THE ADSORPTION CHARACTERISTICS OF SALT MODIFIED ZEOLITE TO AMMONIA NITROGEN

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Abstract. To improve the adsorption capacity of natural zeolite for ammonia nitrogen, zeolite was modified by sodium chloride (NaCl), sodium tungstate (Na_2WO_4), and sodium citrate ($C_6H_5Na_3O_7$) solutions, and the adsorption characteristics of zeolite before and after modification for ammonia nitrogen in water were studied. The properties and structure of zeolite were characterized and analyzed. The adsorption mechanism of modified zeolite for ammonia nitrogen and the effects of environmental factors on the adsorption were studied. The results showed that the modification of NaCl, Na_2WO_4, and $C_6H_5Na_3O_7$ increased the adsorption capacity of zeolite by 60.76%, 58.23%, and 54.43%, respectively. The zeolite modified by NaCl solution had the best adsorption effect for ammonia nitrogen. The optimum concentration, temperature, and time of NaCl modifier was 1.5 mol/L, 85 ℃, and 12 h. The adsorption of ammonia nitrogen on zeolites before and after modification was more consistent with the pseudo-second-order kinetic model. Under the conditions of particle size of 60-80 mesh, pH of 7, temperature of 30 ℃, and dosage of 10 g/L, the removal rate of ammonia nitrogen by zeolites increased from 54.89% to 90.39% after adsorption of wastewater with initial ammonia nitrogen concentration of 50 mg/L. The adsorption of ammonia nitrogen in wastewater by natural zeolite modified by salt solution is an environmentally friendly and effective method.
Keywords: *sodium chloride, sodium tungstate, sodium citrate, adsorption kinetics, adsorption mechanism*

Introduction

In recent years, the high concentration of ammonia nitrogen in water has become a common problem faced by various fields such as agriculture, aquaculture, and industry (Li et al., 2020). Long-term exposure to high ammonia nitrogen levels can lead to physiological hypoxia and tissue damage in aquatic organisms (Cong et al., 2021), affecting their growth and development (Kim et al., 2019). At the same time, high concentration of ammonia nitrogen wastewater can also easily cause eutrophication of lakes, groundwater, and other water sources, affecting normal human production and life. So, solving the problem of excessive ammonia nitrogen content in water bodies and establishing efficient, environmentally friendly, and low-cost treatment methods for ammonia nitrogen wastewater is one of the hot research topics for scholars at home and abroad. Thus, extensive research studies have been conducted on the treatment of ammonia nitrogen wastewater, striving to find treatment technologies that are easy to operate, cost-effective, and efficient’mes of authors, e.g. Ye et al. (2021) etc.

Currently, the methods of treating ammonia-nitrogen wastewater can be divided into physical, chemical, and biological methods. The biological method uses the metabolic

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process of specific microorganisms to remove ammonia nitrogen in water, which has the characteristic of no secondary pollution and can recover available substances after treatment (Yang et al., 2022). However, toxic substances such as heavy metals can inhibit microorganisms and reduce their activity (Zahri et al., 2021). As a physical method, adsorption has the advantages of simple operation and low cost (Mehdi et al., 2022), that is why so many researchers favor it.

The adsorbent is the key to the treatment of ammonia nitrogen wastewater by adsorption. The common adsorbents are zeolite (Yang et al., 2017), activated carbon (Ren et al., 2020), diatomite, etc. Zeolite is a natural mineral with good stability, high exchange capacity, and low material cost (Ma et al., 2022). Zeolite is a suitable adsorbent for ammonia nitrogen removal due to its high affinity for NH_4^+, porous structure and polar surface, so it can also be used for pollution control (Suprihatin et al., 2020). However, the adsorption capacity of natural zeolite to ammonia nitrogen is low. In order to make it a more effective adsorbent, various methods must be used to improve its characteristics. After modification, internal porosity and surface activity of natural zeolite are improved, and the ability to adsorb pollutants is enhanced (Rakhym et al., 2021). Zieliński et al. (2016) modified zeolite with 35 kHz ultrasonic wave for 45 minutes, and the removal rate of ammonia nitrogen was 30% higher than that of natural zeolite. Soetardji et al. (2015) found that the adsorption rate of ammonia nitrogen by sodium hydroxide (NaOH) solution modified zeolites was 30% higher than that of natural zeolites. At present, experts and scholars at home and abroad have studied many modification methods of natural zeolite, but there are still some deficiencies in exploring the specific modification conditions, so this experiment will optimize the modification concentration, modification time and modification temperature in detail. comprehensive and comprehensive exploration of natural zeolite modification methods. In addition, tungstate has good adsorption performance and excellent removal effect of organic pollutants (Jiahui et al., 2018). It has a good application prospect in the field of wastewater treatment, but the related research on using tungstate as a zeolite modifier has not been reported. Therefore, in this study, zeolite was modified with NaCl, Na_2WO_4, and $C_6H_5Na_3O_7$ solution, the best modification method was optimized, and the modification method with the best adsorption effect was selected to study the adsorption characteristics of ammonia nitrogen, which provides a new treatment idea and application reference for the modification of natural zeolite.

