

# Effect of Calcination Temperature on the Adsorption Performance of Tanggamus Natural Zeolite for Ammonium Removal from Shrimp Pond Wastewater

Latif Al Qadri<sup>1</sup>, Gita Aldira Abelta<sup>1</sup>, Melany Febrina<sup>1\*</sup>, Abdul Rajak<sup>1</sup>, Sena Maulana<sup>2</sup>, Meezan Ardhanu Asagabaldan<sup>3</sup>, Tarmizi Taher<sup>4\*</sup>

<sup>1</sup>Master's Program in Physics, Department of Physics, Institut Teknologi Sumatera (ITERA), South Lampung, Lampung, 35365, Indonesia

<sup>2</sup>Department of Forestry Engineering, Institut Teknologi Sumatera (ITERA), South Lampung, Lampung, 35365, Indonesia

<sup>3</sup>Department of Marine Environmental Science, Institut Teknologi Sumatera (ITERA), South Lampung, Lampung, 35365, Indonesia

<sup>4</sup>Department of Environmental Engineering, Institut Teknologi Sumatera (ITERA), South Lampung, Lampung, 35365, Indonesia

\*Corresponding author: melany.febrina@fi.itera.ac.id, tarmizi.taher@tl.itera.ac.id

## Abstract

This research explores the potential of locally sourced natural zeolite from the Tanggamus District, Indonesia, for the removal of ammonium from shrimp pond wastewater. The study utilizes a comprehensive approach involving desilication modification, batch adsorption experiments, and field-scale application. The zeolite, predominantly composed of clinoptilolite, undergoes calcination at varying temperatures, with 200°C proving to be optimal for enhancing ammonium adsorption capacity. The study also highlights the efficient use of zeolite at a lower dosage of 5 g/L, yielding high removal efficiency. The real-world effectiveness of this method was confirmed by field experiments, where the application of calcined zeolite resulted in lower ammonium concentrations in shrimp ponds. The results demonstrate that the application method, specifically direct spreading in the ponds, affects adsorption performance. These findings underscore the potential of using Tanggamus Natural Zeolite as a cost-effective and eco-friendly solution for ammonium control in shrimp pond wastewater. This work paves the way for future research focusing on the long-term application effects and zeolite regeneration methods to further improve the economic and environmental efficiency of this approach.

## Keywords

Natural Zeolite Calcination, Adsorption, Ammonium, Shrimp Pond Wastewater

Received: 30 June 2023, Accepted: 17 January 2024

<https://doi.org/10.26554/sti.2024.9.1.198-206>

## 1. INTRODUCTION

Water pollution remains one of the most pressing environmental issues worldwide (Tom et al., 2021). Among the numerous pollutants, ammonium contamination holds a significant position due to its potential to cause eutrophication, drastically altering the balance of aquatic ecosystems (Lahav and Green, 1998; Nguyen et al., 2022). Particularly in the aquaculture industry, with shrimp farming as a salient example, the issue becomes more pronounced (Bernardi et al., 2018). Shrimp ponds are known to produce wastewater with high ammonium levels (Lin et al., 2002). This pollution not only directly affects the health and survival of aquatic species within these farming environments but also substantially impacts the receiving water bodies when discharged untreated (Ahmad et al., 2021). Given the critical environmental implications and the burgeoning growth of the aquaculture industry, it is imperative to find efficient, affordable, and eco-friendly methods to reduce ammonium levels in shrimp pond wastewater.

While traditional methods to address ammonium contami-

nation in wastewater, such as biological nitrification or physicochemical methods, can be effective, they often come with notable drawbacks (Muscarella et al., 2021; Guida et al., 2020). For instance, biological nitrification processes necessitate precise control over environmental conditions and long retention times, limiting their practical application (Yang et al., 2017). Similarly, physicochemical methods, including air stripping or ion exchange, often involve high operational costs and the use of chemicals, which may pose additional environmental concerns (Lahav and Green, 1998). These challenges underscore the need for alternative ammonium removal strategies that are effective, cost-efficient, operationally simple, and environmentally friendly (Muscarella et al., 2021; Serafin et al., 2021). One such promising avenue is the use of natural adsorbents like zeolites (Rožić et al., 2000), montmorillonite (Taher et al., 2023), layered double hydroxide (LDH) (Palapa et al., 2020; Taher et al., 2019), and biochar (Lesbani et al., 2021), which have demonstrated potential in wastewater treatment. However, to fully leverage their potential, it is essential to understand and optimize the factors that influence their adsorption

performance.

Zeolites, naturally occurring aluminosilicates, have attracted considerable attention in recent years due to their unique properties, such as high porosity, large surface area, and ion exchange capacity, making them promising for water and wastewater treatment (Akgül and Karabakan, 2011). Tanggamus Natural Zeolite has been shown to exhibit high ammonium adsorption capacity. Previous studies have evaluated various methods to enhance the ammonium adsorption performance of zeolites, such as ion exchange and chemical modification (Ates, 2019; Gackowski et al., 2018; Reeve and Fallowfield, 2018). However, calcination, a thermal treatment process, has emerged as a promising approach, potentially enhancing the adsorption capacity of the zeolite by altering its physicochemical properties (Sodha et al., 2022).

Despite the potential benefits of calcination, there is still a gap in understanding how the calcination temperature affects the ammonium adsorption performance of Tanggamus Natural Zeolite. Existing research has primarily focused on the effect of calcination on other types of zeolites or on zeolite's adsorption of other pollutants (Li et al., 2011). Therefore, there is a significant need for a focused study investigating how varying calcination temperatures impact Tanggamus Natural Zeolite's ability to remove ammonium from shrimp pond wastewater. Given the identified research gap, the primary objective of this study is to investigate the effect of calcination temperature on the ammonium adsorption performance of Tanggamus Natural Zeolite. This study seeks to provide a comprehensive understanding of calcination temperature's influence on the zeolite's physicochemical properties and, subsequently, its ammonium removal efficiency from shrimp pond wastewater.

