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Modification of clinoptilolite zeolite adsorbent from Miyaneh mines to remove ammonia from the water environment

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ABSTRACT

Zeolite is well known for its excellent adsorption properties, making it a popular choice for water and wastewater treatment. However, clinoptilolite, the most common type of natural zeolite, has a relatively low capacity for ammonium adsorption. This study aimed to improve its performance by treating natural clinoptilolite with 1 M NaOH and KOH solutions. Batch experiments were conducted to examine how solution pH, contact time, initial ammonium concentration, adsorbent amount, and type of chemical modifier affect adsorption efficiency. The highest adsorption capacity was achieved with NaOH-treated clinoptilolite under optimal conditions: pH 8, 120 minutes contact time, 100 mg/L initial ammonium, and 4 g/L adsorbent, reaching a capacity of 17.03 mg/g. Desorption tests using 0.1 M NaCl over five cycles confirmed the reusability of the modified material with minimal performance loss. Isotherm modeling closely matched both Langmuir and Freundlich models, suggesting the coexistence of monolayer and multilayer adsorption processes. Overall, the modified clinoptilolite shows strong potential as an efficient and economical adsorbent for ammonium removal in wastewater treatment.

Highlights

- NaOH-modified clinoptilolite achieved 17.03 mg/g NH_4^+ adsorption capacity
- Optimal adsorption occurred at pH 8, 120 min, and 4 g/L adsorbent dose
- Adsorbent retained efficiency over 5 desorption–regeneration cycles
- Adsorption fitted well with the Langmuir and the Freundlich isotherm models

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1. Introduction

Water is a vital resource for life, and its contamination by industrial effluents poses a significant threat to the environment. Among industrial pollutants, ammonia is particularly harmful due to its high toxicity, ability to deplete dissolved oxygen, and adverse impact on aquatic ecosystems. Moreover, ammonia can alter the pH of water and soil, leading to biodiversity loss and increased toxicity. Therefore, developing effective methods to remove ammonia from industrial wastewater is crucial for preserving water resources and protecting the environment (Dong et al., 2019).

Various methods, including biological, chemical, and physical processes, have been explored for ammonia removal. Biological methods utilize microorganisms to convert ammonia into less harmful substances, while chemical methods involve reagents such as ferric sulfate for ammonia removal. Adsorption-based techniques are particularly attractive due to their high efficiency, low cost, and simplicity (Majid et al., 2019). Biological treatments, such as bacterial and fungal processes, effectively reduce ammonia concentrations and are considered sustainable because of their environmental compatibility (Morral et al., 2021). Chemical processes also play a major role, transforming ammonia into insoluble compounds for easy removal (Kartohardjono et al., 2012). Advanced technologies like photodegradation, membrane filtration, and electrocoagulation have shown to be effective in ammonia removal, offering benefits such as high efficiency at low concentrations and scalability. However, these methods can be costly and energy-intensive, and membrane filtration may experience fouling issues over time (Zolfaghari et al., 2020).

Adsorption has proven to be an effective method for reducing ammonia levels in water. Adsorbents such as activated carbon, zeolites, and silica gel have demonstrated excellent ammonia removal capabilities, particularly at low to moderate concentrations. This method has gained widespread attention due to its high efficiency, relatively low cost, ease of implementation, and lack of harmful by-products. A significant advantage of adsorption is the potential for adsorbent regeneration, either through thermal decomposition or acidic washing, enabling their reuse. Natural adsorbents such as zeolites are particularly attractive due to their environmental compatibility and ability to perform under diverse conditions. Furthermore, their capacity to simultaneously remove multiple pollutants and their adaptability to various scales make them a promising solution for water treatment. Studies have shown that by selecting the appropriate adsorbent and optimizing operational parameters, ammonia can be effectively removed from industrial wastewater and contaminated water sources (Yadav et al., 2023).

Among various adsorbent materials, zeolites are recognized as the most widely used aluminosilicates. Their key features include high abundance, excellent chemical and thermal resistance, a large specific surface area, and notable ion exchange capacity. Zeolites have a tetrahedral framework in which the central atom is either silicon (Si^{4+}) or aluminum (Al^{3+}), surrounded by four oxygen atoms. When Si^{4+} is present, the framework remains electrically neutral; however, substitution by Al^{3+} introduces a negative charge, which is balanced by exchangeable cations within the zeolite's channels and pores. This enables the adsorption of organic vapors, water pollutants, metal ions, and other contaminants. Moreover, their unique structure supports the decomposition and separation of adsorbed molecules, facilitating adsorbent regeneration and reuse (Stocker et al., 2019).

Zeolites are categorized as either natural or synthetic, with clinoptilolite being the most abundant natural zeolite in Iran. Clinoptilolite has received significant attention in water and wastewater treatment applications due to its high porosity, excellent ion exchange capacity, and cost-effectiveness. Notably, it exhibits strong selectivity toward ammonium ions, with ammonia removal occurring via ion exchange with cations such as sodium and potassium. The efficiency of this process depends on various factors, including the nature and concentration of coexisting ions, pH levels, and the crystalline structure of the zeolite. The properties of natural zeolites vary depending on the geological conditions under which they were formed. Consequently, modifying zeolite structures to enhance their adsorption performance has become a key area of research (Huang et al., 2018).

Among adsorbents, zeolites, particularly clinoptilolite, stand out due to their high ion exchange capacity and cost-effectiveness. Clinoptilolite's ability to adsorb ammonia through ion exchange with cations like sodium and potassium makes it a promising solution for wastewater treatment. Structural modifications, such as surface treatments, have been shown to enhance its adsorption capacity (Zolfaghari et al., 2020).

Recent research has shown that surface modification of clinoptilolite with compounds such as magnetite, sodium chloride, and cationic surfactants can increase its ammonia adsorption capacity by up to 40% (Zolfaghari et al., 2024). Additionally, reducing the particle size of this adsorbent from 2 mm to 0.5 mm has improved the removal efficiency from 82% to 93%. Another study revealed that incorporating clinoptilolite with iron nanoparticles enhanced adsorption capacity by 78%, reaching 22.3 mg/g (Taghizadeh et al., 2021). Moreover, regeneration studies have demonstrated that clinoptilolite can recover up to 85% of its adsorption capacity through washing with saline solutions (Fadillah and Chasanah., 2020).