Materials and methods

Test materials, reagents, and instruments

The adsorption material selected in the experiment was natural zeolite produced in Gongyi City, Zhengzhou, China. The zeolite was granular, and the color was milky white. After cleaning repeatedly with distilled water before using, put it into the oven, heated it at 85°C for 3 hours, took it out, dried it to room temperature, sealed and stored it. The experiments were all carried out in China.

The experimental reagents including rochelle salt ($NaKC_4H_4O_6$), potassium iodide (KI), mercuric iodide (HgI_2), NaOH, hydrochloric acid (HCl), ammonium chloride (NH_4Cl), NaCl, Na_2WO_4, $C_6H_5Na_3O_7$, potassium chloride (KCl), magnesium chloride ($MgCl_2$) and aluminium chloride ($AlCl_3$) were all analytically pure. In the experiment, 50 mg/L NH_4Cl solution was used to simulate wastewater.

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The main instruments of the experiment are shown in *Table 1*.

Table 1. *Main instrument of the experiment*

Instrument name	Model	Manufacturer
Electric blast drying box	101AB	Hangzhou Zhuochi instrument
Ultraviolet-visible spectrophotometer	UVWin6	Beijing Pusan General instrument Co., Ltd.
Air bath constant temperature oscillator	THZ-82A	Marine energy instrument
Analytical balance	AR224CN	Ohaus instruments co., Ltd.
pH meter	PHS-3E	Shanghai Yidian Scientific Instruments Co., Ltd.
X-ray powder diffractometer	XRD-7000	Shimadzu co., Ltd.
Fourier transform infrared spectrometer	FTIR-8400S	Shimadzu co., Ltd.
Scanning electron microscope	JSM-7900F	Japan Electronics Co., Ltd.

Preparation of modified zeolites

A certain concentration of NaCl solution (0.5, 1, 1.5 and 2 mol/L) (Yu, 2021), Na_2WO_4 solution (0.01, 0.05, 0.1 and 0.15 mol/L) and $C_6H_5Na_3O_7$ solution (0.01, 0.05, 0.1 and 0.15 mol/L) (Lin et al., 2015) were prepared and added dry natural zeolite of corresponding quality according to the solid-liquid ratio at 1:15. Then put them into a water bath constant temperature oscillator with a speed of 200 r/min at a specific temperature (25, 35, 45, 55, 65, 75, 85, 95 and 100°C). After oscillating for a certain period (1, 2, 4, 6, 8, 10, 12 and 24 h), taken out and washed repeatedly with distilled water, dried and sealed at 85°C. Taking the adsorption capacity of ammonia nitrogen as the evaluation index, the optimum modification conditions were optimized by a single-factor test to obtain zeolite with better adsorption capacity.

Experimental methods

Exploration experiment of the optimal modification method

0.5 g of zeolite materials with different modifier concentrations, modification time, and modification temperature were added to centrifuge tubes, followed by 25 mL and 50 mg/L of ammonium chloride solution with a concentration of 50 mg/L, with a concentration of 50 mg/L. The samples were taken after 2 h of oscillation in a gas-bath constant temperature oscillator at 30°C and 200 r/min, and then filtered through a double layer of filter paper, and the filtrate diluted by a certain number of times. The concentration of ammonia nitrogen was determined by Nessler's reagent colorimetric method, the experiment was repeated three times in each group, and the optimal modification method was determined.

Adsorption kinetics experiment

The same zeolites content and solution volume were taken, and the adsorption kinetics curves were determined after oscillating 0, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 420, 540, 720 and 1440 min under the same conditions.

Adsorption isothermal thermodynamics experiment

The experiment was conducted with 0.5 g of zeolites with 25 mL of ammonium chloride solution (0, 20, 40, 60, 80, 100, 120 and 140 mg/L) at 15, 25 and 35°C. Then,

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their adsorption isotherm and adsorption thermodynamics were determined, the experiment was repeated three times in each group.