In this study, we investigate the existence of an optimal calcination temperature that maximizes the ammonium adsorption capacity of Tanggamus Natural Zeolite. We postulate that calcination at this optimal temperature alters the zeolite's surface properties and pore structure to enhance ammonium uptake. This hypothesis is based on previous studies that have reported improved adsorption capacity of zeolites for various pollutants after calcination (Wang and Peng, 2010; Fu et al., 2020; Pérez-Botella et al., 2022). However, given the lack of specific studies on Tanggamus Natural Zeolite and ammonium adsorption, this hypothesis will be rigorously tested through a series of carefully designed experiments. In order to test our hypothesis and meet our research objectives, we conducted an experimental study involving the calcination of Tanggamus Natural Zeolite at different temperatures, followed by a series of adsorption tests. We began by sourcing and preparing the natural zeolite, then subjected it to calcination processes at varying temperatures, ranging from 200 to 600°C (Lin et al., 2013). Following calcination, the zeolite samples were tested for ammonium removal from shrimp pond wastewater in both laboratory and field scales. Furthermore, the method for zeolite spreading in the field scale study was investigated.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

The materials employed in this study include Tanggamus Natural Zeolite and several chemical reagents. Tanggamus Natural Zeolite was sourced from the zeolite mining located in Tengor Village, Cukuh Balak Subdistrict, Tanggamus District, Lampung Province, Indonesia, obtained in its raw form and used without further purification. Prior to the experiments, the zeolite was crushed and sieved to attain a uniform particle size range suitable for the adsorption tests.

Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and Nessler reagent were acquired in reagent grade and used as received from Merck. The ammonium chloride was used to prepare simulated shrimp pond wastewater, mimicking the typical ammonium concentrations found in such environments. The Nessler reagent, employed for its sensitivity to the presence of ammonium ions, was utilized for the quantitative analysis of ammonium concentration in the wastewater samples before and after treatment with the calcined zeolite. All chemicals were used without further purification.

### 2.2 Natural Zeolite Calcination

The calcination process was carried out to investigate the effect of varying temperatures on the adsorption performance of the Tanggamus Natural Zeolite. The zeolite samples were subjected to calcination at three different temperatures: 200°C, 400°C, and 600°C. This range of temperatures was selected to provide insights into how moderate to high calcination temperatures influence the zeolite's physicochemical properties and, subsequently, its ammonium adsorption capacity.

Each calcination process was conducted in a muffle furnace for a duration of 3 hours. The zeolite samples were placed in the furnace at the desired temperature and maintained at that temperature for the entire period to ensure uniform treatment. Following calcination, the zeolite samples were carefully removed from the furnace and allowed to cool to room temperature. Once cooled, the samples were stored in a desiccator to prevent exposure to atmospheric moisture and other potential contaminants. The calcined zeolite samples were preserved in this manner until further use for the adsorption experiments.

### 2.3 Material Characterization

The natural and calcined Tanggamus Natural Zeolite samples underwent rigorous characterization using a combination of three analytical techniques: X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), and  $\text{N}_2$  adsorption-desorption analysis. XRD was employed to examine the crystalline structures of the zeolite samples before and after calcination. This analysis provided critical insights into any alterations in the zeolite's crystal structure as a result of the calcination process. The samples were recorded using Rigaku Miniflex Benchtop Powder X-Ray Diffraction (XRD) Instrument, Japan, under a scanning speed of 5°/min.

FTIR spectroscopy was used to analyze the functional groups present on the zeolite's surface. This characterization method

helped to identify any changes in the surface chemistry of the zeolite due to calcination, potentially providing a deeper understanding of how calcination temperature influences ammonium adsorption. The FTIR spectra were recorded using the Shimadzu IRSpirit apparatus. The samples were scanned under a wavenumber range of 4000 to 400  $\text{cm}^{-1}$ .

$\text{N}_2$  adsorption-desorption analysis was performed to assess the textural properties of the zeolite, such as surface area, pore volume, and pore size distribution. These parameters can significantly influence the adsorption capacity of the zeolite, and any changes induced by calcination were carefully evaluated. The samples were measured using the Quantachrome Nova-touch Lx4 BET instrument. Prior to  $\text{N}_2$  adsorption-desorption measurement, the samples were first degassed under vacuum conditions at 200  $^{\circ}\text{C}$  for 2 h. Total pore volume was estimated by measuring the volume of  $\text{N}_2$  adsorbed at  $P/P_0 \approx 0.99$ . To calculate the specific surface area, the Brauer-Emmett-Teller (BET) equation was applied to the adsorption branch of the isotherms, whereas the pore size distribution was calculated from the desorption branch using the Barret-Joyner-Halenda (BJH) model.

#### 2.4 Ammonium Adsorption from Aqueous Solution (Lab Scale)

To evaluate the ammonium adsorption capacity of the calcined Tanggamus Natural Zeolite, a series of batch adsorption experiments were conducted in the laboratory. These tests were designed to simulate the conditions likely to be encountered in real-world shrimp pond wastewater treatment applications. For each test, a 0.1 g sample of calcined zeolite was added to an Erlenmeyer flask containing 100 mL of an ammonium chloride solution. The solution was prepared to a concentration of 20 mg/L to reflect typical ammonium levels found in shrimp pond wastewater.

The adsorption process was allowed to proceed for a duration of 1 hour, with the solution being continuously stirred at a speed of 250 rpm. This stirring speed was selected to ensure homogeneity and effective contact between the zeolite particles and the ammonium ions in the solution. Upon completion of the adsorption period, the remaining concentration of ammonium in the solution was determined using the Nessler method. This analysis provided a quantitative measure of the amount of ammonium adsorbed by the zeolite, thereby offering insights into the zeolite's adsorption capacity following calcination at various temperatures. The adsorption capacity of the calcined zeolite was determined by the following Equation 1:

$$Q_e = \frac{(C_0 - C_t)}{m} V \quad (1)$$

Where  $Q_e$  is the equilibrium adsorption capacity (mg/g),  $C_0$  is the initial ammonium concentration (mg/L),  $C_e$  is the equilibrium ammonium concentration (mg/L),  $m$  is the amount of the employed calcined zeolite sample (g), and  $V$  is the volume of the ammonium solution (L).

