**Advances in Bioresearch**
Adv. Biores., Vol 12 (4) July 2021: 72-83
©2021 Society of Education, India
Print ISSN 0976-4585; Online ISSN 2277-1573
Journal’s URL:http://www.soeagra.com/abr.html
CODEN: ABRDC3
DOI: 10.15515/abr.0976-4585.12.4.7283

Advances
in
Bioresearch

## ORIGINAL ARTICLE

# Excellent adsorption of ammonium nitrogen from water sources using natural Japanese zeolite: Characterization, kinetics and adsorption isotherms model

**Salma Tabassum**
[1]Department of Chemistry, Faculty of Science, Taibah University, Yanbu Branch, 46423, Yanbu, Saudi Arabia
[2]School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.
Email: stabassum@taibahu.edu.sa

### ABSTRACT

*The present study was conducted to evaluate the possibility of using natural Japanese zeolite for ammonium nitrogen (*$NH_4^+$*-N) removal from water sources. Batch experiments were performed under several reaction conditions such as zeolite type, particle size, adsorbent dosage, pretreatment, initial ammonium concentration, contact time, stirring speed, temperature, coexistence of cations, flow dynamic and flow rate. For the micro-polluted source water whose ammonium (*$NH_4^+$*) concentration was 10 mg-N/L, the effluent concentration can reach below 1 mg-N/L within 5 minutes, and the removal efficiency can reach 94.6%. The *$NH_4^+$* conc. range of 0~50 mg-N/L, under any initial conditions can be quickly removed by 0.5 g zeolite in a short time, and most of the *$NH_4^+$*-N can be adsorbed and removed by zeolite within 5 min. *$NH_4^+$* removal capacity per unit mass of zeolite increases as the initial concentration increases. The zeolite adsorption capacity of *$NH_4^+$*-N was in the range of 2.4~22 ml/min. The adsorptive capacity of zeolite in the retention column (9.72~11.73 mg-N/g-zeolite) was far greater than the adsorption capacity of zeolite under static conditions (only 1.59 mg-N/g-zeolite). The obtained adsorption data of *$NH_4^+$*-N by clinoptilolite is in good agreement with isotherm models. Regeneration cycles (desorption efficiency of *$NH_4^+$* adsorption on zeolite was almost 100%) for natural zeolite was also determined. This study can be used to build a low-cost multi-stage parataxis mini adsorption column system for continuous removal of low-concentration ammonia.*

**Keywords:** *Zeolite, Clinoptilolite, regeneration, ammonium removal, ammonia nitrogen.*

Received 12.02.2021 Revised 23.03.2021 Accepted 06.04. 2021

**How to cite this article:**
S Tabassum. Excellent adsorption of ammonium nitrogen from water sources using natural Japanese zeolite: Characterization, kinetics and adsorption isotherms model. Adv. Biores. Vol 12 [4] July 2021. 72-83

## INTRODUCTION

Nitrogenous compounds in wastewater are of significant concern due to their undesirable effects on the environment. Release of excessive wastewater nutrients in the form of ammonia into surface water is a root cause of many environmental problems such as eutrophication, corrosion and fouling [1, 2]. The main sources of ammonium contamination are from coke firing stations, tanneries, food processing, fertilizer manufacturing, slaughter houses, industrial waste, domestic wastewater, landfill leachate, and agricultural runoff [3-5]. Excess levels of ammonia in the drinking water cause potential health risks [6] like methemoglobinemia or blue baby syndrome, formation of carcinogens in stomach and other organs [7]. Ammonia can dissociate into ionized ammonium ($NH_4^+$) in water. However, it is only the non-ionized ammonia ($NH_3$) that is toxic to aquatic life. $NH_4^+$, even a few parts-per-million in oxygen-poor environments may cause toxicity to aquatic animals and ecosystems [8-10]. It can cause gill damage, hyperplasia, and substantial reduction in growth rates [11]. Rising industrialization in countries has instigated regulators to set stricter limits on the ammonia content in wastewater. The maximum limit of ammonia set by the European Association for drinking water is around 0.5 mg $l^{-1}$ and also a guide level is set as 0.05 mg $l^{-1}$ [12, 13].

Various ammonium treatment technologies su ch as air stripping, breakpoint chlorination, reverse osmosis, ion exchange, biological denitrification and chemical reduction processes [7, 14]. Technologies like reverse osmosis and ion exchange are rather expensive and may produce brine water [10, 15]. Though biological denitrification is most effective but hard to maintain and operate [16], during the condition when the effluent ammonium concentration shock load and unacceptable peak appear [17]. The ion exchange method usually employs organic resins, which are very selective and expensive [18, 19]. There is a strong need for technologies that can provide short contact time, low energy consumption, easy operation, economic and environmental friendly for removal of ammonia from wastewater.

Ion exchange with natural zeolites is more competitive due to its low cost and relative simplicity of application and operation [20]. Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment [21]. Zeolites are crystalline, hydrated aluminosilicates of alkali and earth metals that possess infinite, three-dimensional crystal structures. They are further categorized by a capability to lose and gain water reversibly and to exchange some of their constituent elements without major change in structure [22].The discovery of natural zeolite deposits has lead to an increasing use of these minerals for the purpose of eliminating, or at least reducing, many long standing pollution problems [8]. Zeolite adsorption process is the most suitable for use in the in situ treatment of ammonium nitrogen ($NH_4^+$-N) contaminated groundwater as they can be easily injected, dispersed and transported in groundwater and soil. The ammonium ion uptake behavior of zeolite is connected to the processes of ion exchange [23]. Clinoptilolite, a naturally occurring zeolite is an abundant natural zeolite found in igneous, sedimentary and metamorphic deposits in the form of aluminosilicate minerals with high cation-exchange capacity [19, 21, 24]. It has a two-dimensional channel system that allows the mineral to act as a molecular sieve [25, 26]. Clinoptilolite shows a highly selective capacity of adsorption towards $NH_4^+$, and is very effective in removing ammonia from water by means of its excellent ion exchange capacity [27].

Zeolite is a natural adsorbent material and ion exchange material that has been widely used in water treatment [28]. In the past two decades, the research on zeolite in the field of water pollution control has been deepened, and the engineering application of zeolite in water treatment has been continuously expanded. The applications and potential applications of both synthetic and natural zeolites vary based on their primary physical and chemical properties. These properties are in turn linked directly to the chemical composition and crystal structure of specific species [29]. The main objective of this present study is to evaluate the in-depth adsorption capacity of Japanese natural zeolite (Clinoptilolite) for ammonianitrogen. Experiments were investigated to determine the kinetic and adsorption isotherms with respect to coexisting metal cations on zeolite. In addition, NaCl regeneration performance was performed to obtain the relevant parameters.

## MATERIAL AND METHODS

### *Zeolite raw materials*

The experiment was carried out using the clinoptilolite provided by Japan Zeolite Co., Ltd, Japan. The zeolite sample was pulverized and sieved to various types of required particle size (such as <0.08mm, 0.55~1.30mm and 2~4mm, etc.) and washed with water to remove water-soluble impurities and other unwanted substances. Then dried at 100±5 °C. The various physical properties and chemical compositions of zeolites are shown in Tables 1.

### Influent composition

Simulated water distribution was used in this experiment. Ammonium standard stock solution: Weigh 3.819 g of ammonium chloride ($NH_4C1$) that has been pulverized, sieved, washed with water and dried at 100±5 °C. It was transferred to a 1000 ml volumetric flask and diluted to the mark with water. This solution NH4+-N conc. was 1000 mg/L. Simulated $NH_4^+$-N water distribution: Pipette 5.00 ml of ammonium standard stock solution into a 500 ml volumetric flask and dilute to the mark with water. The solution $NH_4^+$-N conc. was 10 mg/L.

