Science and Technology Indonesia
*e*-ISSN:2580-4391 *p*-ISSN:2580-4405
Vol. 9, No. 2, April 2024

Research Paper

# Enhanced Ammonium Adsorption from Aqueous Solutions Using Ethylenediaminetetraacetic Acid (EDTA) Modified Lampung (Indonesia) Natural Zeolite: Isotherm, Kinetic, and Thermodynamic Studies

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## Abstract

The environmental concern related to excessive ammonium in water bodies necessitates efficient and cost-effective removal techniques. This study investigated the modification of natural zeolite collected from the Tanggamus district of Lampung Province, Indonesia, with ethylenediaminetetraacetic acid (EDTA) to enhance its performance for ammonium adsorption from aqueous solution. The modified and natural zeolites were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), $N_2$ adsorption-desorption isotherm, and scanning electron microscopy (SEM). Results indicated that the modification did not cause significant structural changes but increased the mesoporosity of the zeolites, which was beneficial for ammonium adsorption. The adsorption studies revealed that the EDTA-modified zeolites consistently outperformed the natural zeolite and that the adsorption process was exothermic in nature. The Langmuir and Freundlich isotherm models fit the adsorption data well, indicating that the adsorption process occurs on both homogenous and heterogeneous surfaces. Thermodynamic studies confirmed that the adsorption process was exothermic and that the EDTA modification increased the spontaneity of the ammonium adsorption process. Overall, this study highlights the potential of EDTA-modified zeolites as an effective material for ammonium removal from aqueous solutions.

**Keywords**
EDTA-modified Zeolite, Ammonium Adsorption, Adsorption Isotherms, Clinoptilolite

Received: 6 October 2023, Accepted: 24 January 2024
https://doi.org/10.26554/sti.2024.9.2.224-234

## 1. INTRODUCTION

Ammonium, which is commonly found in various water sources such as industrial effluents, agricultural runoff, and municipal wastewater, is a contaminant that poses a significant threat to the environment and human health (Nguyen et al., 2022; Vamvuka et al., 2024). High levels of ammonium in water can cause eutrophication, leading to the excessive growth of algae and other aquatic plants (Chen et al., 2021). This can result in the depletion of oxygen and harm to aquatic life. Moreover, the presence of high ammonium concentrations in drinking water can lead to health issues in humans, such as irritation of the eyes, nose, throat, and respiratory tract. It can also affect the nervous system and cause symptoms such as headache, nausea, vomiting, dizziness, and convulsions (Alkhaldi et al., 2023). Therefore, it is crucial to remove ammonium from water sources effectively to protect public health and the environment. Several methods are available for ammonium removals, such as biological treatments, ion exchange, adsorption, and membrane processes (Chang et al., 2022; Vaičiukynienė et al., 2020; Han et al., 2021). Among these methods, adsorption has gained significant attention due to its cost-effectiveness, simplicity, and potential for high removal efficiency (Han et al., 2021; Khalil et al., 2018; Taher et al., 2023b).

Zeolites are a type of aluminosilicate material that can be found naturally or created synthetically (Maesen, 2007; Taher et al., 2023a). They are often studied for their potential in a variety of environmental applications, including gas separation, ion exchange, and removing pollutants from water (Li et al., 2017; Sun et al., 2022). Zeolites are highly porous and have a large surface area, making them ideal for the adsorptive removal of ammonium from water sources (Taher et al., 2023a; Misaelides, 2011). They can selectively take up ammonium ions through ion exchange processes due to exchangeable cations such as sodium, potassium, calcium, and magnesium within their framework (Hu et al., 2021). Zeolites are also environmentally friendly and stable, and they can be obtained from natural sources or synthesized at a low cost, making them a great option for sustainable water treatment solutions (Gao et al., 2023; Khaleque et al., 2020; Ahmad et al., 2023).

Despite the fact that natural zeolites show promise for ammonium removal, there are several limitations that prevent their widespread use in water treatment processes (Guida et al., 2020; Palapa et al., 2020). One of the main challenges is that they have a lower adsorption capacity for ammonium ions compared to other adsorbents, such as activated carbon or synthetic ion exchange resins (Wang and Peng, 2010; Wu et al., 2022). This is due to the limited availability of exchangeable cations and the heterogeneous pore structure of natural zeolites, which may restrict ion diffusion and access to active sites (Wang and Peng, 2010). Additionally, the selectivity of natural zeolites for ammonium ions can be adversely affected in the presence of other competing cations like sodium, potassium, or calcium, which are commonly found in real water matrices (Maghfiroh et al., 2023). Furthermore, the performance of natural zeolites may decrease over time due to fouling or structural degradation, particularly in harsh operating conditions (Wang and Peng, 2010). These limitations highlight the importance of tailored modifications to zeolite materials to improve their ammonium adsorption capacity, selectivity, and stability for practical water treatment applications (Pérez-Botella et al., 2022).

To improve the adsorption performance of zeolites for ammonium removal, several modification strategies have been explored (Wu et al., 2022; Alshameri et al., 2014). These modifications aim to increase the ion exchange capacity, modify the surface properties, and optimize the pore structure of the zeolites. Some of the most common modification methods include acid treatment, alkali treatment, thermal activation, surfactant modification, and impregnation with metal ions or functional groups (Vaičiukynienė et al., 2020). For example, acid treatment can partially dissolve the aluminosilicate framework of zeolites, enhancing its ion exchange capacity and surface area (Feng et al., 2019). On the other hand, alkali treatment can modify the surface charge and pore structure, improving the accessibility of active sites (Sadowska et al., 2013). Surfactant-modified zeolites can exhibit enhanced selectivity for ammonium ions due to the formation of organophilic domains on the zeolite surface (Reeve and Fallowfield, 2018). However, some of these modification methods may lead to undesirable side effects, such as reduced stability, increased cost, or environmental concerns. Therefore, it is essential to develop novel and sustainable modification approaches that can overcome these limitations.