To further understand the effectiveness of calcined Tanggamus Natural Zeolite for ammonium adsorption, a series of experiments were conducted varying both zeolite dose and contact time. Three different doses of the calcined zeolite were tested: 1 g/L, 2 g/L, and 5 g/L. These doses were selected to provide a range of zeolite concentrations that could feasibly be used in practical wastewater treatment scenarios, allowing us to gauge the impact of zeolite dose on ammonium removal efficiency. The adsorption process for each dose was conducted in an Erlenmeyer flask containing 100 mL of a 20 mg/L ammonium chloride solution under continuous stirring at a speed of 250 rpm. Moreover, the effect of contact time was investigated by varying the duration of the adsorption process from 0 to 64 hours. This allowed us to evaluate how quickly the zeolite can effectively adsorb ammonium and whether extending the contact time further improves ammonium removal efficiency.

#### 2.5 Ammonium Adsorption from Shrimp Pond (Field Scale)

Building upon our laboratory-scale investigations, we extended our study to a more practical and ecologically relevant context through a series of field experiments in constructed shrimp ponds. The schematic figure of the field experiments is presented in Figure 1. Three different treatments were tested during these experiments. The first treatment served as a control, with no zeolite added to the pond. The second treatment involved the direct application of calcined zeolite into the pond at a dosage of 5 g/L. For the third treatment, the calcined zeolite was packed into bags before being placed in the pond to explore whether this method of application influenced the adsorption process. Each of these treatments was replicated in two separate ponds, enhancing the reliability of our findings.

The conditions in each pond were carefully controlled to simulate realistic shrimp farming conditions. Each pond had a volume of 180 L and was populated with 50 shrimp. The shrimp were fed at a rate equivalent to 4% of their total biomass, with the feed having a protein content of 36.5%. The ammonium concentration in each pond was closely monitored on an hourly basis throughout the experiment. By comparing the ammonium levels in the different treatment ponds over time, we aimed to evaluate the effectiveness of calcined Tanggamus Natural Zeolite for in-situ ammonium removal in shrimp pond wastewater and to understand how the method of zeolite application influences its adsorption performance.

### 3. RESULTS AND DISCUSSION

#### 3.1 Materials Characterization

X-ray diffraction (XRD) analysis was conducted to examine alterations in the crystalline structure of Tanggamus Natural Zeolite following calcination at varied temperatures. Figure 2 presents the XRD patterns for the natural zeolite (ZA) and the calcined zeolites at temperatures of 200 $^{\circ}\text{C}$  (ZB), 400 $^{\circ}\text{C}$  (ZC), and 600 $^{\circ}\text{C}$  (ZD). The XRD pattern of the natural zeolite (ZA) displayed prominent peaks at 2-theta angles of 9.9 $^{\circ}$ , 11.14 $^{\circ}$ , 13.08 $^{\circ}$ , 17.42 $^{\circ}$ , 19.02 $^{\circ}$ , 22.46 $^{\circ}$ , 26.1 $^{\circ}$ , 28.1 $^{\circ}$ , 30.12 $^{\circ}$ , 31.04 $^{\circ}$ ,

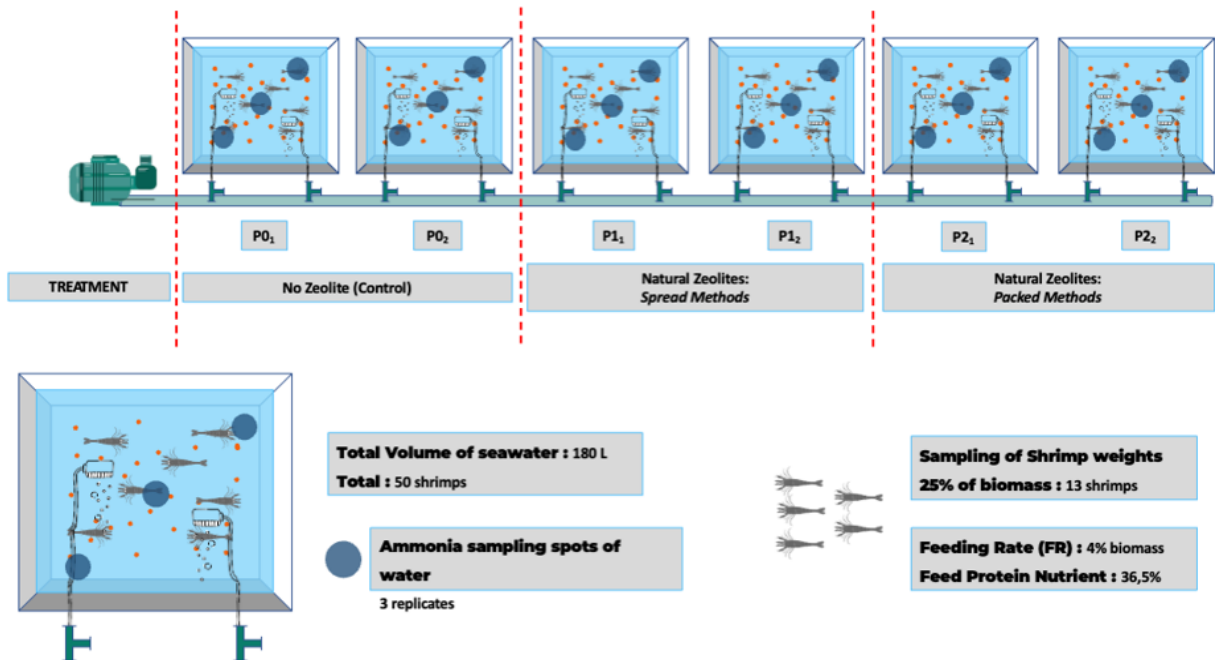


Figure 1. Schematic Figure of the Field Scale Experiments

31.96°, 32.76°, and 36.56°. These peaks, indicative of the zeolite's crystalline structure, match those found in the JCPDS No. 47-1870 reference chart, suggesting that Tanggamus natural zeolite predominantly consists of clinoptilolite. This type of zeolite has also been widely reported to constitute the majority of natural zeolite from various geological sources (Akgül and Karabakan, 2011; Wang et al., 2022; Karadag et al., 2006; Vassileva and Voikova, 2009; Kurniawan et al., 2022).

