radian}$$

From *Scherrer's Formula*

$$t = \frac{0.9 \times 1.54}{0.003 \cos(0.697)} = 603.133 \text{ \AA}$$

The crystal size of activated zeolite measured 603.133 Å.

Crystal size affects the width of the diffraction peaks (full width at half maximum, FWHM). Larger crystals tend to have narrower and sharper peaks, while smaller crystals usually exhibit broader peaks. Crystal size can affect the intensity of peaks in XRD patterns. Larger crystals generally produce sharper and more intense diffraction peaks because more crystal planes contribute to forming these peaks. FWHM can determine crystal size using the Scherrer equation, which relates peak width to crystal size in a specific direction [31].

The three highest peaks indicating SiO₂ crystals, as observed in the XRD test of the modified zeolite, are associated with the following 2θ values:

Table 2. Interpretation of modified zeolite (XRD)

2θ (°)	FWHM (°)	Intensity (Counts)
25.505	0.504	157
22.160	0.625	155
9.523	0.713	138

Table 2 shows that the XRD analysis interpreted the FWHM (β) as 0.504°; 2θ as 25.505°; λ as 3.489°; K as 0.9 which should be converted to:

$$\theta = \frac{25.505^\circ \pi}{2} = 40.079^\circ$$

$$\theta = \frac{40.079 \pi}{180} = 0.699 \text{ radian}$$

$$\beta = \frac{0.504 \pi}{180} = 0.008 \text{ radian}$$

From *Scherrer's Formula*

$$t = \frac{0.9 \times 1.54}{0.008 \cos(0.699)} = 514.285 \text{ \AA}$$

The crystal size of modified zeolite measured 514.285 Å, indicating a difference between both zeolite treatments. It showed that modified zeolite's crystal size is smaller than activated zeolite. Zeolites with smaller crystal sizes can have a larger specific surface area and more active sites, which is beneficial for catalytic applications. Smaller crystal sizes can enhance the catalyst's efficiency by improving the accessibility of active sites for chemical reactions. However, reducing crystal size may also affect the pore structure of the zeolite. If smaller crystal sizes change the pore structure, this can impact the zeolite's adsorption capacity and selectivity.

This study is similar to Reference [30] in that it correlates the number of nucleation sites for zeolite deposition and the amount of PDDA (poly(diallyldimethylammonium chloride)) used. The larger the number of nucleation sites, the crystal size decreases with increasing the amount of polymer used. This effect is in good agreement with previous observations by [40] in the formation of ZSM-5 films by adsorption of organic surfactants. Also, Reference [3] stated that the cations occupy positions that tend to block part of the pores. Monovalent cations occupy every cationic site and lead to lesser pore sizes than in those zeolites with divalent cations, which occupy only every other cationic position, thus leaving bigger spaces on the zeolite pores.

The results of the interpretation of this data are from the journal [20], which shows that the results of the XRD test on zeolite with KNO₃ characterization show that skeletal decomposition

occurs partly due to the influence of high-temperature activation. On the other hand, the KNO_3 addition treatment also improved the total intensity of all peaks and stabilized the zeolite baseline.

3.3. AAS Analysis

Atomic Absorption Spectrophotometry is a chemical instrument used to determine the concentration of metals and metalloids based on the absorption of radiation by free atoms [25]. Measurements with the K parameter on natural zeolite samples, natural zeolite, modified zeolite, and activated zeolite are shown in Table 3.

Table 3. shows a significant increase in potassium levels in zeolite, rising from 3,062 $\mu\text{g/g}$ in natural zeolite to 102,713 $\mu\text{g/g}$ in modified zeolite, an increase of 99.6%. This indicates that potassium has been effectively absorbed in the modified zeolite due to the addition of KNO_3 and high-temperature heating. The calcination process enlarges the zeolite's pores, facilitating potassium absorption, and the addition of KNO_3 further enhances the potassium content. Reference [39] stated that the characterization of zeolites causes dealumination and deionization, resulting in reduced levels of the element Alumina and several cations such as Calcium, Manganese, and Barium, resulting in increased potassium levels after characterization to reach 61.5%.

Table 3. Interpretation of various zeolite variables (AAS)

Sample	Measurement (mcg/g)			Average of measurement (mcg/g)
	I	II	III	
A	3.062	3.062	3.062	3.062
B	102.713	102.713	102.713	102.713
C	1.124	1.124	1.124	1.124

^a. Natural zeolite.

^b. Modified zeolite

^c. Activated zeolite

4. Conclusion

The characterization of zeolite as a metal absorbent can be achieved through physicochemical activation, such as the treatment described in this research, which involves calcination at a temperature of 500°C and adding KNO_3 . Using KNO_3 , combined with high-temperature combustion, increases the adsorptive capacity by reducing the zeolite crystal size and increasing the pore volume. These changes contribute to an enhanced adsorption capacity in the modified zeolites. However, chemical analysis using FT-IR shows the appearance of a P-H stretch in the modified zeolite, which likely indicates the introduction of a phosphorus-containing species, either from the modification process or as an impurity. XRD analysis in this work has demonstrated that potassium can affect the adsorption capacity of zeolites. An increase in potassium may enhance the zeolite's ability to interact with target molecules during adsorption. However, pore structure or ion distribution changes may impact the selectivity and overall adsorption capacity.

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