The present study proposes an innovative approach to improve the adsorption performance of locally sourced natural zeolites for enhanced ammonium removal from wastewater. ethylenediaminetetraacetic acid (EDTA) was employed as a modifying agent in this research, as it is a well-known chelating agent with a strong affinity for meta ions (Dashtpeyma et al., 2022). By interacting with the zeolite framework, EDTA can introduce new functional groups, which alter the surface properties and pore structure of the zeolite, creating more active sites for ammonium ion exchange (Agudelo et al., 2014). EDTA also contains carboxylate and amine functional groups, which can facilitate hydrogen bonding and electrostatic interactions with ammonium ions, enhancing the selectivity of the modified zeolite. This approach is simple, cost-effective, and environmentally friendly, avoiding the use of harsh chemicals or high-energy treatments typically employed in other modification methods.

Although several natural zeolite modification methods have been reported in the literature, the use of EDTA for enhancing ammonium adsorption performance has not been widely explored (Agudelo et al., 2014; Pliekhov et al., 2020). Most existing studies focus on conventional modification techniques, which may have limitations in terms of cost, environmental impact, or stability (Wang and Peng, 2010). Moreover, there is a limited understanding of the interaction mechanisms between EDTA and zeolite, as well as the specific effects of EDTA modification on the zeolite's physicochemical properties and ammonium adsorption performance. In this context, the present study aims to address these knowledge gaps by investigating the synthesis, characterization, and ammonium removal performance of EDTA-modified zeolite. The novelty of this research lies in the development of an innovative, environmentally friendly, and potentially more effective natural zeolite modification approach using EDTA, which can offer new insight into the design and optimization of zeolite-based adsorbent for water treatment applications.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

Natural zeolite used in this study was collected from natural zeolite deposit mined by PT. Paragon Perdana Mining located in Tengor Village, Cukuh Balak Sub District, Tanggamus District, Lampung Province, Indonesia. Ethylenediaminetetraacetic acid (EDTA) was purchased from Merck and used as received without further purification.

### 2.2 Natural Zeolite Collection and Preparation

Natural zeolite samples were collected from a natural zeolite deposit in the form of zeolite stone. The collected zeolite stones were first subjected to size reduction using a laboratory grinding machine. The stones were crushed and ground until a relatively uniform particle size was obtained. After grinding, the zeolite powder was thoroughly cleaned using distilled water to remove any impurities or adhering particles. The powder was then filtered and washed several times with distilled water until the filtrate appeared clear and free of contaminants. The cleaned zeolite powder was sieved using a 100-mesh sieve to select particles with the desired size range. The fraction passing through the sieve was collected, while the coarser particles were discarded or further ground, if necessary. The sieved zeolite powder was dried in an oven at 110°C for 12 h to remove any residual moisture. The dried zeolite powder was stored in airtight containers until further use in the modification and adsorption experiments.

### 2.3 EDTA Modification of Natural Zeolite

Before modification, natural zeolite (NZ) powder was calcined in a muffle furnace at 200°C for 2 hours to remove any remaining organic contaminants and micropore water content. After calcination, the zeolite powder was allowed to cool down to room temperature before proceeding with the modification process. Aqueous solutions of ethylenediaminetetraacetic acid (EDTA) were prepared at various concentrations (0.05, and 0.1 M) by dissolving the appropriate amounts of EDTA in distilled water. The calcined zeolite powder was mixed with the prepared EDTA solutions at a ratio of 2:10 (NZ:EDTA) in separate beakers. The mixtures were then stirred for 2 hours at 60°C and a speed of 250 rpm using a magnetic stirrer to ensure proper contact between the zeolite particles and the EDTA solution. After the modification process, the zeolite was separated from the EDTA solutions using a centrifuge operated at 6000 rpm for 15 minutes. The separated zeolite was then washed several times with distilled water to remove any unbound EDTA or residual contaminants. The washed zeolite sediments were dried in an oven at 110°C for 4 hours to remove any remaining moisture. After drying, the zeolite powder was sieved through a 100-mesh sieve to obtain a uniform particle size. The obtained EDTA-modified zeolite samples were labeled according to their respective EDTA concentrations: ZE_0.05 and ZE_0.1. The samples were stored in airtight containers until further characterization and adsorption experiments.

### 2.4 Material Characterization

The synthesized materials have been characterized using several characterization techniques. The crystallographic structures of the natural and EDTA-modified zeolite samples were analyzed using X-ray diffraction (XRD). The samples were scanned over a specified $2\theta$ range (5-80°) using an X-ray diffractometer (Rigaku MiniFlex, Japan) operated at a specific voltage and current (40 kV and 30 mA). The surface functional groups of the natural and EDTA-modified zeolite samples were investigated using Fourier-transform infrared (FTIR) spectroscopy. The samples were prepared as KBr pellets and measured over a wavenumber range of 400-4000 $cm^{-1}$ using an FTIR spectrometer (Shimadzu, Japan).

The Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size distribution of the natural and EDTA-modified zeolite samples were determined using $N_2$ adsorption-desorption analysis. The samples were degassed under vacuum at a specified temperature (200°C) for 4 h prior to analysis. $N_2$ adsorption-desorption isotherms were recorded using a gas adsorption analyzer (Quantachrome, USA). The BET method was applied to calculate the specific surface area, while the pore size distribution and pore volume were determined using the Barrett-Joyner-Halenda (BJH) method. The morphology, particle size, and elemental composition of the natural and EDTA-modified zeolite samples were examined using scanning electron microscopy (SEM). The samples were coated with a thin layer of conductive material and observed under accelerating voltage of 15-20 kV using an SEM system (Themo Scientific, Germany).