Upon calcination at 200°C (ZB), minor shifts in peak positions were observed, along with changes in peak intensities. Most notably, the intensity of the peak at 22.44° decreased relative to the natural zeolite, suggesting possible structural alterations in the zeolite framework due to calcination (Zhang et al., 2022). By increasing the calcination temperature, the XRD pattern of exhibited more pronounced changes. For ZC, although the general pattern of its peaks remained similar to the natural zeolite, there were noticeable shifts in peak positions and variations in intensity, suggesting further changes to the zeolite framework (Kubota et al., 2021). For ZD, significant changes were evident. Some of the initial peaks disappeared, and new peaks emerged at 17.68°, 21.24°, 22.92°, 24.32°, 26.14°, 30.84°, and 71.88°. This drastic transformation in the XRD pattern indicates major structural changes in the zeolite framework at higher calcination temperatures (Saikumari et al., 2021).

The Fourier-transform infrared spectroscopy (FTIR) analysis was employed to further discern the structural transformations occurring within the Tanggamus Natural Zeolite following calcination at varying temperatures which can be seen in Figure

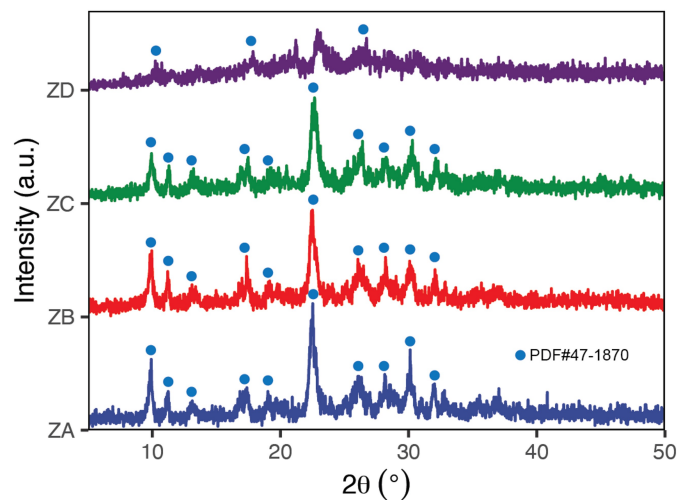
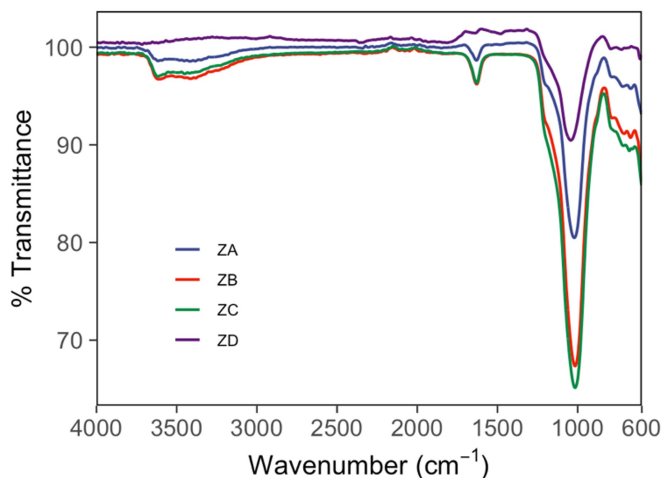


Figure 2. XRD Pattern of Natural and Calcined Tanggamus Zeolite; Natural Zeolite (ZA), Calcined Zeolite at 200°C (ZB), 400°C (ZC), and 600°C (ZD)

3. The FTIR spectrum of the natural zeolite (ZA) revealed distinct absorption bands at 3413, 1635, and 1026  $\text{cm}^{-1}$ . The band observed at 3413  $\text{cm}^{-1}$  is attributed to the O—H stretching vibration of the hydroxyl group (—OH) present within the zeolite structure (Hui et al., 2022; Derbe et al., 2021). These groups are usually associated with water molecules, either adsorbed onto the zeolite surface or trapped within its

porous structure. The absorption band at  $1635\text{ cm}^{-1}$  is likely related to the H—O—H bending or 'scissoring' vibrations of these encapsulated water molecules (Derbe et al., 2021). The most pronounced band, observed at  $1026\text{ cm}^{-1}$ , is typically linked to the asymmetric stretching vibration of the Si—O—Si or Al—O—Si bonds. These are the predominant bonds forming the crystalline framework of the zeolite (Wang et al., 2014).

The FTIR analysis indeed revealed noteworthy changes upon calcination. ZB, which was subjected to calcination at  $200^\circ\text{C}$ , displayed an FTIR spectrum highly resembling that of the natural zeolite, suggesting only minimal alterations to its molecular structure at this temperature. However, a significant decrease in the intensity of the bands at  $3413$  and  $1635\text{ cm}^{-1}$  became evident as the calcination temperature rose to  $400^\circ\text{C}$  (ZC). This trend became more pronounced for ZD, which was calcined at  $600^\circ\text{C}$ , leading to the total disappearance of these bands. These observations indicate that calcination resulted in the elimination of hydroxyl groups and associated water molecules from the zeolite structure, consistent with the recognized effects of calcination, which include the removal of physically adsorbed water and possible dehydration of the zeolite surface (Wang et al., 2014). Concurrently, the observed changes in the reduced intensity of the band at  $1026\text{ cm}^{-1}$  hint at alterations in the zeolite's crystalline framework. This could likely be due to the rearrangement or breaking of the Si—O—Si or Al—O—Si bonds brought about by the increasing calcination temperature (Derbe et al., 2021).