### Analytical Methods

The measurement of $NH_4^+$-N was carried out by the DR/2400 portable spectrophotometer method No. 8038-Nessler method, and the measurement range was water, wastewater, seawater, etc. with a conc. of 0.02 to 2.50 mg/L $NH_3$-N. The measurement of the metal cations was carried out using an ion chromatography IC and ICP-MS (Wellthy Corporation, Tokyo, Japan).

TABLE1: PHYSICAL PROPERTIES OF CLINOPTILOLITE.

| | **Value** | | **Value** |
|---|---|---|---|
| Cation Exchange Capacity | 1.957meq/g | Hardness | 5~6 |
| Specificsurfacearea | 18m$^2$/g | pH ($m_{zeolite}/m_{H2O}$=1) | 6.8 |
| Molar Ratio ($SiO_2/Al_2O_3$) | 10 | Purity | 79.0% |
| Aperture<br>(dry state)<br>(wet state) | 4.0×4.5 Å<br>4.0×9.2 Å | Proportion | 2.8 (true weight)<br>1.0 (visible weight) |
| | | C.E.C. theoreticalvalue (dehydrated Na-Type) | 2.6 |
| cation selectivity sequence | $Ca>Rb>K>NH_4^+>Ba_2>Sr_2>Na>Ca_2>Fe_3>Al_3>Mg_2>Li$ | | |

CHEMICAL COMPOSITION OF CLINOPTILOLITE

| **Composition** | **Specific gravity (wt. %)** | **Composition** | **Specific gravity (wt. %)** |
|---|---|---|---|
| $SiO_2$ | 69.67 | MgO | 1.60 |
| $Al_2O_3$ | 12.15 | $K_2O$ | 3.73 |
| $Fe_2O_3$ | 1.07 | $Na_2O$ | 3.52 |
| $TiO_2$ | 0.13 | Ig, loss | 7.59 |
| CaO | 0.65 | Composition Formula : $Na_6[Al_6Si_{30}O_{72}]\cdot 24H_2O$ | |

## RESULT AND DISCUSSION

*Batch process on ammonia nitrogen removal by zeolite*

*Initial study on denitrification performance of zeolite*

0.5 g of clinoptilolite with a particle size of <0.08 mm pretreated (screened, washed and dried) was placed in a glass beaker with an $NH_4^+$-N concentration of 10mg-N/L (50 ml $NH_4Cl$ simulated water), and then the beaker was placed on a stirrer at about 20 °C. Water sample was taken every 5 minutes, filtered with a membrane with a pore size of 0.45 µm. $NH_4^+$-N conc. was measured.

It can be seen from Table 2a that the $NH_4^+$-N conc. in the effluent rapidly dropped from 10 mg-N/L to 0.54 mg-N/L within 5 min, and then slowly declined. At this time, the zeolite has adsorbed $NH_4^+$-N to saturation, and the ion exchange approached equilibrium. It exhibited that the zeolite has a good rapid adsorption and removal effect on the low $NH_4^+$-N conc. in aqueous solution.

TABLE2: BATCH EXPERIMENTS: $NH_4^+$ REMOVAL BY CLINOPTILOLITE (<0.08MM).

| Time (min.) | 0 | 5 | 10 | 20 | 30 | 40 | 60 |
|---|---|---|---|---|---|---|---|
| Conc. (mg·L$^{-1)}$ | 10 | 0.54 | 0.32 | 0.30 | 0.29 | 0.28 | 0.27 |
| Remov. Efficiency(%) | 0 | 94.6 | 96.8 | 97.0 | 97.1 | 97.2 | 97.3 |

EFFECTS OF ZEOLITE TYPE AND PARTICLE SIZE ON $NH_4^+$ REMOVAL.

| *Time (min)* | *$NH_4^+$-N conc. in effluent (mg·N·L$^{-1}$)* | | | |
|---|---|---|---|---|
| | *Clinoptilolite 2~4mm* | *Clinoptilolite <0.08mm* | *Mordenite 2~4mm* | *Mordenite <0.08mm* |
| *0* | *10* | *10* | *10* | *10* |
| *10* | *3.05* | *0.21* | *3.60* | *0.27* |
| *20* | *2.35* | *0.19* | *2.50* | *0.22* |
| *40* | *1.60* | *0.18* | *1.85* | *0.21* |
| *60* | *0.72* | *0.18* | *0.43* | *0.20* |

EFFECTS OF ZEOLITE TYPE AND PARTICLE SIZE ON THE CAPACITY OF ADSORBING $NH_4^+$.

| | *Clinoptilolite 2~4mm* | *Clinoptilolite <0.08mm* | *Mordenite 2~4mm* | *Mordenite <0.08mm* |
|---|---|---|---|---|
| *RawwaterCo(mg·N·L$^{-1}$)* | *10* | *10* | *10* | *10* |
| *Treated waterCe(mg·N·L$^{-1}$)* | *4.0* | *0.79* | *4.5* | *0.84* |
| *Qe (mg·N·(g-zeolite)$^{-1}$* | *1.20* | *1.84* | *1.10* | *1.83* |

*3.1.2. Effect of zeolite type and particle size on isothermal exchange of $NH_4^+$-N*

Pretreated zeolite (4 types: clinoptilolite with a particle size <0.08 mm and 2~4 mm, mordenite with particle size <0.08 mm and 2~4 mm). 2 g of each zeolites were placed in a beaker with an $NH_4^+$-N concentration of 10 mg-N/L (100 ml $NH_4Cl$ simulated water). Stirred with a magnetic stirrer at about 20

°C. Water sample was taken at regular intervals, filtered with a membrane with a pore size of 0.45 µm. $NH_4^+$-N Conc. was measured. Similar to the above experiment, 0.5 g of each of the four types of zeolites was placed in 100 ml of $NH_4Cl$ simulated water (with an initial $NH_4^+$-N concentration of 10 mg-N/L). Stirred at about 20 °C for about 40 h to ensure sufficient reaction time. The effluent was filtered with a membrane with a pore size of 0.45 µm. $NH_4^+$-N Conc. was measured to determine the zeolite type and particle size impact.

The results for 2 g of zeolite are shown in Table 2b. The order of zeolite adsorption to remove $NH_4^+$-N was [<0.08 mm clinoptilolite] ≈ [<0.08 mm mordenite] >> [2~4 mm clinoptilolite] ≥ [2-4 mm mordenite]. The amount increases significantly with the decrease of zeolite particle size. For zeolite with a particle size <0.08 mm, more than 90% of $NH_4^+$-N can be removed with in 10 min. whereas, for particle size 2~4 mm zeolite removal for $NH_4^+$-N was relatively slow, and it took about 1 h to increase the removal efficiency to over 90%. The clinoptilolite and mordenite at the same particle size have comparable removal effects, and the clinoptilolite has a slight advantage. This may be due to the fact that the exchangeable cations in the small particle size zeolite are easily ion exchanged with $NH_4^+$ in the solution.