Building on these advancements, this study aims to enhance the ammonia removal capacity of clinoptilolite through chemical modification with KOH and NaOH. It focuses on comparing the efficiency of modification techniques and optimizing operational parameters for improved performance in wastewater treatment.

2. Materials and Methods

2.1 Materials

In this study, clinoptilolite zeolite sourced from the Miyaneh mines was used as the adsorbent. For the modification process, potassium hydroxide (KOH, analytical grade, ≥85% purity, Merck, Germany) and sodium hydroxide (NaOH, analytical grade, ≥98% purity, Merck, Germany) were employed. Sodium hydroxide (NaOH) and hydrochloric acid (HCl, analytical grade, 37% w/w, Merck) were utilized for pH adjustment. Ammonium chloride (NH_4Cl, ≥99.5%, Merck, Germany) was used to prepare the standard ammonia solution, while potassium iodide (KI, ≥99%, Merck) and mercuric chloride ($HgCl_2$, ≥99.5%, Merck) were utilized in the preparation of Nessler's reagent. Distilled water was used throughout all experimental procedures.

2.2 Preparation of adsorbents

Initially, clinoptilolite was ground and sieved through a 200 µm mesh. To remove impurities, the sieved zeolite was continuously stirred in distilled water for 60 min. Subsequently, the solid phase was separated through filtration and washed multiple times with deionized water to ensure the complete removal of contaminants. The obtained sample was then dried in an oven at 100 °C for 2 h to eliminate residual moisture, and this processed zeolite was designated as Clin (Fu et al., 2020).

For chemical modification, 1 M solutions of KOH and NaOH were used. Specifically, 5 g of Clin was placed in glass containers, and 100 ml of the respective alkaline solutions was added to each container. The resulting mixtures were stirred magnetically for 24 h at a temperature range of 80–100 °C. Following the modification process, the solid phase was separated using 0.45 µm membrane filters and washed with deionized water until the pH of the effluent reached 7. Finally, the obtained material was dried in an oven at 100 °C for 24 h. To ensure uniform particle size, the modified samples were re-sieved using a 200 µm mesh. The zeolites modified with

NaOH and KOH were denoted as NaOH/Clin and KOH/Clin, respectively (Yuan et al., 2018).

2.3 Preparation of standard ammonium chloride solution

To prepare a 1000 ppm standard solution of ammonium chloride, the ammonium chloride salt was first dried in an oven at 100 °C for 1 h. Then, 3.813 g of the dried salt was accurately weighed and transferred into a 1000 ml volumetric flask. The volume was adjusted with distilled water, and the solution was stirred using a magnetic stirrer to ensure complete dissolution of the ammonium chloride powder (Safie et al., 2020).

2.4 Measurement of Ammonia Concentration Using the Nessler Method

Ammonia concentration was determined using the Nessler method, following the NH_3-N-4500 standard protocol, within the concentration range of 0.1 – 3 mg/l. A spectrophotometer was used for measurement (Safie et al., 2020), with the maximum absorbance wavelength set at $\lambda_{max} = 425$ nm, and all experiments were conducted at this wavelength.

For calibration curve preparation, a 1000 ppm standard ammonium chloride solution was diluted to prepare solutions with concentrations of 0.2, 0.4, 0.6, 0.8, 1, 1.4, 1.8, 2.2, 2.6, and 3 ppm. If the ammonia concentration exceeded this range, the sample was diluted accordingly (Cheng et al., 2017).

Per the standard protocol, 50 ml of the wastewater sample and distilled water (as a blank) were separately transferred into graduated cylinders. To each cylinder, 3 drops of mineral stabilizer solution (tartrate) were added to eliminate interference from magnesium and calcium cations, followed by 3 drops of polyvinyl alcohol to aggregate the ammonia. After homogenization, 1 ml of Nessler's reagent was added to each cylinder. Finally, the ammonia concentration was determined using the pre-constructed calibration curve (Fig. 1).

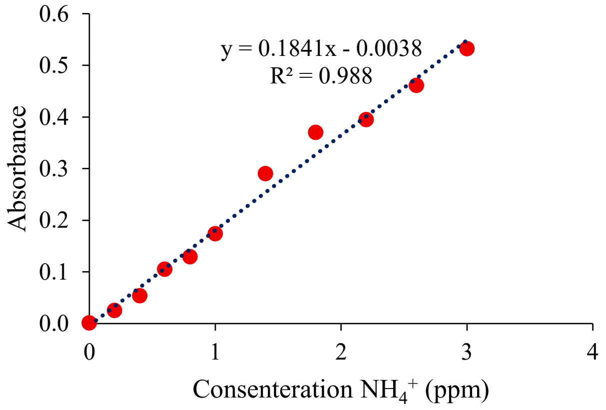


Fig. 1 Calibration curve for measuring ammonia concentration

2.5 Conducting ammonia adsorption experiments

The adsorption experiments were conducted in a batch system using 100 ml samples containing ammonia at concentrations ranging from 25 to 200 mg/l. The experimental conditions were set with a pH range of 2 to 12, adsorbent dosage of 1.0 to 6.0 g/l, and contact times between 20 - 240 min. The samples were agitated at a speed of 180 rpm at a temperature of 25 °C. After the contact time was completed, the liquid phase of the solution was separated by centrifugation, and the ammonia concentration was measured using a Nessler reagent. The removal percentage (R%) and the amount of substance removed (q_t) were calculated using Eqs. 1 and 2, respectively (Benmessaoud et al., 2020).

$$R\% = \frac{C_i - C_t}{C_i} \times 100 \tag{1}$$

$$q_t = \frac{V \times (C_i - C_t)}{m} \tag{2}$$

In these equations, q_t is the amount of ammonia adsorbed per unit mass of adsorbent (mg/g), C_i is the initial ammonia concentration (mg/l), C_t is the ammonia concentration (mg/l) at time t (min), V is the solution volume (l), mmm is the adsorbent mass (g), and R is the adsorption efficiency (%) (Elwakeel et al., 2021).