**Figure 3.** FTIR Spectra of Natural and Calcined Tanggamus Zeolite

The isotherm of nitrogen adsorption-desorption for the natural and calcined zeolite samples and their pore size distribution is shown in Figure 4. The acquired curves were found to align with a Type IV isotherm according to the IUPAC classification. The Type IV isotherm is characteristic of mesoporous materials, which corresponds well to the expected properties of the zeolite under study (Pérez-Botella et al., 2022; Delgado

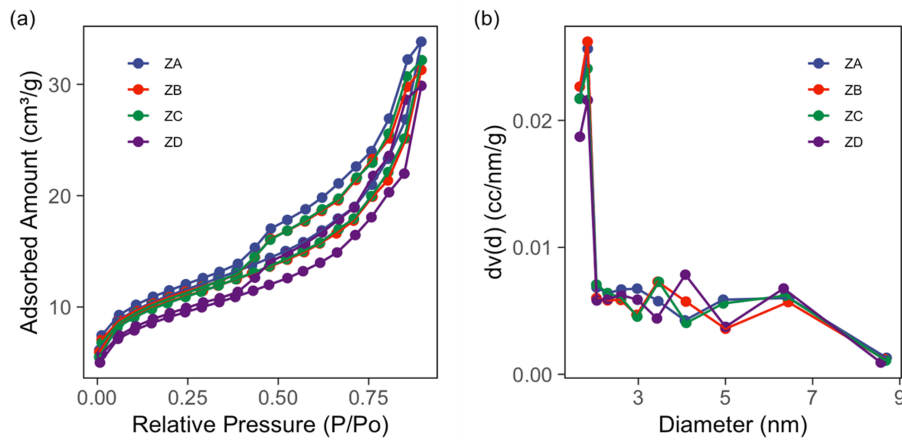
and Areal, 2018). More significantly, a hysteresis loop became discernible at a relative pressure ( $P/P_0$ ) of around 0.4. This phenomenon is typically indicative of capillary condensation occurring within mesopores and further confirms the mesoporous structure of the zeolites (Pan et al., 2017). The hysteresis loop also suggests the presence of networked irregularly shaped pores, which is a common characteristic of these natural zeolite materials (Liu et al., 2011).

The calculated BET surface area and pore properties of the zeolite samples are summarized in Table 1. Notably, the specific surface area ( $S_{BET}$ ) of the zeolites showed a decreasing trend with increasing calcination temperature, going from  $37.84\text{ m}^2/\text{g}$  for ZA to  $31.39\text{ m}^2/\text{g}$  for ZD. This finding suggests that the calcination process may lead to the collapse of the porous structure, causing a decrease in the available surface area for adsorption (Seraj et al., 2016). Similarly, the micropore area and micropore volume also exhibited a decline with increasing calcination temperature. This is consistent with the proposed idea that the calcination might lead to the collapse of the microporous structure, causing a decrease in the microporous volume (Florez et al., 2021). In contrast, the mesoporous volume of the zeolites did not show a significant change as the calcination temperature increased, suggesting that the mesoporous structure of the zeolites remained relatively stable under these conditions. The total pore volume also slightly decreased as the calcination temperature increased, but the effect was less pronounced than for the micropore volume, confirming the impact of calcination on the microstructure more than the mesostructure.

### 3.2 Lab Scale Ammonium Adsorption Test

The influence of calcination temperature on the ammonium adsorption capacity of the calcined zeolite samples was investigated. The result, as shown in Figure 5(a), demonstrates a decreasing trend in the ammonium adsorption capacity ( $Q_e$ ) with increasing calcination temperature. The zeolite sample calcined at  $200^\circ\text{C}$  exhibited the highest ammonium adsorption capacity, with a  $Q_e$  value of approximately  $5.88\text{ mg/g}$ . This high adsorption capacity can be attributed to the presence of a substantial number of active adsorption sites, providing an ideal surface for ammonium ion interaction.

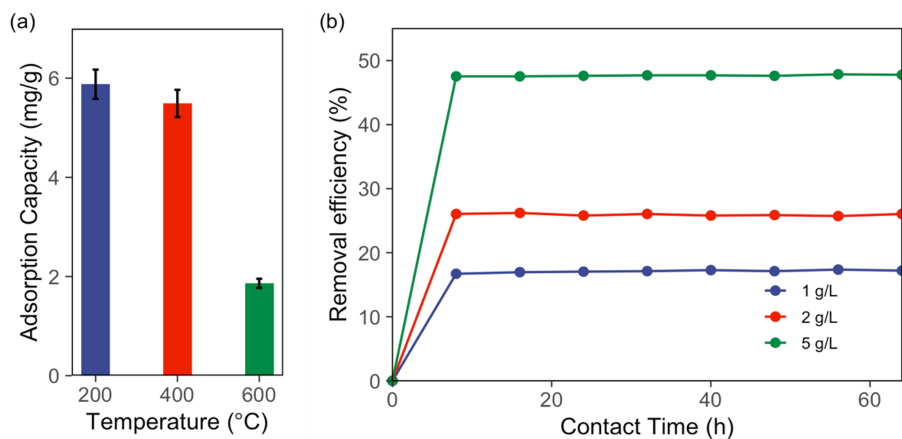
For the zeolite calcined at  $400^\circ\text{C}$ , a slight reduction in the adsorption capacity was observed, where the  $Q_e$  value was approximately  $5.49\text{ mg/g}$ . Despite the increase in calcination temperature, the zeolite maintains a reasonable capacity for ammonium adsorption, suggesting a moderate transformation in its microporous structure (Lin et al., 2013). A significant drop in adsorption capacity was detected for the zeolite sample calcined at  $600^\circ\text{C}$ , with a  $Q_e$  value of approximately  $1.86\text{ mg/g}$ . This substantial decrease indicates that high calcination temperatures lead to a major transformation of the zeolite structure, resulting in the reduction of active adsorption sites for ammonium ions (Liu et al., 2022). In addition, the zeolite structure at high temperatures could become more hydrophilic, which in turn reduces the affinity toward ammonium.