The results for 0.5 g of zeolite obtained in the experiment are shown in Table 2c. According to the results, the adsorption capacity of zeolite for $NH_4^+$-N was [<0.08 mm clinoptilolite] ≈ [<0.08 mm mordenite] >> [2~4 mm clinoptilolite] ≥ [2-4 mm mordenite]. The maximum was <0.08 mm clinoptilolite corresponding to 1.84 mg-N/(g-zeolite). It showed smaller the particle size faster the adsorption of $NH_4^+$-N as the specific surface area of the zeolite increases significantly with the decrease in the particle size. Small particle zeolite can have better mixing and contact with the matrix in the solution to achieve efficient adsorption [30].

*Effect of pretreatment on zeolite structure and $NH_4^+$-N exchange capacity*

12 g of washed and dried clinoptilolite (particle size 2 to 4 mm) and mordenite (2 to 4 mm) were placed in a beaker having 200 ml of RO water, 2 mol/L of NaCl solution and 2 mol/L of hydrochloric acid, respectively. After immersing for 24 h, the solid zeolite was separated from the solution (effect of $Cl^-$ ions washed away) and dried at room temp.

It can be seen from Table 3a that only $Na^+$ and a small amount of $K^+$ ions are dissolved in the RO aqueous solution, which may be due to the ion exchange between these cations in the zeolite and the $H^+$ generated by the electrolysis of water molecules. While in the 2 mol/L hydrochloric acid solution a large amount of metal cations were dissolved, and the order of solubility according to their concentration was $Al^{3+}>Mg^{2+}>Na^+=K^+>Ca^{2+}>Fe_{total}$. Among them, $Al^{3+}$ ion was the most influential. $Al^{3+}$ ion dissolves very little in RO water, but dissolves in a large amount in HCl solution [31].

TABLE3: (A)CONCENTRATIONS OF DISSOLVED METAL CATIONS OF ZEOLITE IN 2 mol/L HYDROCHLORIC ACID (HCl) AND RO WATER ($H_2O$).

| Clinoptilolite | HCl | | | $H_2O$ | | |
|---|---|---|---|---|---|---|
| | mg/L | mg/gzeolite | meq/gzeolite | mg/L | mg/g zeolite | meq/gzeolite |
| $Na^+$ | 206 | 3.43 | 0.15 | 41.5 | 0.69 | 0.030 |
| $K^+$ | 355 | 5.92 | 0.15 | 7.0 | 0.12 | 0.003 |
| $Ca^{2+}$ | 68 | 1.13 | 0.056 | 3.0 | 0.05 | 0.0025 |
| $Mg^{2+}$ | 136 | 2.27 | 0.189 | 4.0 | 0.067 | 0.0056 |
| $Al^{3+}$ | 250 | 4.17 | 0.463 | 0.2 | 0.003 | -- |
| Fe | 37 | 0.62 | 0.011 | 0.3 | 0.005 | -- |
| Mordenite | HCl | | | $H_2O$ | | |
| | mg/L | mg/gzeolite | meq/gzeolite | mg/L | mg/gzeolite | meq/gzeolite |
| $Na^+$ | 633 | 10.55 | 0.459 | 16 | 0.267 | 0.012 |
| $K^+$ | 527 | 8.78 | 0.225 | 1.0 | 0.017 | -- |
| $Ca^{2+}$ | -- | -- | -- | -- | -- | -- |
| $Mg^{2+}$ | 82 | 1.37 | 0.114 | -- | -- | -- |
| $Al^{3+}$ | 320 | 5.33 | 0.592 | -- | -- | -- |
| Fe | 180 | 3.00 | 0.054 | -- | -- | -- |

(B)THE CONCENTRATIONS OF DISSOLVED METAL CATIONS OF CLINOPTILOLITE AND MORDENITE AFTER PRETREATMENT IN 2mol/L SODIUM CHLORIDE (NaCl).

| NaCl 2M | Clinoptilolite | | | Mordenite | | |
|---|---|---|---|---|---|---|
| | mg/L | mg/gzeolite | meq/gzeolite | mg/L | mg/gzeolite | meq/gzeolite |
| $K^+$ | 431 | 7.18 | 0.18 | 427 | 7.12 | 0.18 |
| $Ca^{2+}$ | 537 | 8.95 | 0.45 | 107 | 1.78 | 0.09 |
| $Mg^{2+}$ | 69 | 1.15 | 0.096 | -- | -- | -- |
| $Al^{3+}$ | -- | -- | -- | -- | -- | -- |
| Fe | -- | -- | -- | -- | -- | -- |

It can be seen from Table 3b that after treatment with 2 mol/L NaCl solution, the $K^+$ and $Ca^{2+}$ ions in the zeolite, especially the clinoptilolite, are dissolved into the solution in large quantities. This was due to the high conc. of $Na^+$ ions in the solution. Under the driving force of concentration gradient, a large amount of $K^+$ and $Ca^{2+}$ ions in the zeolite are ion exchanged with the high conc. of $Na^+$ ions in the solution i.e. a large amount of $K^+$ and $Ca^{2+}$ ions in the zeolite are replaced by $Na^+$ ions, that have the weakest connection with the parent crystal frame structure and are mostly replaced. But $Al^{3+}$ and Fe are completely fixed in the zeolite structure without being affected. Therefore, it is beneficial to the subsequent ion exchange removal process of $NH_4^+$-N. In short, $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ ions are exchangeable active ions. $Al^{3+}$ and Fe are the basic framework and composition of the zeolite structure.

0.5 g of each of the pre-treated zeolite samples was placed in 50 ml of a $NH_4Cl$ solution having an initial conc. of 20 mg-N/L. Stirred with a magnetic stirrer, sampled at regular intervals, and filtered through a 0.45 μm membrane and $NH_4^+$-N concentration was determined. According to the experimental data, the plot is shown in Fig. 1. Zeolite pretreated by 2 mol/L NaCl solution had better performance in the exchange and adsorption of $NH_4^+$-N. This was due to the large amount of $K^+$ and $Ca^{2+}$ ions in the zeolite being replaced by the high concentration of $Na^+$ ions in the solution. The $Na^+$ ion, which had a weak binding force to the parent structure, was easily replaced by $NH_4^+$ to achieve the effect of exchange adsorption to remove ammonia nitrogen [27, 32-34].