### 2.5 Ammonium Adsorption Studies

A series of batch adsorption experiments were conducted to evaluate the ammonium removal performance of the natural and EDTA-modified zeolite samples. For each experiment, 1 g of adsorbent was added to a known volume 1000 mL of the prepared ammonium solution in a conical flask. The flasks were then placed on an orbital shaker and agitated at 250 rpm and temperature of 30°C for a predetermined contact time.

After the adsorption process, the suspensions were centrifuged or filtered to separate the solid adsorbent from the liquid phase. The residual ammonium concentration in the supernatant or filtrate was analyzed using the Nessler method, which involves the formation of a colored complex between ammonium ions and Nessler's reagent (potassium tetraiodomercurate(II)). The absorbance of the complex was measured at 425 nm using a UV-Vis spectrophotometer (Thermo Scientific Genysis 20). The ammonium adsorption capacity were calculated based on the following Equation (1).

$$q = \frac{(C_0 - C_t)}{m} \cdot V \tag{1}$$

Where $q$ is the adsorption capacity of the adsorbent (mg/g), $C_0$ is the initial dye concentration (mg/L), $C_t$ is the remaining dye concentration (mg/L), $m$ is the amount of the employed adsorbent (g), and $V$ is the volume of the dye (L).

The effects of various adsorption parameters, such as initial ammonium concentration, contact time, and temperature on the ammonium removal performance of the zeolite samples were investigated by conducting a series of batch experiments under different experimental conditions. The equilibrium adsorption data obtained from the batch experiments were fitted to various isotherm models (Langmuir and Freundlich) to determine the best-fit model that describes the adsorption process. Similarly, the adsorption kinetics data were fitted to different kinetic models (pseudo-first-order and pseudo-second-order) to understand the rate-controlling mechanisms and predict the adsorption behavior. Moreover, the adsorption thermodynamic behavior including the enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) at different temperatures were calculated.

## 3. RESULTS AND DISCUSSION

### 3.1 Materials Characterization

The XRD pattern of the natural zeolite sample is presented in Figure 1. The diffraction peaks observed at $2\theta$ angles of 17°, 19°, 22°, 26°, 28°, 30°, 32°, and 35° suggest the presence of clinoptilolite and possibly other zeolite phases or minerals in the sample (Assar et al., 2020; Adam et al., 2023). Several peaks can be attributed to the characteristic reflections of clinoptilolite (JCPDS 47-1870), including those at 19°, 22°, 26°, and 30°, which correspond to the (040), (031)/(040), (002), and (060) planes, respectively (Rodríguez-Iznaga et al., 2011). These peaks are in agreement with the literature values for clinoptilolite, indicating that the sample contains a significant amount of this zeolite phase (Alshameri et al., 2014; Alshameri et al., 2014).

The presence of additional peaks at 17°, 28°, and 32°, which are not commonly associated with pure clinoptilolite samples, suggests that the natural zeolite sample might also contain other zeolite phases, minerals, or impurities (Fajdek-Bieda et al., 2021). The XRD patterns of the EDTA-modified zeolite samples did not show significant changes compared to the NZ sample, suggesting that the modification process with EDTA did not alter the primary crystal structure of the zeolite (Wu et al., 2022). This result indicates that the modification likely occurred on the surface of the zeolite particles without disrupting the overall crystalline framework. The absence of new diffraction peaks in the modified zeolite samples also implies that no new crystalline phases were formed during the modification process.

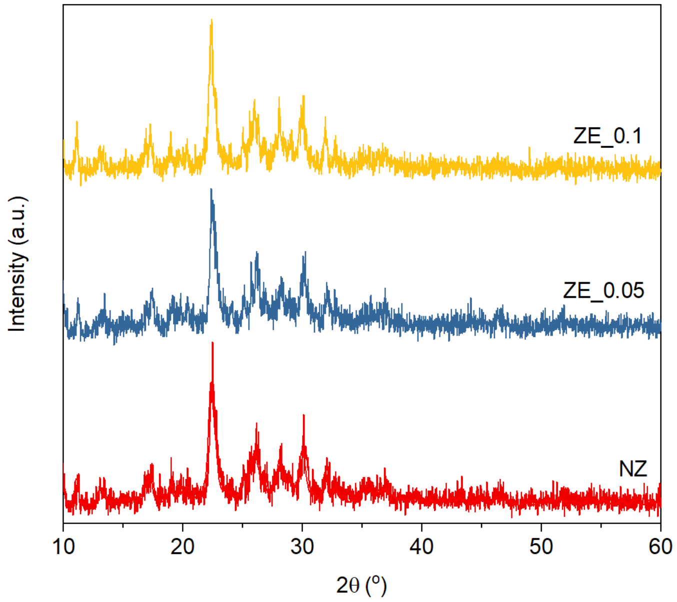

**Figure 1.** XRD Pattern of Natural Zeolite (NZ) and EDTA-modified Zeolite (ZE_0.05 and ZE_0.1)

The FTIR spectra of the natural zeolite and EDTA-modified zeolite samples are presented in Figure 2. The spectra display several peaks, which can be assigned to various functional groups and structural features of the zeolite. A small peak at 3660 $cm^{-1}$ was observed, which can be attributed to the O−H stretching vibrations of hydroxyl groups (OH) which could be present on the surface of the zeolite or within its structure (Fu et al., 2020). Since the natural zeolite sample was calcined before it was characterized, it can be observed that OH stretching vibration peaks was not intense as widely reported in zeolite samples. The small peaks observed at 2100–2400 $cm^{-1}$ is likely associated with the C−H stretching vibrations of organic impurities, such as aliphatic hydrocarbons, in the sample. The peak at 1640 $cm^{-1}$ corresponds to the bending vibrations (deformation vibrations) of the O−H groups of adsorbed water molecules or hydroxyl groups in the zeolite structure (Akgül and Karabakan, 2011).