**Figure 4.** N<sub>2</sub> Adsorption Desorption-Desorption Isotherm (a) and Pore Size Distribution (b) of Natural and Calcined Zeolite

**Table 1.** The Calculated BET Surface Area and Pore Properties of the Zeolite Samples

Sample	$S_{BET}$ (m <sup>2</sup> /g)	Micropore Area (m <sup>2</sup> /g)	Mesopore Volume (cm <sup>3</sup> /g)	Mesopore Volume (cm <sup>3</sup> /g)	Total Volume (cm <sup>3</sup> /g)
ZA	37.84	10.54	0.0052	0.0472	0.0524
ZB	35.76	10.15	0.0050	0.0434	0.0485
ZC	35.85	9.23	0.0045	0.0453	0.0498
ZD	31.39	7.72	0.0037	0.0425	0.0463

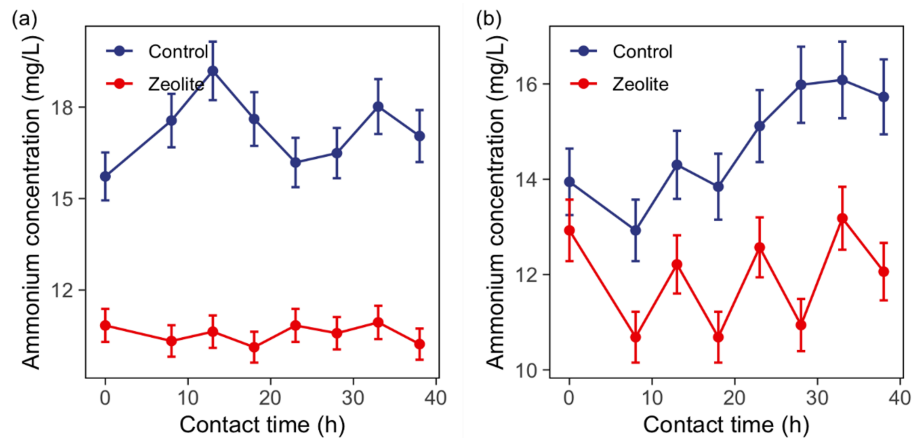


**Figure 5.** Effect of Zeolite Calcination Temperature (a) and the Effect of Contact Time (b) on the Removal Efficiency of Ammonium onto Calcined Tanggamus Zeolite at 200°C

In subsequent experiments, the focus was shifted toward zeolite sample ZB, which was calcined at 200°C. This decision was based on the previous result that showed ZB to have a reasonably high ammonium adsorption capacity. An investigation was then conducted on the effect of zeolite dosage on the adsorption capacity, with the aim of determining the optimal zeolite dosage for maximum ammonium removal. Three different dosages were tested, including 1, 2, and 5 g/L.

The results of these tests are illustrated in Figure 5(b). The

removal efficiency of ammonium was observed to increase with zeolite dosage (Guida et al., 2020). At a dosage of 1 g/L, the removal efficiency rose from 16.71% at 8 h to 17.36% at 56 h. When the zeolite dosage was increased to 2 g/L, the removal efficiency improved significantly, reaching 26.05%. The highest removal efficiency was observed at a zeolite dosage of 5 g/L, reaching up to 47.86% (Ham et al., 2018). These findings suggest that the removal efficiency of ammonium could be enhanced by increasing the zeolite dosage. This can be



**Figure 6.** The effect of Zeolite Treatment, (a) Under Direct Spreading, (b) Under the Packed Bag

attributed to the increased availability of adsorption sites as the zeolite dosage increase.

### 3.3 Application of Zeolite in the Field Scale

Following our laboratory-scale experiments, we sought to understand how our findings translated to a field-scale context. Our field studies were carried out in constructed shrimp ponds, simulating practical shrimp farming conditions. The experiment was conducted in three different treatment conditions. The experiment consisted of three different treatments. The first was a control treatment where no zeolite was added to the pond. The second involved the spreading of 5 g/L of calcined zeolite directly into the pond, while the third involved packing the same quantity of zeolite into bags before being placed into the pond. This was intended to explore the effect of zeolite application methods on its adsorption performance. The two variations of each treatment were implemented in separate ponds to improve the robustness of our findings.

The concentration of ammonium in each pond was monitored hourly and compared to evaluate the effectiveness of the applied treatments. Figure 6 shows the effect of each treatment on the concentration of ammonium. As expected, in the control ponds where no zeolite was added, the concentration of ammonium increased over time, reaching as high as 18.01 mg/L (Fu et al., 2020). In contrast, for the ponds where zeolite was directly spread, a significant reduction in ammonium concentration was observed. The concentration levels fluctuated between 10.12 and 10.94 mg/L, indicating an overall improved ammonium control compared to the control treatment. In the case where the zeolite was packed into bags before being placed into the pond, the ammonium concentration varied between 10.68 and 13.18 mg/L, which was lower than the control but slightly higher than the direct spreading method.

These findings suggest that the application of calcined zeolite effectively reduces the concentration of ammonium in shrimp ponds (Guida et al., 2020). The method of zeolite ap-

plication also appears to influence the adsorption performance, with the direct spreading method showing a slightly better performance than the packed method. The results from the field-scale experiment align with our laboratory-scale findings and demonstrate the practical applicability of using calcined zeolite for ammonium removal in shrimp pond wastewater. This further validates the potential of using calcined zeolite as a low-cost and efficient solution to manage ammonium levels in shrimp farming practices.