Exploration experiment of the optimal particle size

The zeolites with particle sizes of 20-40 mesh, 40-60 mesh, 60-80 mesh, 80-100 mesh, and 100-120 mesh were applied to investigate the effect of particle size on adsorption capacity, the experiment was repeated three times in each group.

Exploration experiment of the optimal pH

The initial pH values of the ammonium chloride solution were adjusted to 3, 5, 7, 9, and 11 with 0.5 mol/L HCl and NaOH solution, respectively, and then the optimal pH for the experiment was determined, the experiment was repeated three times in each group.

Exploration experiment of the optimal temperature

The temperature was adjusted to 5, 15, 25, 30, 35 and 40°C, respectively, to explore the effect of temperature on adsorption capacity, the experiment was repeated three times in each group.

Exploration experiment of the optimal dosage

The dosages of zeolites were 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5 g, respectively, to explore the effect of dosage on adsorption capacity, the experiment was repeated three times in each group.

Effect of interfering ions on the adsorption of ammonia nitrogen by zeolites

KCl, $MgCl_2$ and $AlCl_3$ solution with different concentrations of 0.01, 0.05, 0.10, 0.15 and 0.20 mol/L were added to the solution to explore the effects of ion types and ion concentrations on zeolites' adsorption of ammonia nitrogen, the experiment was repeated three times in each group.

Characterization of zeolites

In this experiment, the surface morphology of zeolites was observed by scanning electron microscope, the infrared spectrometer analyzed the surface functional groups of zeolites, and the crystal structure of zeolites was determined by X-ray diffraction spectrum.

Data analysis and processing

Adsorption capacity

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{Eq.1}$$

where Q_e is the amount of adsorption, mg/g; V is the volume of the solution, L； m is the mass of the material, g; C_0 and C_e are the initial concentration and equilibrium concentration of ammonia nitrogen in the solution, mg/L.

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Adsorption kinetics

Pseudo-first-order kinetic equation:

$$Q_t = Q_e\left(1 - e^{-kt}\right) \quad \text{(Eq.2)}$$

Pseudo-second-order kinetic equation:

$$Q_t = \frac{{Q_e}^2 k_2 t}{1 + Q_e k_2 t} \quad \text{(Eq.3)}$$

where Q_t is the adsorption amount of ammonia nitrogen at t time, mg/g; Q_e is the adsorption amount of ammonia nitrogen per unit mass of zeolite at adsorption equilibrium, mg/g; $k_1$and k_2 are the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic equations, respectively.

Adsorption isotherms

Langmuir equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \text{(Eq.4)}$$

Freundlich equation:

$$Q_e = K_F {C_e}^{1/n} \quad \text{(Eq.5)}$$

Separation factor:

$$R_L = 1/(1 + K_L C_0) \quad \text{(Eq.6)}$$

where Q_e is equilibrium adsorption capacity, mg/g; Q_m is the theoretical maximum adsorption capacity, mg/g; C_e is the concentration of ammonia nitrogen in the solution when the adsorption reaches equilibrium, mg/L; K_L is Langmuir constant, L/mg; Both K_F and n are related constants of Freundlich model; R_L is a separation factor, also known as equilibrium parameter; C_0 is the initial concentration of ammonia nitrogen, mg/L.

Adsorption thermodynamics

The Gibbs free energy equation calculated the change of thermodynamic parameters (ΔH enthalpy change, ΔS entropy change) of the adsorption process, and the effect of temperature on equilibrium adsorption was analyzed. The formulas are as follows:

$$\ln k_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{(Eq.7)}$$

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$$\Delta G = -RT\ln k_0 \quad \text{(Eq.8)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(Eq.9)}$$

where G is Gibbs free energy change, kJ/mol; ΔH is enthalpy change, kJ/mol; ΔS is entropy change, kJ/mol/K; R is the ideal gas constant, 8.314 J/mol/K, T is Kelvin temperature, K; In the relationship line between $\ln k_0$ and 1/T, the slope and intercept correspond to the values of ΔH and ΔS, respectively.

Results and analysis

Characterization of zeolites

Analysis of zeolites by scanning electron microscope

The scanning electron microscope of zeolites is shown in *Figure 1*. *Figure 1d* shows that the surface of natural zeolites is relatively smooth, and the pores are relatively few. In contrast, (a), (b) and (c) we can see that the surfaces of the three kinds of salt modified zeolites are rough and the porosity is larger. Among them, the surface of NaCl modified zeolite is more irregular and the porous structure is more pronounced.