2.6 Adsorption Isotherm Study

Analyzing and quantifying equilibrium data in the adsorption process is among the most crucial methods for improving the results obtained in the final design, aiming to introduce a suitable adsorbent. Several different isotherm equations have been proposed to model adsorption data. In this study, both Langmuir and Freundlich adsorption isotherms were used. The Langmuir adsorption isotherm is expressed by Eq. 3 (Elwakeel et al., 2020).

$$\frac{C_e}{q_e} = \frac{1}{q_0 \cdot K} + \frac{C_e}{q_0} \tag{3}$$

where, q_0 and K_L are Langmuir constants, which are related to the adsorption capacity and energy of adsorption, respectively. q_m represents the maximum adsorption capacity of the adsorbent, which is covered by the adsorbate in a monolayer. K_L is considered a measure of the adsorption enthalpy. By plotting the linear curve of c_e/q_0 versus C_e, the slope of the line will be equal to $1/q_0$, and the intercept will be equal to $1/q_0 \, . \, k$. These relationships allow for the calculation of the maximum adsorption capacity and K_L (Zhao et al., 2010). The Freundlich adsorption isotherm is also presented by Eq. 4 (Khalil et al., 2018).

$$q_e = K_f \, . \, C_e^{1/n} \tag{4}$$

where, K_f and n are the constants of the Freundlich model. To calculate these constants, the logarithm of Eq. 4 must first be taken, and by plotting the linear curve of $\ln C_e$ versus $\ln C_e$ in Eq. 5, the slope of the line will be $\frac{1}{n}$, and the intercept will be $ln\, K_f$ (Zolfaghari et al., 2024).

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

3. Results and Discussion

3.1 FTIR

FTIR spectroscopy was used to identify functional groups and confirm the chemical modification process of natural clinoptilolite. The results from this analysis are shown in Fig. 2. The peaks in the 1450-1550 cm^{-1} range are attributed to the vibrations of Na-O and K-O bonds. Smaller peaks in the 600-1850 cm^{-1} range are related to bending vibrations of Si-O and Al-O bonds (Majid et al., 2019). The sharpest peak at 1054 cm^{-1} corresponds to the asymmetric vibrations of Si-O-Si and

Si-O-Al. Additionally, the change in peak intensity in the 1650-1630 cm^{-1} range indicates the presence of adsorbed water.

The increase in peak intensity in the 3400-3600 cm^{-1} range, characteristic of the stretching vibrations of OH groups, confirms the increase in hydroxyl groups on the surface of the zeolite after alkaline modification (Radoor et al., 2021). These spectral changes indicate the successful alkaline modification process and the creation of favorable structural changes in the zeolite.

Overall, the FTIR results suggest that alkaline modification leads to significant changes in the surface structure of the zeolite. Particularly, the increase in hydroxyl groups after modification reflects chemical changes that could improve the adsorption performance of the zeolite. These spectral changes also indicate the success of the alkaline modification process, which effectively alters the surface characteristics of the zeolite and enhances its adsorption capacity.

Fig. 2 FTIR analysis of natural clinoptilolite, Clin, KOH/Clin, and NaOH/Clin adsorbent

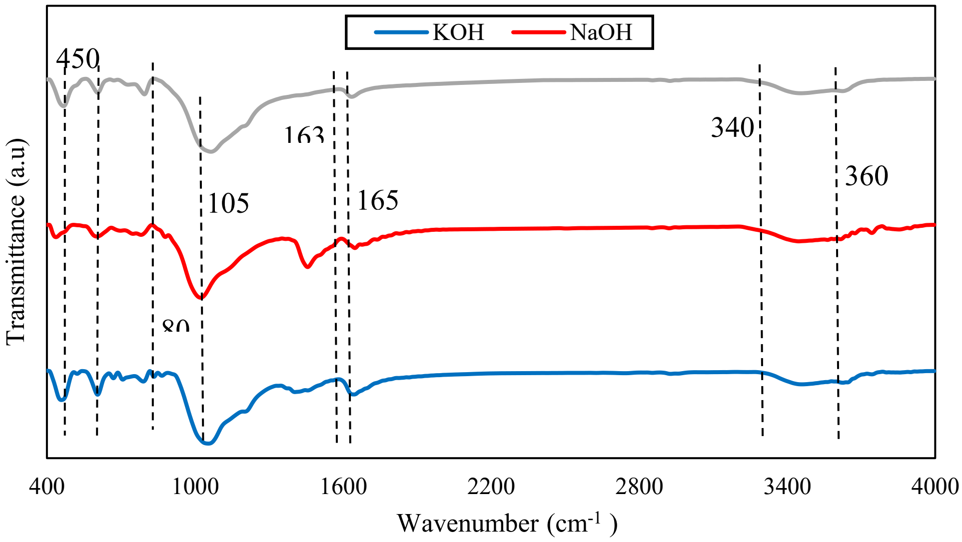


Table 1 shows the correlation matrix, highlighting the interactions among every pair of water quality factors. In statistical analysis, this matrix is a useful instrument since it helps one understand the interactions among several parameters. Regarding water quality, it improves knowledge of interdependence among several indicators. Dissolved oxygen (DO) shows a notable negative correlation with respect to parameters including nitrate, phosphate, biochemical oxygen demand (BOD), and chemical oxygen demand (COD.). This inverse link implies that DO levels drop as the organic load in the water rises, mostly from microbial activity consuming oxygen to break down organic matter. Reflecting the biological state of the water body, this correlation is a major in evaluations of water quality. Usually, this negative correlation highlights the detrimental impact of organic and nutrient pollution on aquatic ecosystems, as it leads to reduced oxygen availability, which can harm aquatic life and disrupt ecological balance.