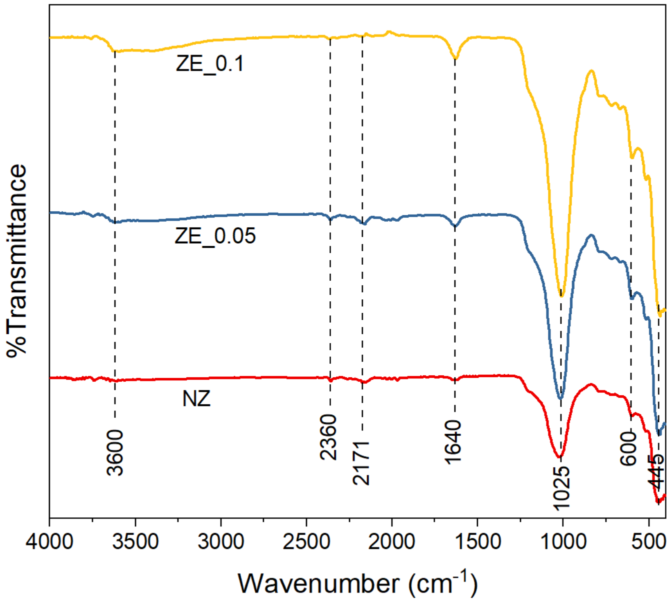

**Figure 2.** FTIR Spectra of Natural Zeolite and its Modified Form

The peak at 1025 $cm^{-1}$ represents the asymmetric stretching vibrations of the Si−O and Al−O tetrahedral units in the zeolite framework, which is confirming the presence of the zeolite structure in the sample (Ma et al., 2021). The peak at 441 $cm^{-1}$ is attributed to the bending vibrations of the O−Si−O or O−Al−O linkages in the zeolite framework, further supporting the presence of the zeolite structure in the sample (Skorynina et al., 2023). The FTIR spectrum of the EDTA-modified zeolite (ZE_0.05, ZE_0.1) showed no significant differences compared to the natural zeolite sample, suggesting that the modification process did not introduce new functional groups or significantly alter the existing ones. This observation aligns with the XRD results, which indicated that the modification took place on the zeolite surface without disrupting the overall crystal structure.

The $N_2$ adsorption-desorption isotherms of natural zeolite and EDTA-modified zeolite, which provided valuable insight into the surface and pore properties, are presented in Figure 3. It can be signed that all the samples were classified as Type IV according to IUPAC classification, which indicates the presence of abundant mesopores in the natural zeolite and its modification form (Lin et al., 2017; Thommes et al., 2015). Moreover, the present of a distinct hysteresis loop in the $P/P_0$ range of 0.4–0.95 further confirmed the microporosity of the samples, which could be attributed to the aggregation of particles or the formation of interparticle voids, which migh have been influenced by the EDTA modification process.

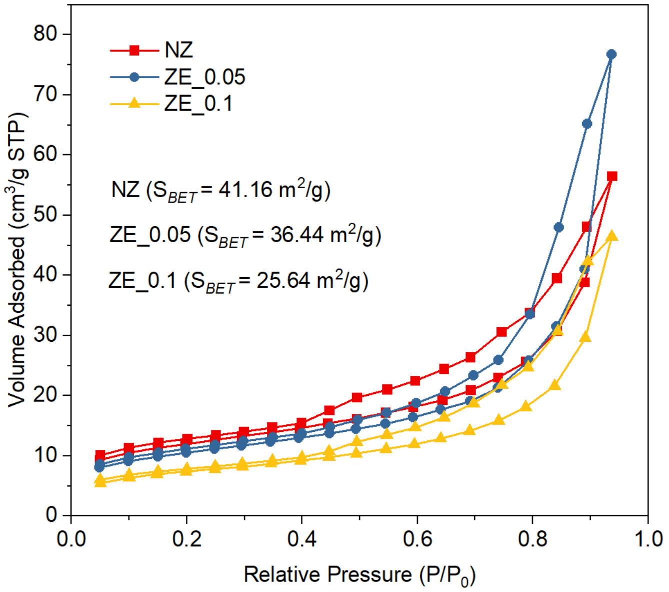

**Figure 3.** $N_2$ Adsorption-desorption Isotherm of the Natural Zeolite (NZ) and Modified Zeolite Samples (ZE_0.05 and ZE_0.1)