## 4. CONCLUSION

In conclusion, the investigation of the potential of calcined Tanggamus Natural Zeolite for the in-situ removal of ammonium from shrimp pond wastewater has been investigated. First, it can be found that calcination at 200°C was the optimal temperature to enhance the removal of ammonium from the aqueous solution, yielding a higher adsorption capacity than zeolite calcined at higher temperatures. In zeolite dosage investigation, it was found that 5 g/L dosage provided the highest ammonium removal efficiency. The field experiments in constructed shrimp ponds confirmed the laboratory finding. The ponds where calcined zeolite was applied demonstrated lower ammonium concentrations than the control ponds, validating the effectiveness of zeolite as an ammonium adsorbent in a practical context. Interestingly, the method of zeolite application influenced the adsorption performance. Directly spreading the zeolite in the ponds was slightly more effective than packing the zeolite into bags before placement. Our findings offer valuable insights that can guide the practical implementation of this method in shrimp farming practices. Future research should focus on long-term application effects and potential regeneration methods of the zeolite to further improve the economic and environmental efficiency of this method.

## 5. ACKNOWLEDGEMENT

The authors extend their acknowledgment to the Institut Teknologi Sumatera for the research funding that enabled the execu-

tion of this study. This endeavor was made possible through the GBU-45 research grant, registered under the contract number B/763d/IT9.C1/PT.01.03/2022. Furthermore, the authors would like to recognize the instrumental support and resources offered by the institution, playing a crucial role in the fruitful culmination of this research.

## REFERENCES

- Ahmad, A., S. R. S. Abdullah, H. A. Hasan, and A. R. Othman (2021). Plant-Based Versus Metal-Based Coagulants in Aquaculture Wastewater Treatment: Effect of Mass Ratio and Settling Time. *Journal of Water Process Engineering*, **43**; 102269
- Akgül, M. and A. Karabakan (2011). Promoted Dye Adsorption Performance Over Desilicated Natural Zeolite. *Microporous and Mesoporous Materials*, **145**(1-3); 157–164
- Ates, A. (2019). The Modification of Aluminium Content of Natural Zeolites with Different Composition. *Powder Technology*, **344**; 199–207
- Bernardi, F., I. V. Zadinelo, H. J. Alves, F. Meurer, and L. D. dos Santos (2018). Chitins and Chitosans for the Removal of Total Ammonia of Aquaculture Effluents. *Aquaculture*, **483**; 203–212
- Delgado, M. R. and C. O. Arean (2018). Non-Linear Enthalpy-Entropy Correlation for Nitrogen Adsorption in Zeolites. *Molecules*, **23**(11); 2978
- Derbe, T., S. Temesgen, and M. Bitew (2021). A Short Review on Synthesis, Characterization, and Applications of Zeolites. *Advances in Materials Science and Engineering*, **2021**; 1–17
- Florez, C., O. Restrepo-Baena, and J. I. Tobon (2021). Effects of Calcination and Milling Pre-Treatments on Natural Zeolites As a Supplementary Cementitious Material. *Construction and Building Materials*, **310**; 125220
- Fu, H., Y. Li, Z. Yu, J. Shen, J. Li, M. Zhang, T. Ding, L. Xu, and S. S. Lee (2020). Ammonium Removal Using a Calcined Natural Zeolite Modified with Sodium Nitrate. *Journal of Hazardous Materials*, **393**; 122481
- Gackowski, M., K. Tarach, J. Podobiński, S. Jarczewski, P. Kuśtrowski, and J. Datka (2018). Hierarchical Zeolites Y Obtained by Desilication: Porosity, Acidity and Catalytic Properties. *Microporous and Mesoporous Materials*, **263**; 282–288
- Guida, S., C. Potter, B. Jefferson, and A. Soares (2020). Preparation and Evaluation of Zeolites for Ammonium Removal from Municipal Wastewater through Ion Exchange Process. *Scientific Reports*, **10**(1); 12426
- Ham, K., B. S. Kim, and K.-Y. Choi (2018). Enhanced Ammonium Removal Efficiency by Ion Exchange Process of Synthetic Zeolite After Na<sup>+</sup> and Heat Pretreatment. *Water Science and Technology*, **78**(6); 1417–1425
- Hui, Y., J. Zheng, Y. Qin, X. Du, Y. Zu, J. Yang, S. Sun, X. Gao, Z. Sun, and L. Song (2022). Insight into the Nature and the Transformation of the Hydroxyl Species in the Cey Zeolite. *Inorganic Chemistry Frontiers*, **9**(7); 1354–1365
- Karadag, D., Y. Koc, M. Turan, and B. Armagan (2006). Removal of Ammonium Ion from Aqueous Solution Using Natural Turkish Clinoptilolite. *Journal of Hazardous Materials*, **136**(3); 604–609
- Kubota, K., N. Miyajima, and H. Sakane (2021). Influence of Calcination Atmosphere and Temperature on the Fluorescence Properties of NH<sub>4</sub>-Form Y-Type Zeolite. *Materials Letters*, **303**; 130485
- Kurniawan, T., N. Nuryoto, N. S. Fitri, H. S. Sofiyah, M. R. Bilad, K. Faungnawakij, and S. Thongratkaew (2022). Catalytic Acetalization of Glycerol Waste Over Alkali-Treated Natural Clinoptilolite. *Results in Chemistry*, **4**; 100584
- Lahav, O. and M. Green (1998). Ammonium Removal Using Ion Exchange and Biological Regeneration. *Water Research*, **32**(7); 2019–2028
- Lesbani, A., N. R. Palapa, R. J. Sayeri, T. Taher, and N. Hidayati (2021). High Reusability of NiAl LDH/Biochar Composite in the Removal Methylene Blue from Aqueous Solution. *Indonesian Journal of Chemistry*, **21**(2); 421–434
- Li, M., X. Zhu, F. Zhu, G. Ren, G. Cao, and L. Song (2011). Application of Modified Zeolite for Ammonium Removal from Drinking Water. *Desalination*, **271**(1-3); 295–300
- Lin, L., Z. Lei, L. Wang, X. Liu, Y. Zhang, C. Wan, D. J. Lee, and J. H. Tay (2013). Adsorption Mechanisms of High-Levels of Ammonium onto Natural and NaCl-Modified Zeolites. *Separation and Purification Technology*, **103**; 15–20
- Lin, Y. F., S. R. Jing, D. Y. Lee, and T. W. Wang (2002). Nutrient Removal from Aquaculture Wastewater Using a Constructed Wetlands System. *Aquaculture*, **209**(1-4); 169–184
- Liu, P., A. Zhang, Y. Liu, Z. Liu, X. Liu, L. Yang, and Z. Yang (2022). Adsorption Mechanism of High-Concentration Ammonium by Chinese Natural Zeolite with Experimental Optimization and Theoretical Computation. *Water*, **14**(15); 2413
- Liu, Z., C. A. Grande, P. Li, J. Yu, and A. E. Rodrigues (2011). Adsorption and Desorption of Carbon Dioxide and Nitrogen on Zeolite 5A. *Separation Science and Technology*, **46**(3); 434–451
- Muscarella, S. M., L. Badalucco, B. Cano, V. A. Laudicina, and G. Mannina (2021). Ammonium Adsorption, Desorption and Recovery by Acid and Alkaline Treated Zeolite. *Bioresource Technology*, **341**; 125812
- Nguyen, T. D., T. M. P. Nguyen, H. T. Van, L. H. Nguyen, T. D. Nguyen, T. H. V. Nguyen, T. H. H. Chu, T. H. Nguyen, L. Ha, and N. Vinh (2022). Adsorption Removal of Ammonium from Aqueous Solution Using Mg/Al Layered Double Hydroxides-Zeolite Composite. *Environmental Technology & Innovation*, **25**; 102244
- Palapa, N. R., N. Juleanti, R. Mohadi, T. Taher, A. Rachmat, and A. Lesbani (2020). Copper Aluminum Layered Double Hydroxide Modified by Biochar and Its Application As an Adsorbent for Procion Red. *Journal of Water and Environment Technology*, **18**(6); 359–371
- Pan, M., H. M. Omar, and S. Rohani (2017). Application of Nanosize Zeolite Molecular Sieves for Medical Oxygen