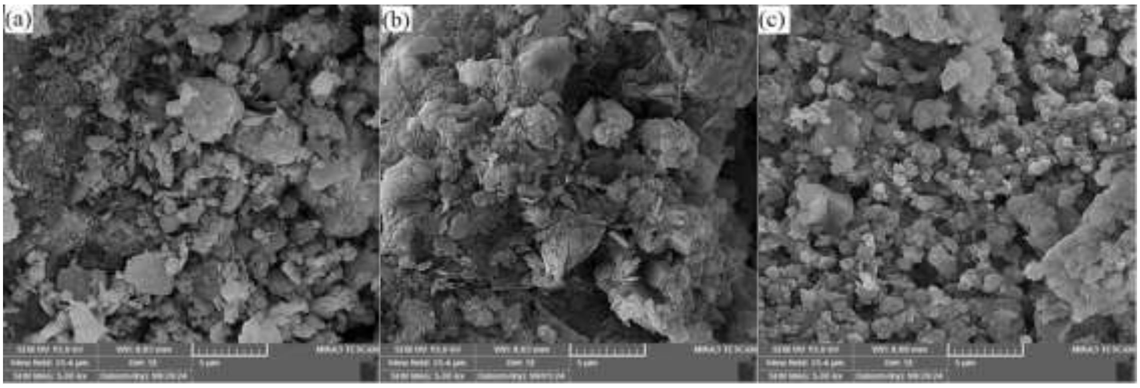


Fig. 3 SEM images of :a) natural clinoptilolite Clin, b) KOH/Clin adsorbent, and c) NaOH/Clin adsorbent

3.2 SEM

To examine the morphology and structural changes of the modified adsorbents, SEM images were used, and the results are shown in Fig. 3 (a-c). Fig. 3a shows that natural clinoptilolite has a crystalline, layered, and irregular structure with a rough surface and limited pore space. In contrast, Fig. 3b, which corresponds to KOH-modified clinoptilolite, shows a significant increase in porosity and surface roughness compared with the natural sample, indicating structural changes due to the alkaline modification. Fig. 3c, representing NaOH-modified clinoptilolite, shows a noticeable increase in porosity and the formation of a more porous and homogeneous structure, which is more uniform compared to the KOH-modified sample. A comparison between KOH- and NaOH-modified clinoptilolite revealed that both methods enhance porosity and improve the adsorbent's surface, but there are differences in the intensity of the structural changes. Modification with NaOH has a milder effect on the zeolite structure, preventing excessive destruction of the crystalline network while increasing porosity and surface area.

Comparing the modified forms with the natural sample showed that alkaline modification significantly increases the adsorbent’s active surface and creates a more porous structure. While natural clinoptilolite has a dense and heterogeneous structure, the modified samples have networks with larger pores and better dispersion, which can lead to higher pollutant removal efficiency. These differences indicate the impact of the modification method on the final performance of the adsorbent in the ammonia removal process (Yin et al., 2018).

These structural changes confirm the effective interaction between the adsorbent surface and the alkaline modifying agents. Alkaline modification with NaOH, compared to KOH, has a milder effect on the zeolite structure, preventing excessive destruction of the crystalline network while increasing porosity and surface area. This characteristic plays a crucial role in enhancing the adsorbent's performance and increases active sites for ammonium ion adsorption. In contrast, modification with KOH, due to its more intense effect, may overly alter the zeolite structure and, in some cases, negatively impact adsorption performance by reducing structural strength. These differences illustrate the impact of the modification method on the final efficiency of the adsorbent in the ammonia removal process (Mirzaei et al., 2019).

3.3 Ammonia adsorption results by adsorbents

3.3.1 pH

One of the most important factors affecting ammonia adsorption is the pH of the contaminant solution. pH, as a key parameter, significantly influences the adsorption process at the water-adsorbent interface. The effect of hydrogen ion (H^+) concentration on the capacity and percentage of ammonia adsorption by natural clinoptilolite and its modified forms with NaOH and KOH is shown in Fig. 4. The adsorption experiments were carried out under controlled conditions with a process time of 120 min and an ammonia concentration of 100 mg/l. As shown, initially, as the pH increases, both capacity and percentage of adsorption increase, reaching their peak around pH 8. After this point, as the pH continues to increase, both capacity and percentage of adsorption begin to decline. This behavior can be explained by the fact that at pH values above 8, ammonium ions (NH_4^+) convert to ammonia (NH_3), and the NH_3 molecules are unable to exchange ionically with the zeolite, leading to a decrease in adsorption. Under acidic conditions (pH<5), ammonia removal is likely reduced due to an increase in hydrogen ion concentration in the solution, which competes with ammonium ions to occupy zeolite exchange sites (Jahangiri et al., 2019).