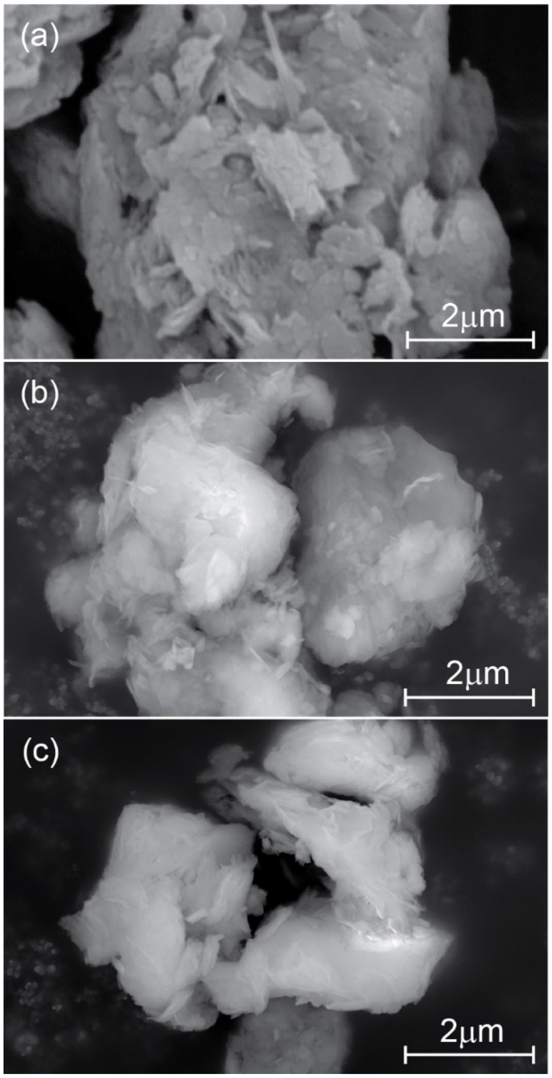

**Figure 4.** Scanning Electron Microscopy (SEM) Images of (a) Natural Zeolite and (b) ZE_0.05, and (c) ZE_0.1

The surface area and porosity properties of the natural zeolite (NZ) and the modified zeolite samples (ZE_0.05, ZE_0.1) were investigated using $N_2$ adsorption-desorption analysis. The results, including the specific surface area ($S_{BET}$), external surface area ($S_{Ext}$), micropore area, micropore volume, mesopore volume, and total pore volume, are presented in Table 1. The Brunauer–Emmett–Teller (BET) surface area ($S_{BET}$) of the natural zeolite (NZ) decreased from 41.168 $m^2/g$ to 36.449 $m^2/g$ and 25.641 $m^2/g$ for ZE_0.05 and ZE_0.1 respectively. This decrease suggests that the EDTA modification resulted in a decrease in the total surface area available for adsorption, possibly due to the partial blocking of pores by EDTA molecules.

Similarly, the micropore area (the area pores with diameters less than 2 nm) and the micropore volume also decreased following EDTA modification. The reduction in microporosity could be due to the EDTA molecules occupying or blocking the micropores (Volavšek et al., 2022). Interestingly, the mesopore volume increased from 0.0825 $cm^3/g$ from NZ to 0.1159 $cm^3/g$ for ZE_0.05 before decreasing to 0.0709 $cm^3/g$ for ZE_0.1. This might suggest that the EDTA modification caused some structural rearrangement or dealumination that led to an initial increase in mesoporosity at lower EDTA concentration, followed by a decrease at higher concentration (Shi et al., 2018). However, despite these changes in surface area and porosity, the total pore volume did not change dramatically, remaining within the range of 0.0885 to 0.0720 $cm^3/g$. This finding suggests that the EDTA modification affected the distribution of pore size, but it did not significantly alter the total porosity of the zeolite.

The morphology and surface characteristics of natural zeolite and EDTA-modified zeolite were investigated using scanning electron microscopy (SEM). As can be seen in Figure 4, The SEM images revealed a flake-like aggregate structure, which is typical for this type of zeolite material (Barus et al., 2021). These aggregates consist of numerous small, interconnected flakes that form the overall porous structure of the

**Table 1.** Surface Area and Porosity Properties of the Natural Zeolite (NZ) and Modified Zeolite Samples (ZE_0.05, ZE_0.1)

| Sample | $S_{BET}$ ($m^2/g$) | $S_{Eks}$ ($m^2/g$) | Micropore Area ($m^2/g$) | Micropore Volume ($cm^3/g$) | Mesopore Volume ($cm^3/g$) | Total Volume ($cm^3/g$) |
|---|---|---|---|---|---|---|
| NZ | 41.168 | 31.370 | 9.798 | 0.0049 | 0.0825 | 0.0875 |
| ZE_0.05 | 36.449 | 30.298 | 6.151 | 0.0030 | 0.1159 | 0.1189 |
| ZE_0.1 | 25.641 | 23.416 | 2.225 | 0.0010 | 0.0709 | 0.0720 |

zeolite, contributing to its adsorption properties. Additionally, a small number of impurities were observed within the natural zeolite sample. These impurities may be due to the presence of mineral impurities or residual organic material from the sample collection and preparation process (Wang et al., 2014). While the impurities may have a minor effect on the overall adsorption capacity of the natural zeolite, they also highlight the importance of thorough sample preparation and cleaning procedures to minimize the impact of impurities on the material's adsorption performance (Sihombing et al., 2018).

Comparing the SEM images of the natural zeolite sample and the EDTA-modified zeolite sample, noticeable differences were observed in the surface properties and particle size of the zeolite material. The SEM image of the EDTA-modified zeolite showed cleaner surfaces compared to the natural zeolite sample. This observation indicates that the modification process with EDTA effectively removed impurities, which could lead to enhanced adsorption performance due to the increased availability of active sites on the zeolite surface (Ramesh et al., 2014). Moreover, the modified zeolite exhibited slit-like structures and smaller particle sizes compared to the natural zeolite. The reduced particle size and the presence of slit-like structures could potentially improve the overall surface area and porosity of the material, further enhancing its adsorption capacity (Wang et al., 2014). The morphological changes observed in the SEM images suggest that the modification process with EDTA not only successfully removed impurities but also altered the zeolite's microstructure, which could have significant implications for its adsorption properties. These findings highlight the effectiveness of the EDTA modification process in altering the morphology and surface properties of the natural zeolite, which could potentially lead to improved ammonium adsorption performance.