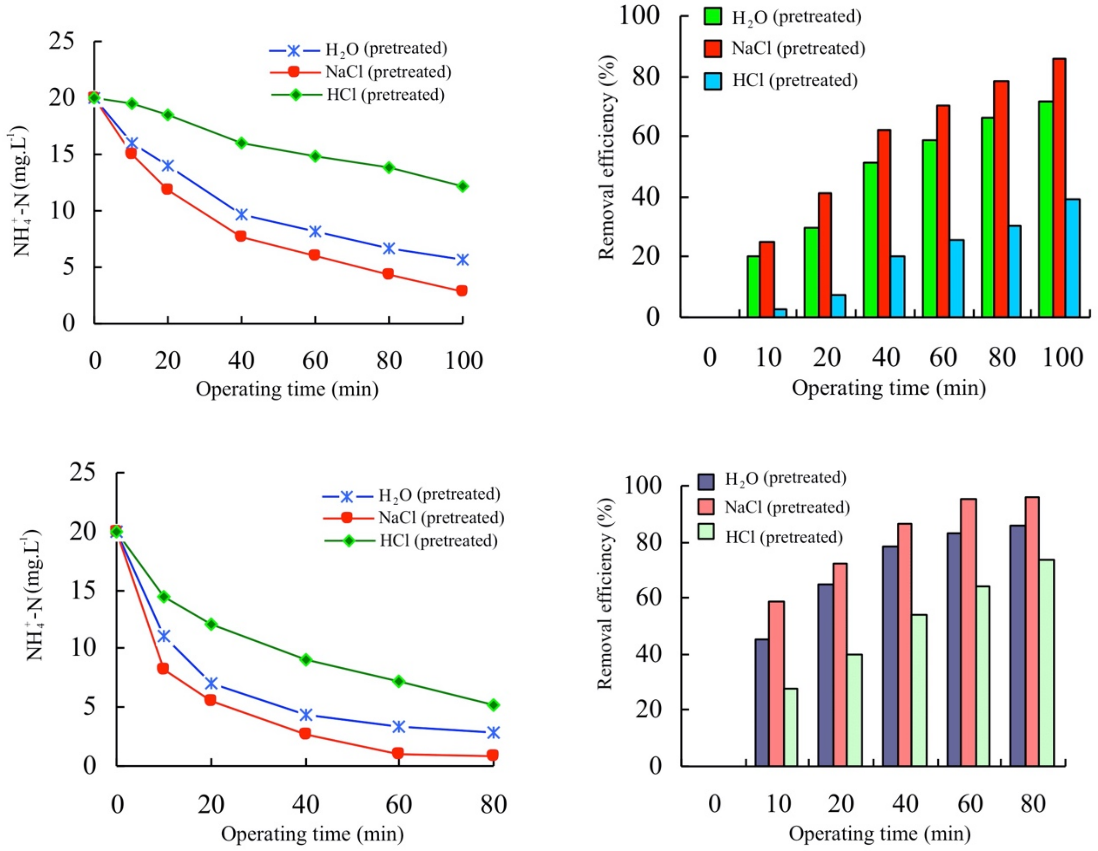

**Figure 1** Effects of pretreatment on $NH_4^+$ removal by zeolite: (a)- (b)Clinoptilite, and (c)-(d)Mordenite.

*Effect of initial $NH_4^+$-N conc. on static exchange capacity of zeolite*

A sufficient contact reaction time was given under static conditions to determine the effect of the initial $NH_4^+$-N conc. on the zeolite exchange adsorption. 0.5 g of zeolite with a particle size of <0.08 mm was placed in 100 ml of $NH_4Cl$ simulated water (with an initial $NH_4^+$-N conc. ranging from 10 to 60 mg-N/L), and allowed to stand for more than 24 hours. Sampled and filtered with a membrane having a pore size of 0.45 µm.

When the initial $NH_4^+$-N conc. was low (10 mg-N/L), the removal efficiency can reach more than 90% even under static conditions. As a small amount of $NH_4^+$-N had a competitive effect on the exchangeable active sites on the zeolite surface. However, the diffusion inhibition of a small part of ammonia nitrogen molecules caused by the standing solution is compensated by sufficient contact time. As the initial concentration increases, the removal efficiency shows a downward trend due to the membrane diffusion of a large number of ammonia nitrogen molecules and ions. The internal diffusion of particles are restricted as the high concentration ammonia nitrogen solution was left standing. Subsequent supply of ion exchange on the particle surface was insufficient. Therefore, the ammonia nitrogen adsorbed on the zeolite at equilibrium was relatively small with the ammonia nitrogen in the aqueous solution. The higher the ammonia nitrogen concentration in the solution, the more obvious the inhibition phenomenon. The $NH_4^+$ removal capacity per unit mass of zeolite increases as the initial concentration increases. This was due to the high conc. of $NH_4^+$-N solution. The ion exchange driving force was larger and the relative adsorption quantity was high.

*Effect of initial $NH_4^+$-N conc. and contact time on zeolite isothermal exchange*

0.5 g of zeolite with a particle size of <0.08 mm was placed in 50 ml of $NH_4Cl$ water with a conc. ranging from 10 to 50 mg-N/L. Stirred at a constant temperature of 20 °C, and samples were taken at regular intervals. After filtration using a membrane with pore size of 0.45 µm, the concentration was measured.

It can be seen from Fig. 2 in the conc. range of 0~50 mg-N/L, $NH_4^+$ under any initial conditions can be quickly removed by 0.5 g zeolite in a short time, and most of the $NH_4^+$-N can be adsorbed and removed by zeolite within 5 min. When the initial conc. was 5~15 mg-N/L, 20~25 mg-N/L and 50 mg-N/L, respectively. The equilibrium can be reached within 5 min, 10 min and 20 min, respectively.

After that, the removal efficiency showed a slow upward trend with the extension of the contact time due to the rapid diffusion of the matrix in the solution to the surface of the zeolite and then the rapid diffusion of the matrix in the internal structure of the zeolite to achieve adsorption equilibrium [35, 36]. The driving force of the concentration of ammonia nitrogen adsorbed by the zeolite in the solution was also beneficial for the smooth progress of ion exchange until the adsorption reaches equilibrium.

It can also be seen from Fig. 2 that the lower the initial $NH_4^+$ conc., the shorter the time required to reach equilibrium between the two phases. Higher the initial $NH_4^+$ conc., longer the equilibrium time. But larger the capacity of adsorbing $NH_4^+$-N, as high concentration of ammonia nitrogen molecules and ions compete more strongly for the active site on the zeolite. So the longer it takes to reach equilibrium. However, the ion exchangeability and adsorption performance of the zeolite can be fully utilized. For the micro-polluted source water whose $NH_4^+$ concentration is 10 mg-N/L, the effluent concentration can reach below 1 mg-N/L within 5 minutes, and the removal efficiency can reach 94.6%.

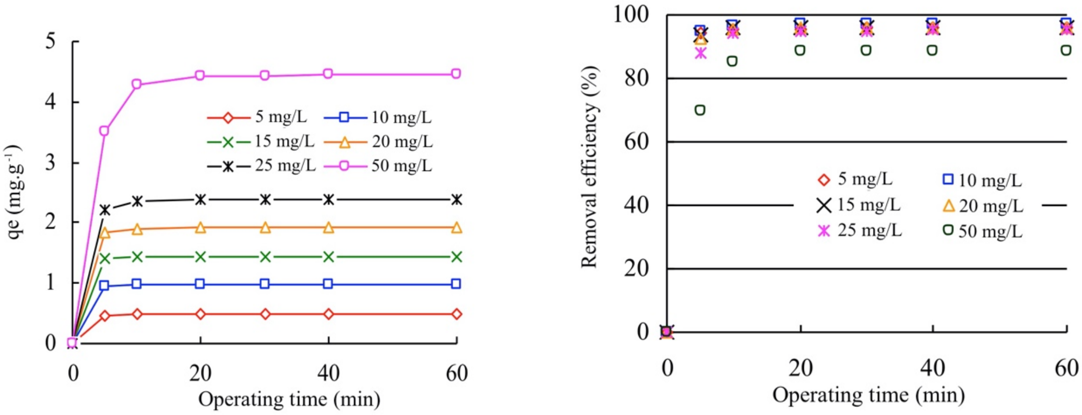

**Figure 2** Effect of contact time and initial conc. on the exchange of $NH_4^+$ onto clinoptilolite (T, 20°C)

*Effect of static and flow dynamic conditions on the $NH_4^+$-N exchange capacity of zeolite*

In order to further understand the difference between static and flow dynamic conditions on the capacity of zeolite to exchange and adsorb $NH_4^+$-N. The static intermittent adsorption experiments under different initial concentration and different flow rates in the flow column were performed, respectively. Static adsorption experiment: 0.5 g of clinoptilolite with a particle size of 0.55~1.30 mm (washed and dried) was added to 50 ml of $NH_4Cl$ (with an initial $NH_4^+$-N conc. of 10~100 mg-N/L), and allowed to stand for 40 h. The liquid phase was filtered through a 0.45 µm membrane and the $NH_4^+$-N conc. was measured.