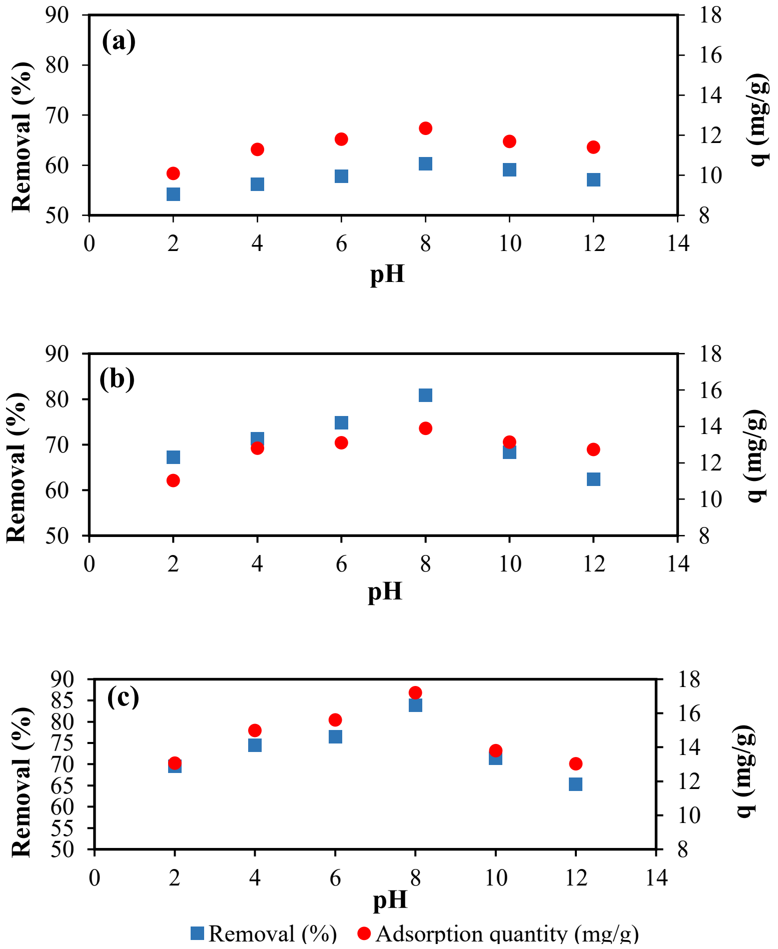


Fig. 4 Effect of solution pH on the removal efficiency and adsorption capacity of ammonia by a) natural clinoptilolite (Clin), b) KOH/Clin adsorbent, and c) NaOH/Clin adsorbent

For a better comparison, the effect of liquid-phase pH on ammonia adsorption efficiency by all three adsorbents is presented in Fig. 5. The results indicate that pH has a significant impact on the adsorption process, with all adsorbents following a distinct pattern in response to pH changes. Notably, among the adsorbents studied, the NaOH-modified adsorbent showed the best adsorption efficiency. This improvement can be attributed to the increased ion exchange capacity resulting from the substitution of sodium (Na^+) ions in the zeolite structure. Sodium has a larger ionic radius compared to potassium (K^+), allowing it to occupy exchange sites more effectively, which leads to an increase in ammonium adsorption capacity (Guo et al, 2016).

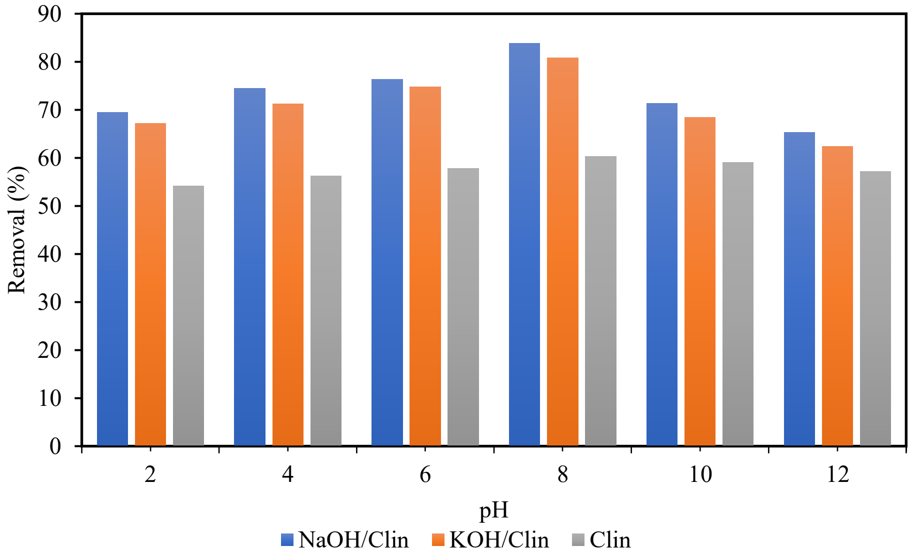


Fig. 5 The effect of environmental pH on the efficiency of ammonia adsorption by different adsorbents

3.3.2 Adsorbent Amount

Another factor affecting the efficiency and amount of adsorption by adsorbents is the quantity of adsorbent used. To investigate the effect of this parameter, the amounts of all three adsorbents (Clin, KOH/Clin, and NaOH/Clin) were varied in the range of 1 to 6 g/l, and an ammonia concentration of 100 mg/l was used at a pH of 8, with a contact time of 120 min and a temperature of 25 °C. The results are shown in Fig. 6. The findings showed an initial increase in ammonia removal efficiency with higher adsorbent dosages, which aligns with results from previous studies (Qin et al., 2020). However, after reaching an optimal adsorbent dose of 4 g/l, the removal efficiency plateaued, indicating the system had reached its saturation point. This phenomenon is commonly attributed to factors such as limited available adsorption sites, particle aggregation, and mass transfer limitations, which reduce the driving force for adsorption (Elgarahy et al., 2019). Moreover, while increasing the adsorbent amount adds more active sites, the lack of sufficient ammonia molecules and the clustering of adsorption sites can reduce the total surface area available for adsorption. This phenomenon has been widely observed in the literature, with similar findings reported for other adsorbents (Majid et al., 2019). Therefore, after the system reaches its maximum adsorption capacity, further increases in adsorbent amount do not significantly improve ammonia removal.