### 3.2 Effect of Contact Time and Adsorption Kinetics

The effect of contact time on the adsorption capacity of ammonium onto the prepared natural and modified zeolite was investigated, and the result is presented in Figure 5. It can be found that the adsorption of ammonium by natural and EDTA-modified zeolites was time-dependent, as also reported by Vaičiukynienė et al. (2020). For the natural zeolite, the adsorption capacity increased rapidly within the first 10 minutes of contact time, indicating the availability of a large number of vacant adsorption sites on the zeolite surface that were easily accessible to the ammonium ions (Nguyen et al., 2022). However, beyond 10 minutes, the adsorption capacity slightly declined, suggesting that as these sites became occupied, the rate of adsorption decreased. This could be attributed to the increased repulsive forces between the adsorbed ammonium ions and those still in the solution or possibly diffusion limitations within the zeolite's microporous structure (Muscarella et al., 2021).

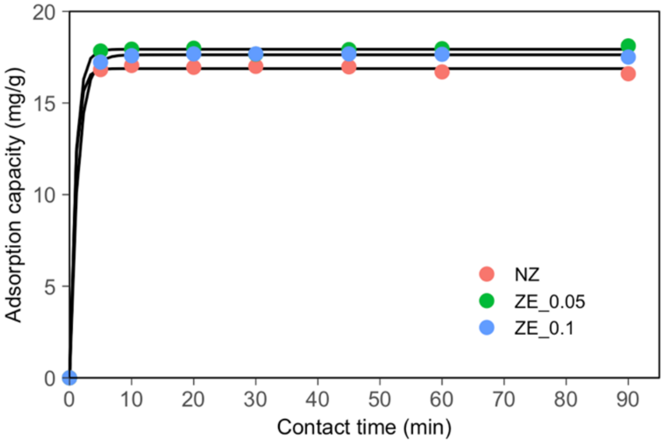

**Figure 5.** Effect of Contact Time on the Adsorption Capacity of Ammonium onto Natural Zeolite (NZ) and EDTA-modified Zeolite (ZE_0.05 and ZE_0.1)

In contrast, the adsorption capacity of the EDTA-modified zeolites, ZE_0.05 and ZE_0.1, generally increased over the contact time, though some fluctuations were observed (Palapa et al., 2023). The continuous increase in adsorption capacity for the modified zeolites, particularly within the initial 20 minutes, suggests that the EDTA modification might have enhanced the selectivity for ammonium ions or altered the surface charge properties, improving the overall adsorption process (Pérez-Botella et al., 2022). Interestingly, the adsorption capacity of ZE_0.05 was consistently higher than that of ZE_0.1, indicating that an EDTA concentration around 0.05 M might provide an optimal balance between improving ammonium selectivity and preventing excessive pore blockage (Shi et al., 2018). As indicated by the results of $N_2$ adsorption-desorption isotherm analysis, the EDTA modification reduced the total surface area and microporosity of the zeolite but caused an initial increase in mesoporosity at lower EDTA concentrations, followed by a decrease at higher concentrations. These changes in surface area and porosity can potentially explain the observed trends in the ammonium adsorption experiments.

In order to gain a deeper understanding of how ammonium ions are adsorbed onto the modified natural zeolite, two kinetic models were utilized: the pseudo-first-order (PFO) (Guo and Wang, 2019) and pseudo-second-order (PSO) (Wu et al., 2009) models. The linear model of these adsorption kinetics models is displayed in Equations (2) and (3), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Where $q_t$ is the adsorption capacity at time $t$ (mg/g), $k_1$ is the equilibrium rate constant for the pseudo-first-order model (min$^{-1}$), $t$ is contact time (min), $q_e$ is the amount of the dye adsorbed at the equilibrium (mg/g), and $k_2$ is the constant of the equilibrium rate of the pseudo-second-order model (g/mg min).

Table 2 displays the kinetic parameters obtained from the adsorption of ammonium into NZ and EDTA-modified zeolite, which includes the equilibrium adsorption capacity ($q_e$), rate constants ($k_1$ for PFO and $k_2$ for PSO), and correlation coefficients (R$^2$). From the results in Table 2, it can be observed that the PSO model provides a better fit for the experimental data compared to the PFO model, as evidenced by the significantly higher R$^2$ values (≈0.9999) for the PSO model (Wu et al., 2009). This suggests that the adsorption of ammonium ions onto the natural and modified natural zeolite follows a chemisorption mechanism (Shi et al., 2018). The higher R$^2$ values for the PSO model also indicate that the rate-limiting step in the adsorption process is likely the formation of chemical bonds between the ammonium ions and the modified zeolite surface rather than diffusion processes such as intraparticle or external mass transport (Manalu et al., 2023). Moreover, the equilibrium adsorption capacities ($q_e$) and rate constants ($k_2$) obtained from the PSO model reveal that the modified zeolite samples generally exhibit higher adsorption capacities and faster adsorption rates for ammonium ions compared to the unmodified natural zeolite (NZ). This highlights the effectiveness of the EDTA modification in enhancing the ammonium removal performance of the natural zeolite.