Dynamic experiment of zeolite adsorption in a flow column: 10 g of clinoptilolite with a particle size of 0.55~1.30 mm was added to a flow column with an inner diameter of 13 mm and a length of about 300 mm. $NH_4Cl$ solution having a conc. of 20 mg-N/L was passed. The flow rates were 2.4 ml/min, 10.8 ml/min and 22 ml/min, respectively. The conc. of $NH_4^+$-N in the effluent was measured. The obtained data was compiled into Fig. 3.

It can be obtained from the above static adsorption experiment that the adsorption capacity of the zeolite to adsorb $NH_4^+$-N increases with the increase of the initial $NH_4^+$-N conc. The main reason was the strong driving force of the conc. gradient caused by the high conc. of $NH_4^+$-N solution. Therefore, the adsorption capacity of the zeolite was relatively large. However, the $NH_4^+$-N removal efficiency under the above stirring conditions was low, and it was not easy to effectively diffuse $NH_4^+$ and contact with the exchangeable cations in the zeolite. When the initial conc. was 20 mg-N/L, the adsorption capacity was 1.59 mg-N/g-zeolite. The zeolite adsorption capacity of $NH_4^+$-N was in the range of 2.4~22 ml/min. As the flow velocity increases, it decreases slightly. This is due to the low flow rate. If the contact time was sufficient, the relative adsorption capacity will be large. However, the difference was not large. During the membrane diffusion process, the exchange rate between zeolite and the cation $NH_4^+$ in the aqueous solution increases with the increase of the solution flow rate. So the influence of the flow rate on the exchange adsorption was more complicated.

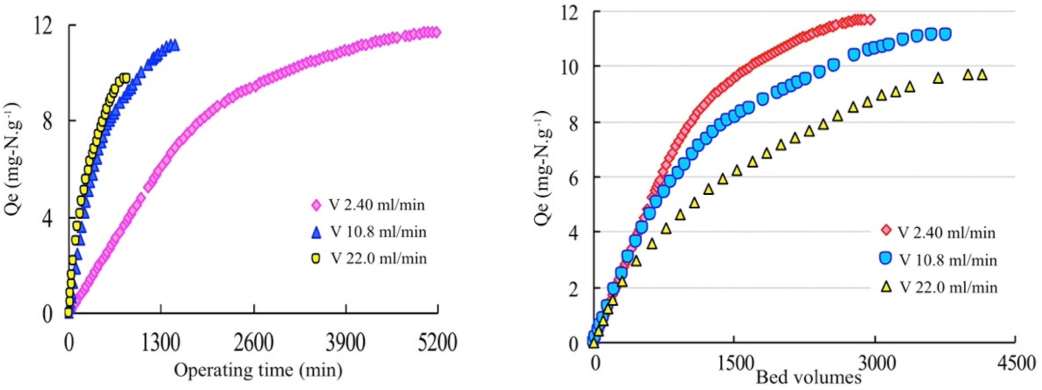

**Figure 3.** Results of $NH_4^+$ removal by zeolite in columns

However, compared with the above-mentioned static adsorption and the amount of $NH_4^+$-N adsorbed by the zeolite in the flow column. It can be seen that the adsorption capacity of zeolite in the retention column (9.72~11.73 mg-N/g-zeolite) was far greater than the adsorption capacity of zeolite under static conditions (Only 1.59 mg-N/g-zeolite). This was due to the conc. of zeolite contact solution was always close to 20 mg-N/L during dynamic adsorption in the flow column. However, under static conditions, with the increasing adsorption capacity, the concentration of ammonia nitrogen in the surrounding environment exhibited a downward trend. The driving force of ammonia nitrogen concentration was relatively smaller than that of dynamic conditions. On the other hand, under dynamic adsorption conditions, metal cations such as $Na^+$, $K^+$, $Mg^{2+}$, and so on replaced from zeolite can be quickly taken out of the system with the water flow. This was beneficial to the smooth progress of the ion exchange reaction in the direction of removing ammonia nitrogen. In addition, dynamic flow adsorption is also beneficial for the membrane diffusion process of $NH_4^+$ions in solution moving to the zeolite. Therefore, the exchange rate between zeolite and cation $NH_4^+$ in the aqueous solution increases significantly with the flow of the solution. The amount of $NH_4^+$ adsorbed by zeolite was also significantly improved.

*Effect of temp. on the exchange capacity of zeolite*

In order to determine the effect of temp. on the exchange capacity of zeolite for $NH_4^+$-N. 0.5 g of zeolite having a particle size of <0.08 mm was placed in a concentration of 50ml of $NH_4Cl$ mixed water with a concentration ranging from 10 to 50 mg-N/L and placed on a magnetic stirrer for batch experiments.

Temperature water bath at 10, 20, 30, 40 and 50 °C, respectively. Samples are taken at regular intervals, and the concentration was determined after filtered through a membrane with a pore size of 0.45 µm. From the perspective of thermodynamics, since the ion exchange process of zeolite adsorption of $NH_4^+$-N is an exothermic process. So, low temperature is good for ion exchange reaction. However, higher the temperature, the larger the molecular thermal energy. Higher the molecular activity, that is more conducive to diffusion and ion exchange reaction. Therefore, it was necessary to choose a suitable temperature to achieve the best effect. As, the zeolite structure is different, the temperature affected it differently. In this experiment, regardless of the initial conc. of 25 mg-N/L or 50 mg-N/L, the temperature 10~50 °C, had little effect on the adsorption of $NH_4^+$-N by zeolite, which was almost negligible.

*Adsorption isotherms*

0.5 g of clinoptilolite with a particle size of <0.08 mm was placed in 50 ml of a $NH_4Cl$ solution having a conc. ranging from 0 to 100 mg-N/L. Than placed on a magnetic stirrer at 20 °C for 36 h. $NH_4^+$ conc. was determined. In order to determine the effect of coexisting metal cations such as $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ on the exchange and adsorption of ammonia nitrogen by zeolite, 40 mg/L of metal cations were added, respectively.

It can be seen from Fig. 4 that as the initial $NH_4^+$ conc. in the solution increases, the amount of $NH_4^+$-N adsorbed per gram of zeolite also increases (i.e. the amount of charge adsorbed per gram of zeolite also increases). The high conc. gradient resulted in a greater driving force for ion exchange. When there are other coexisting metal cations in the water, the $NH_4^+$-N effluent conc. will increase significantly, but the increase was not large. When there are other coexisting metal cations in the solution (such as $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$), the amount of $NH_4^+$-N adsorbed by the zeolite will be obvious.