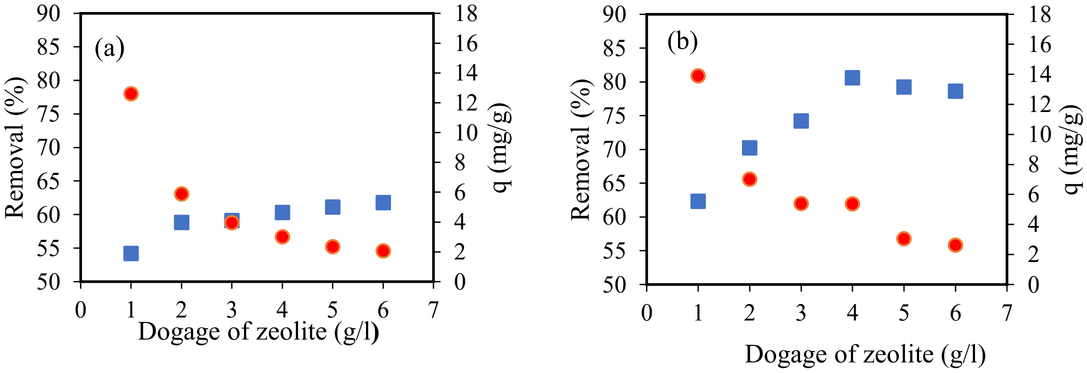
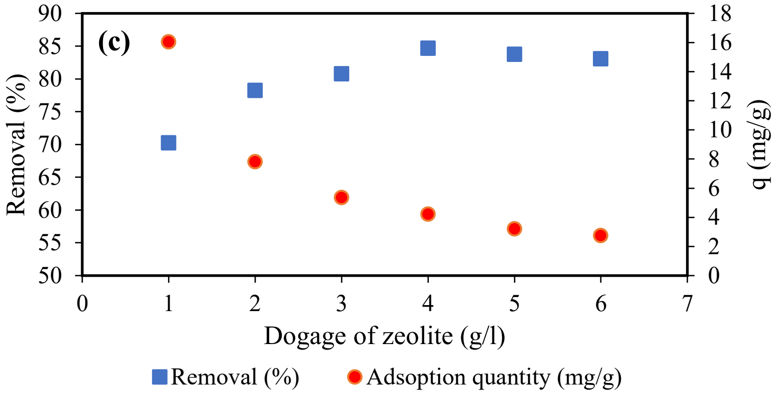


Fig. 6 The effect of adsorbent amount on the efficiency and capacity of ammonia absorption by a) natural clinoptilolite Clin, b) KOH/Clin adsorbent, and c) NaOH/Clin adsorbent



3.3.3 Contact time

Another important factor affecting the adsorption process is the duration of contact between the adsorbent and the contaminant. To investigate this parameter, contact times ranging from 20 to 240 min were considered (Yadav et al., 2023). Other parameters, such as the initial concentration of ammonium chloride in the solution (50 and 100 mg/l), adsorbent dose (4 g/l for both adsorbents), and pH (8 for both adsorbents), were kept constant. The results are shown in Fig. 7. It can be observed that during the initial stages, adsorption progresses rapidly and intensively. The rate of ammonia adsorption is initially fast due to the availability of vacant sites and active functional groups on the adsorbent surface. However, as time passes, these vacant sites become occupied, resulting in reduced access for ammonia molecules to the active sites. Eventually, 120 min was selected as the optimal contact time (Yin et al., 2018).

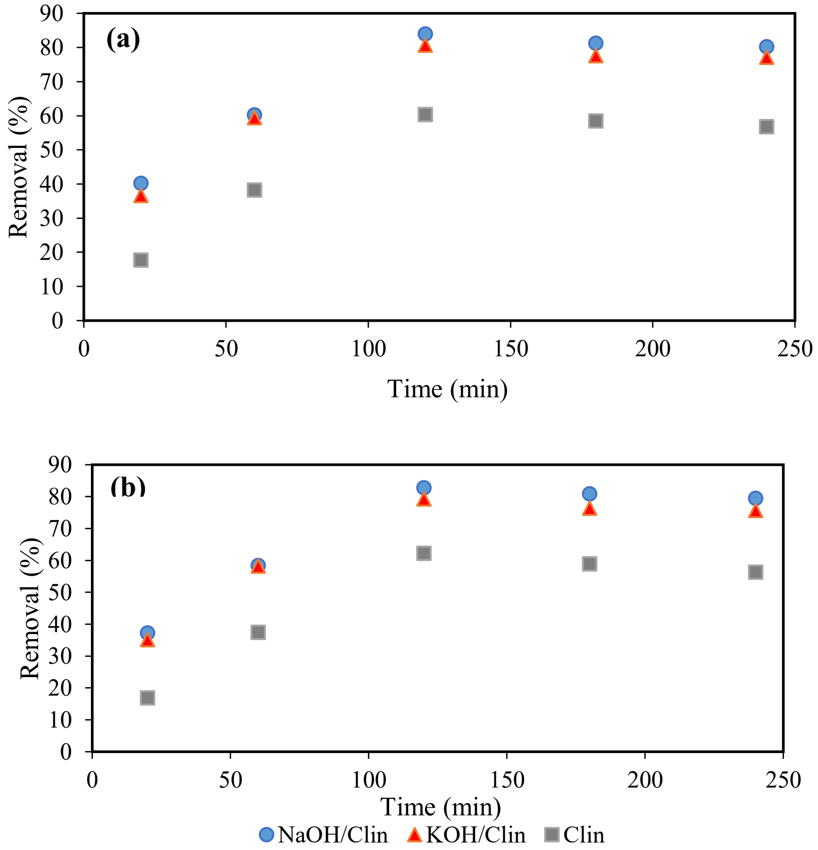
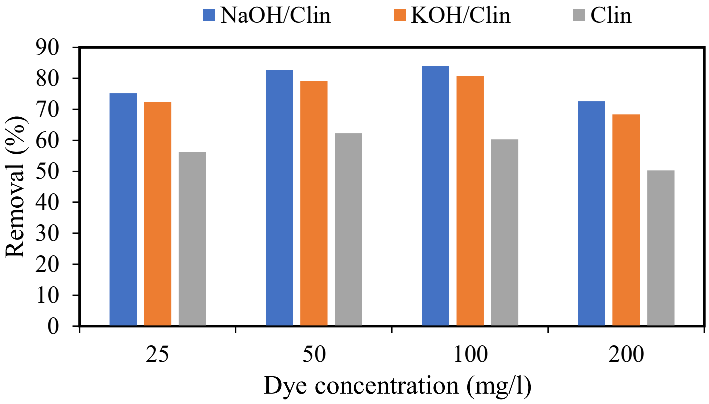