### 3.3 Adsorption Isotherm Equilibrium

Figure 6 shows the adsorption isotherm curve of ammonium removal by NZ and EDTA-modified NZ, which shows the relationship between the amount of adsorbate on the surface of an adsorbent and the concentration of adsorbate in the surrounding phase at a constant pressure (Mourabet et al., 2011). The obtained experimental data were then fitted to the adsorption isotherm models, called Langmuir and Freundlich, in order to comprehend the interaction between the ammonium and zeolite and to derive important characteristics of the adsorption process. The Langmuir model assumes monolayer adsorption onto a surface with identical adsorption sites, while the Freundlich model is empirical, assuming heterogeneous energy distributions and non-uniform distribution of adsorption heat (Wang and Guo, 2020). The linear equation of both Langmuir and Freundlich models are presented in Equations (4) and (5), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \,.\, q_{max}} \tag{4}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{5}$$

Where $C_e$ is the concentration of the ammonium solution at the equilibrium state (mg/L), $q_e$ is the equilibrium adsorption capacity (mg/g), $q_{max}$ is the monolayer adsorption capacity of the adsorbent (mg/g), $b$ is the constant of the Langmuir adsorption (L/g), $k_f$ is the Freundlich adsorption constant (mg g-1 (L g$^{-1}$)$^{-1/n}$), and $1/n$ is an empirical parameter associated with surface heterogeneity.

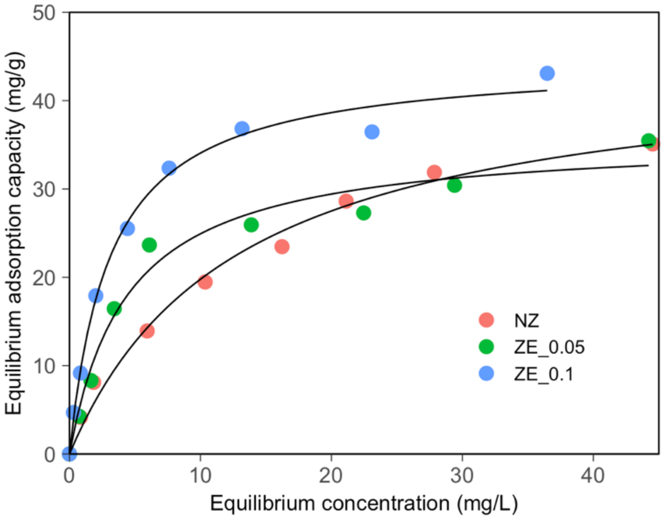

**Figure 6.** Adsorption Isotherm Curve of Ammonium Adsorption onto NZ and EDTA-modified NZ (ZE_0.05 and ZE_0.1)

The calculated adsorption isotherm parameters of ammonium adsorption by NZ, ZE_0.05, and ZE_0.1 are presented in Table 3. It can be found that the Langmuir isotherm model delivered excellent fits to the data with high correlation coefficients (R$^2$) for all samples (>0.98). This finding suggests that the adsorption of ammonium onto the zeolite surfaces takes place as a monolayer and that the adsorption sites are homogenous (Vaičiukynienė et al., 2020). The $q_{max}$ values reveal that the EDTA modification can influence the zeolite's maximum adsorption capacity for ammonium. Interestingly,

**Table 2.** Kinetic Parameters for the Adsorption of Ammonium Ions onto Natural Zeolite (NZ) and Modified Zeolite Samples (ZE_0.05, ZE_0.1)

| Sample | Pseudo-first-order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|
| | $q_e$ (mg/g) | $k_1$ (min$^{-1}$) | R$^2$ | $q_e$ (mg/g) | $k_2$ (g/(mg.min)) | R$^2$ |
| NZ | 0.526 | 0.015 | 0.064 | 16.580 | -0.137 | 0.9999 |
| ZE_0.05 | 1.048 | 0.040 | 0.259 | 18.107 | 0.195 | 0.9999 |
| ZE_0.1 | 1.000 | 0.034 | 0.306 | 17.541 | -0.445 | 0.9999 |

**Table 3.** Adsorption Isotherm Parameters for Ammonium Removal Using NZ, ZE_0.05, ZE_0.1, Samples Fitted with Langmuir and Freundlich Models

| Sample | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ (mg/g) | $K_L$ (L/mg) | R$^2$ | $K_F$ (mg/g) | $1/n$ | R$^2$ |
| NZ | 34.88 | 0.1224 | 0.9952 | 5.1139 | 0.5004 | 0.9744 |
| ZE_0.05 | 32.02 | 0.2694 | 0.9850 | 7.6315 | 0.4166 | 0.8586 |
| ZE_0.1 | 35.40 | 0.3565 | 0.9896 | 9.4690 | 0.3939 | 0.8981 |

the Langmuir constant $K_L$, associated with the affinity between the adsorbate and the adsorbent, displayed an increase with the EDTA modification. This indicates a heightened affinity for ammonium ions upon modification, which is advantageous for the purpose of ammonium removal (Muscarella et al., 2021).

The Freundlich isotherm model also provided reasonable fits to the data, albeit with slightly lower correlation coefficients than the Langmuir model. The Freundlich constant $K_F$ and the heterogeneity parameter $1/n$ both increased with EDTA modification, suggesting enhanced adsorption capacity and intensity (Wang and Guo, 2020). However, as the Freundlich isotherm assumes multilayer adsorption on a heterogeneous surface, the better fit of the Langmuir model indicates that the zeolite surfaces might be more homogenous and that the adsorption process could be predominantly monolayer.