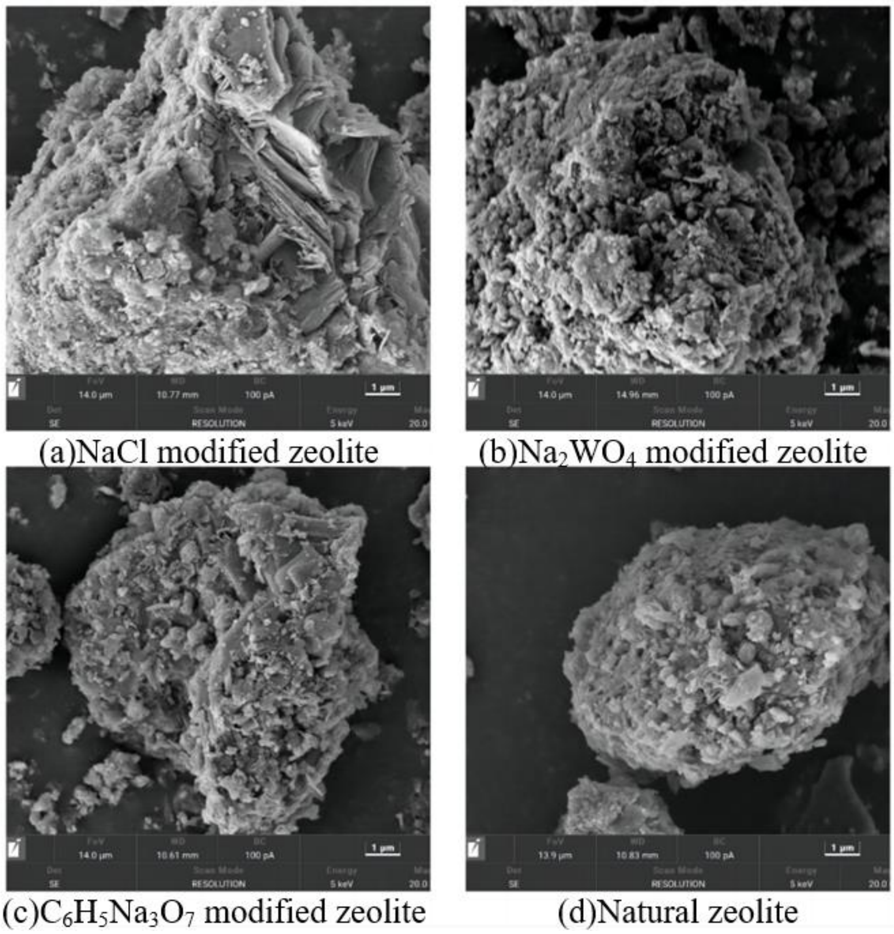

Figure 1. *SEM diagrams of zeolites*

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Infrared spectral analysis of zeolites

Figure 2 shows the infrared spectrum (FTIR) of zeolites. It can be seen from the figure that the zeolites modified by three kinds of salts retain the characteristic peaks of natural zeolite. The characteristic peak at 3502 cm^{-1} is caused by the stretching vibration of O-H (Lian et al., 2024), the zeolite itself may contain a small amount of water before and after modification; The characteristic peak at 2358 cm^{-1} is caused by the stretching vibration of C-H and the stretching vibration of C=O (Li et al., 2023); The characteristic peak at 1647 cm^{-1} is caused by the bending vibration of Si-O and Al-O (Liu et al., 2023); The characteristic peak at 1051 cm^{-1} is caused by the vibration of Si-O-Si skeleton (Liu et al., 2021); The characteristic peak at 793 cm^{-1} is caused by the bending vibration of silicon-oxygen tetrahedron Si-O-Si and aluminum-oxygen octahedron Al-O-Si (Yang et al., 2012). The stretching vibration peak of modified zeolite -OH is weaker than that of natural zeolite, in which the effect of NaCl modification is more prominent.