Fig. 7 Effect of contact time on ammonia absorption efficiency (a) initial concentration of ammonia 100 mg/l and (b) initial concentration of ammonia 50 mg/l

3.3.4 Initial ammonia concentration

The amount of ammonia adsorbed on the adsorbent surface is highly dependent on its initial concentration in the solution. In this study, to evaluate the effect of this parameter, initial ammonia concentrations ranging from 25 to 200 mg/l were examined. Similar to the effects of other factors, the other variables were kept constant at pH 8, adsorbent dose of 4 g/l, and a contact time of 120 min. The results are presented in Fig. 8. It is observed that as the initial ammonia concentration increases from 25 to 100 mg/l, the adsorption efficiency for natural clinoptilolite, KOH/Clin, and NaOH/Clin adsorbents initially increases. This is because the higher concentration results in more collisions between ammonia ions and the adsorbent surface, and the active adsorption sites on clinoptilolite are not yet saturated. However, as the ammonia concentration increases from 100 to 200 mg/l, the adsorption efficiency starts to decrease. This can be attributed to the saturation of the active sites on the adsorbent surface by ammonia molecules. In other words, the active sites on the adsorbent surface are limited, and the number of ammonia molecules continues to increase. When ammonium ions exchange with ions such as Na^+ or K^+, the number of active sites required for ammonia adsorption decreases, which reduces the interaction between ammonia molecules and the adsorbent surface, leading to a decrease in adsorption. In this study, the maximum adsorption efficiency was obtained at an ammonia concentration of 100 mg/l (Ghadiri et al, 2012).

Fig. 8 Effect of initial ammonia concentration on ammonia absorption efficiency



3.4 Desorption Behavior

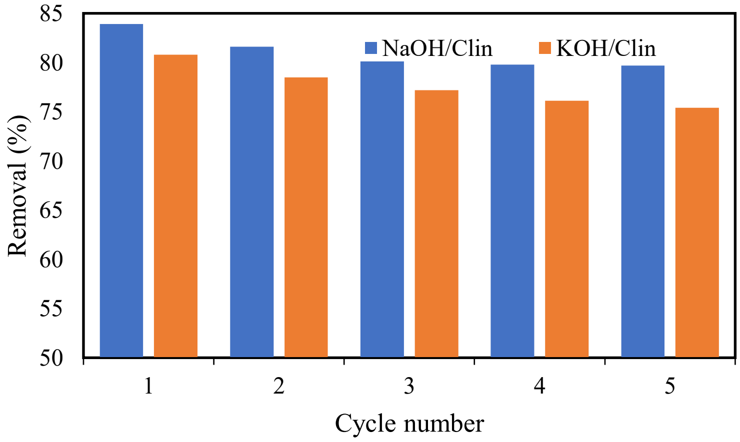
To evaluate the recovery capability and desorption capacity of the NaOH and KOH-modified adsorbents for ammonia removal, a sodium chloride solution was used in the desorption process. The results of the desorption experiments, conducted over five consecutive adsorption-desorption cycles, are presented in Fig. 9.

After each adsorption cycle, the adsorbents were carefully separated from the solution and rinsed with distilled water. To facilitate the desorption process, the adsorbents were agitated in a sodium chloride solution for 6 h. After the required time, the adsorbents were filtered from the solution, and the remaining ammonia concentration in the solution was measured using spectrophotometry. The amount of ammonia desorbed was calculated based on Eq. 6. These results highlight the potential for the recovery and reuse of the adsorbents, emphasizing their stability and cost-effectiveness for practical applications (Han et al., 2021).

$$\text{Desorption\%} = \left(\frac{C_m}{C_e}\right) \times 100 \tag{6}$$

After each adsorption cycle, the adsorbents were thoroughly washed with distilled water and then agitated for 6 hours in the sodium chloride solution. The ammonia removal efficiency gradually decreased, with the NaOH-modified adsorbent efficiency dropping from 83.9% in the first cycle to 81.6%, 80.1%, 79.8%, and 79.7%, and the KOH-modified adsorbent efficiency decreasing from 80.8% in the first cycle to 78.5%, 77.2%, 76.1%, and 75.4% in subsequent cycles, demonstrating the adsorbents' good potential for reuse.

Fig. 9 Desorption behavior of NaOH/Clin and KOH/Clin adsorbent in NaCl solution



3.5 Adsorption isotherm study

The adsorption capacity and Langmuir constant (K_L) coefficients were calculated using linear regression and are presented in Table 1. Additionally, the Freundlich model coefficients were also calculated using linear regression, and the Freundlich constant is provided in the same table. The results in Table 1 indicate that the modified adsorbents show a significant fit to both the Langmuir and the Freundlich isotherms. Among the adsorbents studied, the NaOH-modified adsorbent performed better than the KOH-modified adsorbent. The coefficient of determination (R^2) for the Langmuir and Freundlich isotherm models for the NaOH-modified zeolite in ammonia removal was 0.99 and 0.95, respectively. According to Table 1, the maximum adsorption capacity (q_m) for the NaOH-modified zeolite, as calculated from the Langmuir isotherm model, was 17.03 mg/g.

Table 1 Langmuir and Freundlich isotherm parameters regarding ammonia adsorption on the studied adsorbents

Adsorbent Materials	Langmuir			Freundlich		
	q_m (mg/g)	K_L (l/mg)	R^2	n	K_f	R^2
Clin	10.08	0.044	0.97	1.61	0.58	0.93
KOH/Clin	13.18	0.021	0.98	2.45	0.45	0.98
NaOH/Clin	17.03	0.039	0.99	2.82	0.43	0.95

Furthermore, the separation factor (R_L) for this zeolite, at initial ammonia concentrations ranging from 25 to 100 ppm was between 0.561 and 0.204. The value of $\frac{1}{n}$ for the Freundlich model was calculated as 0.354. Since the R_L and $1/n$ values are between zero and one, it can be concluded that the ammonia adsorption by the NaOH-modified zeolite is favorable according to both the Langmuir and the Freundlich models. These findings emphasize the importance of surface modification of adsorbents and suggest that the use of NaOH in the modification process significantly improves the adsorption performance. In general, the modified zeolites showed a higher ammonia adsorption efficiency compared to the unmodified samples (Han et al., 2021).