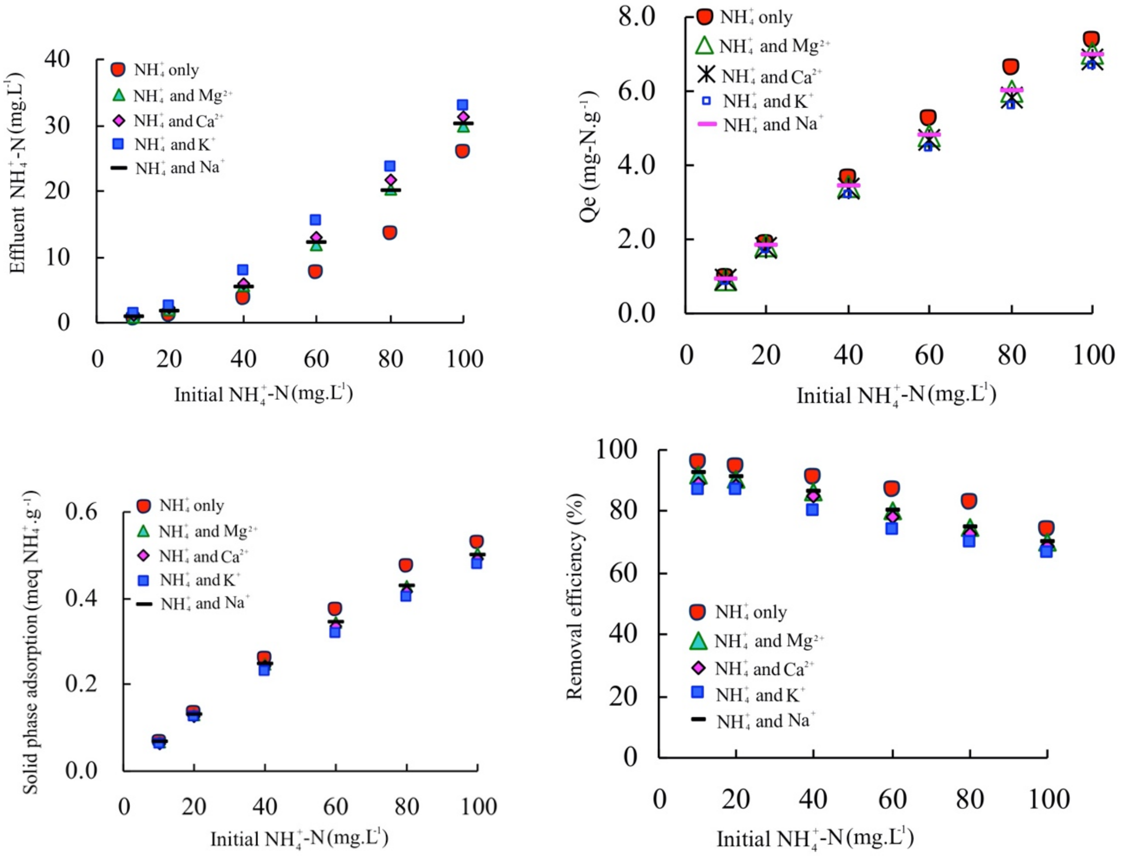

**Figure 4.** Ammonium exchange isotherms and effects of individual cation on the exchange of $NH_4^+$ uptake by zeolite.

In addition, $K^+$ ions had the largest relative influence of metal ions under the same concentration conditions, and $Mg^{2+}$ ions had the smallest relative influence. This is related to the zeolite structure and its selective order to metal cations [37-39]. For example, when the metal ions (40 mg/L) in the water, the corresponding charge of $Mg^{2+}$ was 3.33 meqMg/L, but it showed a small effect. While the corresponding charge of $K^+$ ions was only 1.026 meqK/L, it showed the strongest effect. The impact of the other was 2.0 meqCa/L and 1.74 meqNa/L.

The equilibrium adsorption curve of ion exchange is the key basic data in engineering design [40, 41]. The distribution of $NH_4^+$ ions in liquid phase and solid phase in equilibrium state can be expressed by a series of empirical models, such as Langmuir, Freundlich and Dubinin-Radushkevich. Among them Langmuir and Freundlich models are more commonly used, and are widely used in theoretical research and actual engineering design.

The Langmuir adsorption curve model formula is as follows:

$$Qe = \frac{KbCe}{1+KCe} \quad (1)$$

After linear processing, $\frac{1}{Qe} = \frac{1}{KbCe} + \frac{1}{b}$ (2)

Qe is the amount of $NH_4^+$ adsorbed by the unit zeolite at equilibrium, Ce is the $NH_4^+$ ion conc. at equilibrium, and K and b are Langmuir constants, which represent the adsorption capacity and rate of adsorption capacity, respectively.

The Freundlich model was also applied [42], The Freundlich modelempiricalformulaisas follow

$$Qe = K_f Ce^{(1/n)} \quad (1)$$

After linear processing $\log Qe = \log K_f + \frac{1}{n}\log Ce$ (2)

where $K_f$ is the Freundlich constant and 1/n adsorption intensity. The two models are applied to the experimental data of $NH_4^+$ adsorption by zeolite. Fig. 5 showed that the adsorption of $NH_4^+$-N by clinoptilolite is in good agreement with the Langmuir and Freundlich model. Compared with the Freundlich model (correlation coefficient $R^2$=0.9734 ~ 0.9840). The Langmuir model can better fit the experimental data. The correlation coefficient $R^2$ reached 99.73% ~ 99.97%, especially for low-concentration ammonia nitrogen adsorption. It's correlation fit is more stronger.

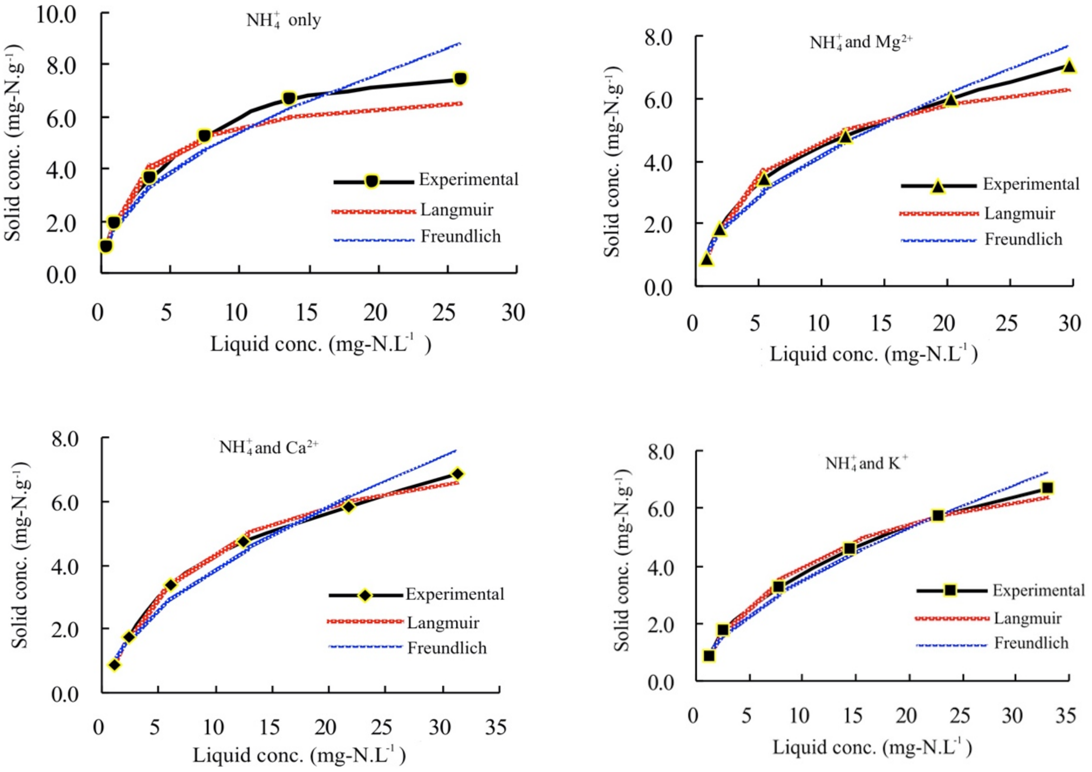

**Figure 5.** Equilibrium isotherm data for $NH_4^+$ uptake onto clinoptilolite fitted to the Langmuir and the Freundlich uptake models under the condition of $NH_4^+$ only, and in the presence of individual $Mg^{2+}$, $Ca^{2+}$, $K^+$ ion.