- Concentration. *Nanomaterials*, **7**(8); 195
- Pérez-Botella, E., S. Valencia, and F. Rey (2022). Zeolites in Adsorption Processes: State of the Art and Future Prospects. *Chemical Reviews*, **122**(24); 17647–17695
- Reeve, P. J. and H. J. Fallowfield (2018). Natural and Surfactant Modified Zeolites: A Review of Their Applications for Water Remediation with a Focus on Surfactant Desorption and Toxicity Towards Microorganisms. *Journal of Environmental Management*, **205**; 253–261
- Rožić, M., Š. Cerjan-Stefanović, S. Kurajica, V. Vančina, and E. Hodžić (2000). Ammoniacal Nitrogen Removal from Water by Treatment with Clays and Zeolites. *Water Research*, **34**(14); 3675–3681
- Saikumari, N., S. M. Dev, and S. A. Dev (2021). Effect of Calcination Temperature on the Properties and Applications of Bio Extract Mediated Titania Nano Particles. *Scientific Reports*, **11**(1); 1734
- Serafin, J., M. Ouzzine, O. F. C. Junior, and J. Sreńscek-Nazzal (2021). Preparation of Low-Cost Activated Carbons from Amazonian Nutshells for CO<sub>2</sub> Storage. *Biomass and Bioenergy*, **144**; 105925
- Seraj, S., R. D. Ferron, and M. C. Juenger (2016). Calcining Natural Zeolites to Improve Their Effect on Cementitious Mixture Workability. *Cement and Concrete Research*, **85**; 102–110
- Sodha, V., S. Shahabuddin, R. Gaur, I. Ahmad, R. Bandyopadhyay, and N. Sridewi (2022). Comprehensive Review on Zeolite-Based Nanocomposites for Treatment of Effluents from Wastewater. *Nanomaterials*, **12**(18); 3199
- Taher, T., Y. Irianty, R. Mohadi, M. Said, R. Andreas, and A. Lesbani (2019). Adsorption of Cadmium (II) Using Ca/Al Layered Double Hydroxides Intercalated with Keggin Ion. *Indonesian Journal of Chemistry*, **19**(4); 873–881
- Taher, T., A. Munandar, N. Mawaddah, M. S. Wisnubroto, P. M. S. B. N. Siregar, N. R. Palapa, A. Lesbani, and Y. G. Wibowo (2023). Synthesis and Characterization of Montmorillonite–Mixed Metal Oxide Composite and Its Adsorption Performance for Anionic and Cationic Dyes Removal. *Inorganic Chemistry Communications*, **147**; 110231
- Tom, A. P., J. S. Jayakumar, M. Biju, J. Somarajan, and M. A. Ibrahim (2021). Aquaculture Wastewater Treatment Technologies and Their Sustainability: A Review. *Energy Nexus*, **4**; 100022
- Vassileva, P. and D. Voikova (2009). Investigation on Natural and Pretreated Bulgarian Clinoptilolite for Ammonium Ions Removal from Aqueous Solutions. *Journal of Hazardous Materials*, **170**(2-3); 948–953
- Wang, C., J. Yu, K. Feng, H. Guo, and L. Wang (2022). Alkali Treatment to Transform Natural Clinoptilolite into Zeolite Na–P: Influence of NaOH Concentration. *Journal of Physics and Chemistry of Solids*, **168**; 110827
- Wang, J. Q., Y. X. Huang, Y. Pan, and J. X. Mi (2014). Hydrothermal Synthesis of High Purity Zeolite a from Natural Kaolin without Calcination. *Microporous and Mesoporous Materials*, **199**; 50–56
- Wang, S. and Y. Peng (2010). Natural Zeolites As Effective Adsorbents in Water and Wastewater Treatment. *Chemical Engineering Journal*, **156**(1); 11–24
- Yang, Y., Z. Chen, X. Wang, L. Zheng, and X. Gu (2017). Partial Nitrification Performance and Mechanism of Zeolite Biological Aerated Filter for Ammonium Wastewater Treatment. *Bioresource Technology*, **241**; 473–481
- Zhang, X., B. Wang, and J. Chang (2022). Effect of Zeolite Calcination Temperature on the Carbonation Degree and Strength of Steel Slag Compacts. *Construction and Building Materials*, **343**; 127987