3.6 Comparison of results

The comparison of the results from this study with previous research on ammonia removal using various adsorbents demonstrates the significant effectiveness of NaOH-modified clinoptilolite. Table 2 provides a summary of key parameters, including maximum adsorption capacity, optimum contact time, ideal pH, and adsorption percentage for the modified adsorbent in this study, along with other adsorbents reported in the literature. The results show that NaOH-modified clinoptilolite in this study, with a maximum adsorption capacity of 17.03 mg/g, exhibits comparable performance to many advanced adsorbents reported in previous studies. For example, Habiba (2017) reported an adsorption capacity of 8.83 mg/g for zeolite modified with polyvinyl alcohol, while our adsorbent showed a higher capacity. The optimum contact time of 120 min obtained in this study is shorter compared to those reported in some other studies (e.g., 600 min in Wang et al., 2016), indicating a faster adsorption rate for our adsorbent. This feature can be highly beneficial in industrial applications where process time is crucial. The optimal pH of 8 for ammonia adsorption in this study aligns with most previous studies that report an optimal pH range of 7-9. This result indicates that our adsorbent performs well under near-neutral to slightly alkaline conditions, typically found in wastewater containing ammonia.

Table 2 Comparison of adsorption capacities and other parameters for ammonia removal by different adsorbents

Adsorbent Materials	Adsorption Capacity (mg/g)	Concentration (mg/l)	Removal (%)	Contact Time (min)	pH	Ref.
Chinese zeolite	13.18	5-500	-	600	6.8	(Wang et al., 2016)
Synthesized zeolite	22.90	100		40	6.0	(Liu et al., 2018)
Modified zeolite	21.31	0-70	95.5	25 h	-	(Zhang et al., 2016)
Iron oxide/zeolite	3.47	5-100	43.3	60	6.4	(Xu et al., 2020)
Natural vermiculite	22.61	10-1000	-	120	7.0	(Alshameri et al., 2018)
Natural Sepiolite	21.51	10-1000	-	120	7.0	(Alshameri et al., 2018)
Zeolite/hydroxyapatite	10.89	5-20	-	20	6.0	(Gupta et al., 2011)
Chitosan/PVA/zeolite	8.83	5-100	-	10	-	(Habiba et al., 2017)
Zeolite HY/magnetic nanoparticle	28.41	10-40	-	40	9	(Majid et al., 2019)
ZSM-5 zeolite/polyvinyl	29.58	10-100	-	220	10	(Radoor et al., 2021)
Polyamide-6/zeolite nanofibers	16.66	20-40	-	80	3.5	(Ghanavati et al., 2021)
Clinoptilolite/NaOH	17.03	50-100	83.9	120	8	This study
Clinoptilolite/KOH	13.18	50-100	81.7	120	8	This study

The high adsorption percentage of 83% obtained for NaOH-modified zeolite highlights the excellent efficiency of this adsorbent in ammonia removal. This level of adsorption is comparable to the results reported by Xu et al. (2020), who used advanced nanocomposites and achieved an adsorption of 43%. Moreover, comparing the performance of NaOH and KOH-modified zeolites in this study showed that although both modifications resulted in significant improvements in ammonia adsorption compared to natural zeolite, the NaOH-modified zeolite outperformed the KOH-modified one. This difference may be attributed to the structural changes induced by the two alkalis. NaOH likely created more pores and active sites in the zeolite structure, leading to increased surface area and, consequently, higher ammonia adsorption. Overall, the comparison of the results from this study with previous research suggests that NaOH-modified clinoptilolite is an efficient, economical adsorbent with high potential for ammonia removal from aqueous solutions. This adsorbent can be considered a suitable option for industrial applications in the treatment of ammonia-laden wastewater.

4. Conclusion

In this study, natural clinoptilolite zeolite from the Miyaneh mines was modified using KOH and NaOH solutions, and its performance in ammonia removal was evaluated. The main findings are as follows.

1. Chemical modification altered the zeolite structure, increasing porosity and active adsorption sites. Modification with NaOH had a milder effect on the zeolite structure than KOH, preventing excessive damage to the crystal network while increasing porosity and specific surface area.

2. The optimal conditions for ammonia removal were found to be pH = 8, an adsorbent dose of 4 g/l, a contact time of 120 minutes, and an initial ammonia concentration of 100 mg/l.

3. NaOH-modified clinoptilolite exhibited the highest adsorption capacity at 17.03 mg/g, performing better than both KOH-modified and natural forms due to improved surface characteristics and more efficient ion exchange.

4. The adsorption process followed both Langmuir and Freundlich isotherms, indicating the presence of both monolayer and multilayer adsorption mechanisms.

The findings of this study can be applied to optimize water and wastewater treatment systems, improve water quality, reduce environmental pollution, and protect aquatic ecosystems.

However, a limitation of this study was the use of only two modifying solutions. Exploring additional modification methods, such as acid, polymer, or nanoparticle treatments, could significantly improve the adsorbent's performance and should be considered in future research. Additionally, the experiments were conducted at a laboratory scale, so evaluating the adsorbent's performance on a larger scale and under more practical conditions is essential. Investigating the adsorbent's efficiency in more complex wastewater systems and its long-term stability are important directions for future research. These findings can play a vital role in optimizing water treatment processes and reducing environmental pollution.

Statements and Declarations

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Data availability

The data used in this research are provided in the text of the article.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

A. Behfrouz: Methodology, Investigation, Conceptualization, Writing Original Draft; M. Tahmasebpoor: Supervision, Review-Editing.

AI Use Disclosure

Artificial Intelligence tools (specifically ChatGPT by OpenAI) were used to enhance the clarity, grammar, and coherence of the English language in the manuscript. All intellectual content, interpretation of results, and scientific conclusions were developed and approved by the authors.

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