Therefore, the process and mechanism of zeolite adsorption of low-concentration ammonia nitrogen can be well expressed by the Langmuir model. The correlation coefficient was obtained based on a series of experimental data, so as to establish a zeolite adsorption $NH_4^+$-N model suitable for the actual conditions. Both the Langmuir model parameter $K_L$ and the Freundlich model parameter $K_F$ decrease with the presence of coexisting metal cations as the coexisting metal cations have a certain competitive effect on the active sites of ammonia nitrogen adsorbed on the zeolite. Through the magnitude of its parameter value, it can be concluded that the order of its influence on zeolite adsorption of ammonia nitrogen is: $K^+>Ca^{2+}>Na^+\approx Mg^{2+}$, which is completely consistent with the previous conclusions. 1/n represents the surface heterogeneity exchange intensity of zeolite for $NH_4^+$-N. The dimension 1/n in the Freundlich modelwas between 0 and 1, which indicated that the adsorption strength of zeolite to $NH_4^+$-N under this condition was ideal [43], and the adsorption performance is better.

*Kinetics of dynamic adsorption of $NH_4^+$-N by zeolite*

In order to further understand the kinetics of zeolite adsorption of $NH_4^+$-N, 10 g of clinoptilolite with a particle size of 0.55~1.30 mm (washed and dried) was added to a flow column with an inner diameter of 13 mm and a length of about 300 mm (volume 2.4 ml). At a flow rate of 2.4 ml/min, $NH_4Cl$ solution with a conc. of 20 mg-N/L was passed. The operation was suspended every night. The experiment of the previous day was continued the next day. The conc. of $NH_4^+$-N in the water was determined.

$NH_4^+$-N was not detected in the effluent within 15 hours of the initial stage. The adsorption of $NH_4^+$-N per unit mass of zeolite per unit time reached the maximum. Within the first 18 h, the removal efficiency of $NH_4^+$ by zeolite exchange adsorption was always 95% or more. After that, the $NH_4^+$-N conc. in the effluent continuously increased, and the removal efficiency showed a gradual decreasing trend. After a period of interruption every night, $NH_4^+$-N in the effluent at the beginning of the next day was stable and even slightly decreased. This is due to the time period of suspension. During this period, there was sufficient time for the zeolite to rearrange the adsorbed $NH_4^+$-N ions and molecules, and gradually enter the adsorption center inside the particle structure through the internal diffusion of the particle. Thus, the ability of zeolite to adsorb $NH_4^+$-N was improved. The total adsorption capacity of zeolite continued to rise throughout this period. The ascending slope decreases continuously until the curve tends to be flat. This is due to the zeolite gradually tends to become saturated with the increase in the amount of $NH_4^+$-N adsorbed by the zeolite.

*Study on NaCl regeneration performance of zeolite*

2 g of clinoptilolite with a particle size of 0.55~1.30 mm was placed in 100 ml of RO water and a saturated NaCl solution with a conc. of about 360 g/L. Stirred on a magnetic stirrer for regeneration experiments to determine the use of neutral NaCl solution for the feasibility and effect of regeneration. In order to further determine the effect of NaCl solution conc. on the regeneration of zeolite, 1 g of clinoptilolite with a particle size of 0.55~1.30 mm was placed in 100 ml of NaCl solution. The conc. of NaCl solution varied from 0 to 180 mg/L, followed by 0 mg/L, 15 mg/L, 30 mg/L, 60 mg/L, 90 mg/L, and 180 mg/L, and was also stirred on a magnetic stirrer. $NH_4^+$-N conc. in the water was measured at regular intervals.

Zeolite adsorbing $NH_4^+$-N was difficult to elute with RO water, but when saturated NaCl solution was used, the $NH_4^+$-N adsorbed by the zeolite particles can be quickly eluted. The high conc. of $Na^+$ ions in the NaCl solution undergoes ion exchange with the $NH_4^+$ ions adsorbed on the zeolite under the driving force of the concentration difference. It is feasible to regenerate the adsorption saturated zeolite with neutral NaCl solution. As the conc. of NaCl solution increases, the amount of eluted $NH_4^+$ was high. The time required for the same regeneration effect was short, and most of the $NH_4^+$ ions are desorbed from the zeolite within 30 minutes after the start. The desorption process then tends to be flat. The desorption efficiency of $NH_4^+$adsorption on zeolite with 100 ml NaCl solution with a conc. of 180 g/L was almost 100%. Whereas, the desorption efficiency of $NH_4^+$adsorption on zeolite with 100 ml of NaCl solution with a conc. of 360 g/L was only 80%. This may be due to the fact that the high conc. of $NH_4^+$ ions resolved from the zeolite into the solution inhibited the further ion exchange between $Na^+$ ions with $NH_4^+$ ions.

## CONCLUSION

This study considered the potential of a natural Japanese zeolite, clinoptilolite, to remove low-concentration ammonia nitrogen. Their use for environmental applications is of high interest mostly due to their rapid adsorption and ion-exchange processes. The main conclusion as follows: the denitrification performance increases with the decrease of the zeolite particle size. The adsorption capacity of zeolite after treatment with neutral NaCl solution increased. However, the ammonia nitrogen adsorption performance of zeolite treated with HCl was significantly reduced. In the zeolite structure, $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ ions are exchangeable active ions, while $Al^{3+}$ and Fe are the basic framework and composition of the zeolite structure. The capacity of zeolite to adsorb ammonia nitrogen increases significantly with the increase of the initial ammonia nitrogen concentration and the extension of the contact time. Adsorption equilibrium can be achieved in a short time. The adsorption capacity of zeolite under stirring and flow dynamic conditions was much greater than static conditions. The optimum flow rate should be adopted according to the actual situation. It should neither be too large nor too small. The influence of temperature in the range of 0~50 °C was small and can be almost ignored. All the results demonstrate that the natural Japanese zeolite (specific physicochemical properties) could be used efficiently as a water treatment agent due to its high selectivity to one of the most potent pollutant ammonia. Moreover, zeolite forms strong bonds with ammonia and heavy metals that are difficult to break. Hence, leaching of contaminants into the environment are avoided. It is very effective to analyze the $NH_4^+$-N adsorbed by saturated zeolite with NaCl solution. Higher the conc. of NaCl solution, the more effective the desorption, but the consumption of NaCl was high. Therefore, it is necessary to comprehensively consider various factors such as optimal regeneration conc. and regeneration flow rate. As this present study provided a theoretical basis, further work in our laboratory is directed towards development and investigation of continuous adsorption-regeneration of Japanese natural clinoptilolite filled in multi-stage parataxis mini adsorption column process for ammonia nitrogen removal from groundwater-based on engineering design.