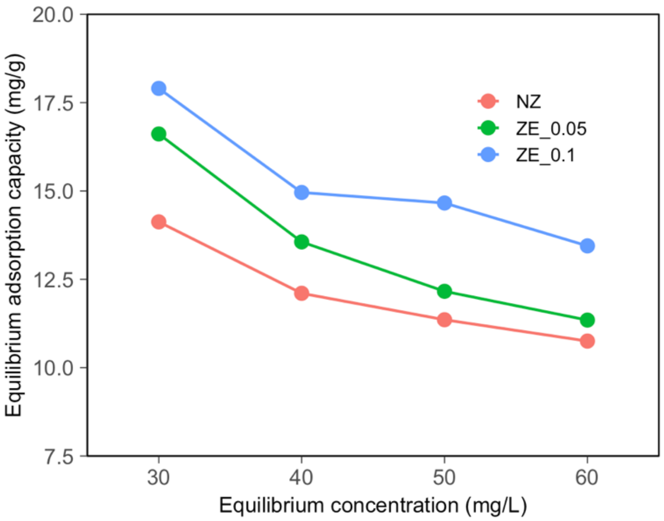

**Figure 7.** Effect of Contact Time on the Adsorption Capacity of Ammonium onto NZ, ZE_0.05, and ZE_0.1

### 3.4 Adsorption Thermodynamics

The effect of temperature on the adsorption performance of ammonium onto NZ, ZE_0.05, and ZE_0.1 was investigated at four different temperatures, i.e., 30°C, 40°C, 50°C, and 60°C. As presented in Figure 7, it can be observed that the adsorption capacity decreases with an increase in temperature for all zeolite samples (Taher et al., 2023b). This trend suggested that the adsorption of ammonium onto these zeolites was an exothermic process characterized by the release of heat, and therefore, it becomes less favorable as the temperature increase (Pérez-Botella et al., 2022). Despite the common decreasing trend, a comparison between the materials at each temperature setting demonstrated the superior adsorption capacity of the modified zeolites. This observation is consistent with previous findings that demonstrated the efficacy of EDTA modification in enhancing the adsorption performance of zeolites.

For a more comprehensive understanding of the temperature dependence of the adsorption process and to confirm the exothermic nature of the adsorption, the obtained results were analyzed using the van't Hoff equation, where the calculating thermodynamic parameters, such as changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), can offer a deeper insight into the underlying mechanisms of the adsorption process. The linear form of the van't Hoff equations is as follows:

$$\ln K_D = \frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT} \tag{6}$$

$$K_D = \frac{q_e}{C_e} \tag{7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

Where $T$ is the absolute temperature, $K_D$ is the distribution constant, and $R$ is the molar gas constant (8.314 J.K$^{-1}$.mol$^{-1}$).

**Table 4.** Adsorption Thermodynamic Parameters of Ammonium Adsorption onto NZ, ZE_0.05, and ZE_0.1

| Sample | ΔH (kJ/mol) | ΔS (J/mol K) | $R^2$ | ΔG (kJ/mol) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 30°C | 40°C | 50°C | 60°C |
| NZ | -26904.35 | -38.01 | 0.9983 | -1538.76 | -1508.71 | -1468.66 | -1428.60 |
| ZE_0.05 | -30916.05 | -88.92 | 0.9749 | -3972.99 | -3083.78 | -2194.57 | -1305.36 |
| ZE_0.1 | -28624.16 | -76.76 | 0.9399 | -5364.79 | -4597.16 | -3829.52 | -3061.89 |

The calculated adsorption thermodynamic parameters are presented in Table 4. The overall results shed light on the spontaneous and temperature-dependent nature of the adsorption process. The negative values of the change in enthalpy (ΔH) for all zeolite samples signify that the adsorption process is exothermic. The magnitudes of ΔH for ZE_0.05 and ZE_0.1 are greater than that for NZ, suggesting that the heat release during the adsorption process is more significant in the modified zeolites. The negative values of the change in entropy (ΔS) indicate a decrease in randomness at the solid-solution interface during the adsorption process. The more negative ΔS for the modified zeolites suggests that the adsorption process becomes less random upon EDTA modification.

The Gibbs free energy change (ΔG) provides valuable information about the spontaneity of the adsorption process. The negative values of ΔG for all zeolite samples at all temperatures indicate that the adsorption of ammonium ions onto the zeolite surfaces is spontaneous. The more negative ΔG for the modified zeolites suggests that EDTA modification increases the spontaneity of the ammonium adsorption process. Interestingly, for each zeolite sample, the ΔG values become less negative with increasing temperature, further confirming that the adsorption process is exothermic. Moreover, this trend also suggests that the adsorption process is more favorable at lower temperatures.

## 4. CONCLUSIONS

In this study, natural zeolite obtained from the Tanggamus district of Lampung Province, Indonesia, was first investigated and modified with EDTA to enhance its performance in ammonium adsorption. The characterization of the modified and natural zeolites through XRD and FTIR revealed that the structure of the zeolite was not significantly affected by the modification process. SEM images illustrated an increase in the surface roughness of zeolite after modification, and $N_2$ adsorption-desorption isotherm indicated an increase in the mesoporosity of the modified zeolites. The adsorption studies exhibited that the EDTA-modified zeolites (ZE_0.05 and ZE_0.1) consistently performed better in removing ammonium from an aqueous solution compared to natural zeolite. Adsorption capacity decreased with increased temperature for all zeolites, suggesting an exothermic nature of the adsorption process. Overall, this study demonstrates the potential of EDTA-modified zeolites for ammonium removal from aqueous solutions. These findings open avenues for further research into the modification of zeolites for enhanced adsorption performance and for exploring other potential applications of modified zeolites in environmental remediation.

## 5. ACKNOWLEDGEMENT

The authors would like to express their sincere gratitude to Institut Teknologi Sumatera for providing the research funding that made this study possible. This work was supported by the GBU-45 research grant under contract number B/763d/IT9.C1/PT. 01.03/2022. The authors also acknowledge the valuable assistance and resources provided by the institution, which significantly contributed to the successful completion of this research.

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