## ACKNOWLEGEMENT

The author expresses her gratitude to Ge Xiaohong for her valuable contribution in this experimental study and also cooperation in contributing to the success of this study. The author would also like to thank Taibah university

## CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## REFERENCES

1. Dong, Y. and L. Xu, (2019). Aggregate risk of reactive nitrogen under anthropogenic disturbance in the Pearl River Delta urban agglomeration. Journal of Cleaner Production; 211: 490-502.
2. Sun, C., et al., (2020). National assessment of nitrogen fertilizers fate and related environmental impacts of multiple pathways in China. Journal of Cleaner Production*;* 277: 123519.
3. Ahn, S.C., S.-Y. Oh, and D.K. Cha, (2008). Enhanced reduction of nitrate by zero-valent iron at elevated temperatures. *Journal of Hazardous Materials;* 156(1):17-22.
4. Cheng, H., Q. Zhu, and Z. Xing, (2019). Adsorption of ammonia nitrogen in low temperature domestic wastewater by modification bentonite. *Journal of Cleaner Production*; 2019. 233: 720-730.
5. Xu, R., et al., (2020). Agricultural nitrogen flow in a reservoir watershed and its implications for water pollution mitigation. J. Clean. Prod., 2020. 267: 122034.
6. Ruiz-Beviá, F. and M.J. Fernández-Torres, (2019). Effective catalytic removal of nitrates from drinking water: An unresolvedproblem? *Journal of Cleaner Production*; 217:398-408.
7. Yang, G.C.C. and H.-L. Lee, (2005). Chemical reduction of nitrate by nanosizediron: kinetics and pathways. Water research; 39(5):884-894.
8. Weatherley, L.R. and N.D. Miladinovic, (2004). Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. Water Research ;38(20): 4305-4312.
9. Zheng, H., et al., (2008). Adsorption characteristics of ammonium ion by zeolite 13X. Journal of HazardousMaterials ;158(2):577-584.
10. Chatterjee, S. and S.H. Woo, (2009). The removal of nitrate from aqueous solutions by chitosan hydrogel beads. Journal of Hazardous Materials; 164(2): 1012-1018.
11. Larmoyeux, J.D. and R.G. Piper, (1975). Effects of Water Reuse on Rainbow Trout in Hatcheries Prog. Fish Culture, 35:2-8.
12. Gaspard, M., A. Neveu, and G. Martin, (1983). Clinoptilolite in Drinking Water Treatment for NH 4+ Removal(Utilisation De La Clinoptilolite En Potabilisation Des Eaux--Elimination De L'Ion NH 4+). Water Research; 17(3).
13. Hill, M.G., (1990). American Water Works Association, Water quality and treatment. Co. New York.
14. Paul Chen, J., M.-L. Chua, and B. Zhang, (2002). Effects of competitive ions, humic acid, and pH on removal of ammonium and phosphorousfrom the synthetic industrial effluent by ion exchange resins. Waste Management; 22(7):711-719.
15. Della Rocca, C., V. Belgiorno, and S. Meriç, (2007). Overview of in-situ applicable nitrate removalprocesses. Desalination; 204(1): 46-62.
16. Imchuen, N., et al., (2016). Using cation exchange resin for ammonium removal as part of sequential process for nitrate reduction by nanoiron. Sustainable Environment Research; 26(4):156-160.
17. Baker, H.M. and H. Fraij, (2010). Principles of interaction of ammonium ion with natural Jordanian deposits: Analysis of uptakestudies. Desalination; 251(1): 41-46.
18. Jorgensen, T.C. and L.R. Weatherley, (2003). Ammonia removal from waste water by ion exchange in the presence of organic contaminants. Water Research; 37(8):1723-1728.

19. Sarioglu, M., (2005). Removal of ammonium from municipal waste water using natural Turkish (Dogantepe) zeolite. Separation and purification technology; 41(1): 1-11.
20. Wen, J., H. Dong, and G. Zeng, Application of zeolite in removing salinity/sodicity from wastewater: A review of mechanisms, challenges and opportunities. J. Clean. Prod., 2018. 197: p. 1435-1446.
21. Nguyen, M.L. and C.C. Tanner, (1998). Ammonium removal from wastewaters using natural New Zealand zeolites. New Zealand Journal of Agricultural Research; 41(3):427-446.
22. Wang, H., J. Xu, and L. Sheng, (2020). Purification mechanism of sewage from constructed wetlands with zeolite substrates: A review. J. Clean. Prod., 2020. 258:120760.
23. Zabochnicka-Świątek, M. and K. Malińska, (2010). Removal of ammonia by clinoptilolite. Global NEST Journal;12(3):256-261.
24. Karadag, D., et al., (2006). Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. Journal of HazardousMaterials, 136(3):604-609.
25. Sullivan, E.J., J.W. Carey, and R.S. Bowman, (1998). Thermodynamics of cationic surfactant sorption onto natural clinoptilolite. Journal of Colloid and Interface Science ; 206(2):369-380.
26. Bowman, R.S., (2003). Applications of surfactant-modified zeolites to environmental remediation. Microporous and mesoporousmaterials ; 61(1-3):43-56.
27. Sprynskyy, M., et al., (2005). Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studiedunderdynamic conditions. Journal of Colloid and Interface Science; 284(2):408-415.
28. Ghasemi, Z., et al., (2018). Application of zeolites in aquaculture industry: areview. Reviews in Aquaculture ;10(1):75-95.
29. Mumpton, F.A., (1999). Uses of natural zeolites in agriculture and industry. Proceedings of the National Academy of Sciences; 96(7):3463-3470.
30. Tantekin-Ersolmaz, Ş.B., et al., (2000). Effect of zeoliteparticle size on the performance of polymer–zeolite mixed matrix membranes. Journal of Membrane Science;175(2):285-288.
31. Oldenburg, M. and I. Sekoulov, (1995).Multipurpose filterswith ion-exchanger for the equalization of ammoniapeaks. Water Science and Technology;32(7):199-206.
32. Murphy, C., O.Hrycyk, and W.Gleason, Natural Zeolites: Occurrence, Properties, Use. 1978, New York: PergamonPress Oxford. 0-471.
33. Demir, A., A. Gunay, and E. Debik, (2002). Ammonium removal from aqueous solution by ion-exchange using packed bed naturalzeolite. Water Sa ; 28(3):329-336.
34. Bogdanov, B., et al., (2009). Natural zeolites: clinoptilolite. Review, Natural & Mathematical science; 4:6-11.
35. Semmens, M.J. and W.P. Martin, (1998). The influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions. Water Research; 22(5):537-542.
36. Ho, Y.-S., T.-H. Chiang, and Y.-M. Hsueh,(2005). Removal of basic dyefrom aqueous solution using tree fern as a biosorbent. Process Biochemistry; 40(1):119-124.
37. Zendelska, A., et al., (2018). Characterization and application of clinoptilolite for removal of heavymetal ions from water resources. Geologica Macedonica ; 32(1):21-32.
38. Elboughdiri, N., (2020). The use of naturalzeolite to remove heavy metals Cu (II), Pb (II) and Cd (II), fromindustrialwastewater. Cogent Engineering; 7(1):1782623.
39. Zinicovscaia, I., et al., (2020). Selective metal removal from chromium-containing synthetic effluents using *Shewanella xiamenensis* biofilm supported on zeolite. Environmental Science and Pollution Research; 27(10):10495-10505.
40. Namasivayam, C. and R.T. Yamuna, (1995). Adsorption of direct red 12 B by biogas residual slurry: equilibrium and rate processes. Environ. Pollut., 1995. 89(1): p. 1-7.
41. Fertu, D.I.T. and M. Gavrilescu, (2012). Application of naturalzeolites as sorbents in the clean-up of aqueousstreams. Environ. Eng. Manag. J; 11(4):867-878.
42. Treybal, R.E., (1981). Mass transfer operations. McGrawHill Book Co.Singapore.Özcan, A.S., B. Erdem, and A.
43. Özcan, (2004). Adsorption of Acid Blue 193 from aqueous solutions onto Na–bentonite and DTMA–bentonite. Journal of Colloid and Interface Science ; 280(1): 44-54.