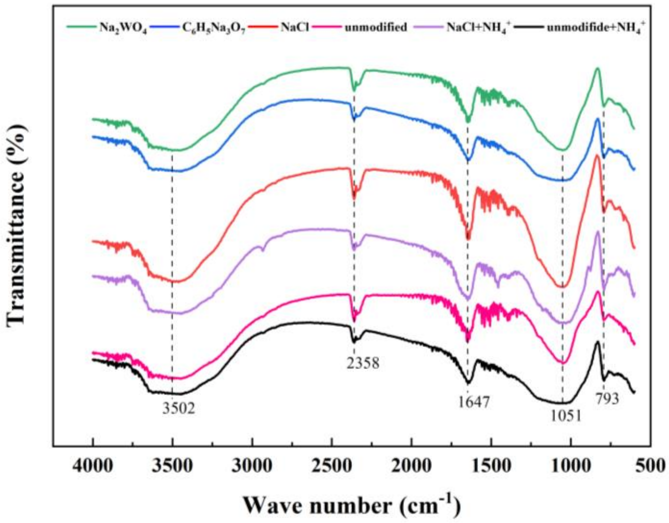

Figure 2. *FTIR spectra of zeolites. Note: Na_2WO_4 is sodium tungstate modified zeolite, $C_6H_5Na_3O_7$ is sodium citrate modified zeolite, NaCl is sodium chloride modified zeolite, unmodified is natural zeolite, NaCl+NH_4^+ is sodium chloride modified zeolite after adsorption of ammonia nitrogen, unmodified+NH_4^+ is natural zeolite after adsorption of ammonia nitrogen*

After ammonia nitrogen adsorption, zeolites' characteristic peaks become weaker at 3502 cm^{-1} and 1647 cm^{-1}. The infrared spectra before and after adsorption show that O-H, C-H and C=O on the surface of zeolites are all involved in the adsorption reaction.

XRD analysis of zeolites

Figure 3 shows the XRD spectrum of zeolites. It can be seen from the diagram that there are no new characteristic peaks in XRD scanning of modified zeolites compared with natural zeolite. There are sharp diffraction peaks at 22.38°. Zeolites before and after modification contain both sodium and calcium zeolites, but the characteristic peaks of sodium zeolites of natural zeolite are not as significant as those of modified zeolites. The formation of sodium zeolites can promote ammonia nitrogen adsorption and improve zeolites' adsorption capacity for ammonia nitrogen. This is consistent with the

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experimental results that the adsorption effect of modified zeolites on ammonia nitrogen is better than that of natural zeolite and is consistent with the results obtained by other researchers using sodium salts to modify natural zeolite.

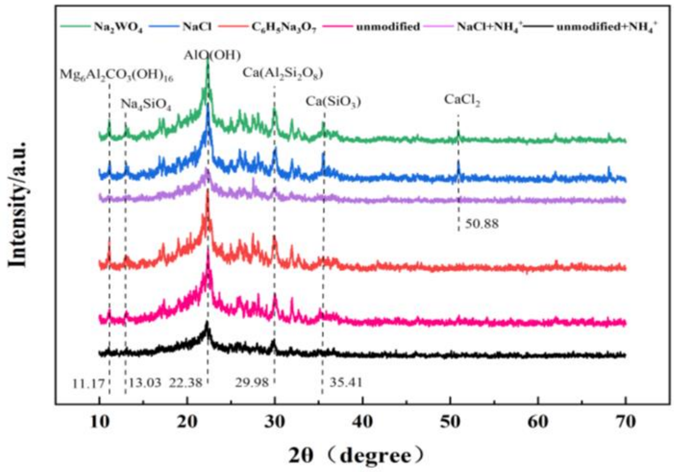

Figure 3. *XRD patterns of zeolites. Note: Na_2WO_4 is sodium tungstate modified zeolite, $C_6H_5Na_3O_7$ is sodium citrate modified zeolite, NaCl is sodium chloride modified zeolite, unmodified is natural zeolite, $NaCl+NH_4^+$ is sodium chloride modified zeolite after adsorption of ammonia nitrogen, unmodified+NH_4^+ is natural zeolite after adsorption of ammonia nitrogen*

In addition, it can be seen from the diagram that there is no new characteristic peak after the adsorption of ammonia nitrogen. Still, the intensity of the diffraction peak decreases at 22.38°, indicating that the dealumination effect of zeolite is noticeable after the adsorption of ammonia nitrogen.

Effect of different modification methods on adsorption of ammonia nitrogen

Effect of modifier concentration on adsorption of ammonia nitrogen by zeolites

Figure 4 shows the adsorption effect of zeolites on ammonia nitrogen after modification with different concentrations of NaCl, Na_2WO_4 and $C_6H_5Na_3O_7$ solution. It can be seen from *Figure 4* that the adsorption capacity and removal rate of ammonia nitrogen by zeolites also change with the change of modifier concentration. The adsorption effect of zeolites for ammonia nitrogen in *Figure 4a* increases with NaCl concentration. When the NaCl concentration is more than 1.5 mol/L, the adsorption effect of zeolite for ammonia nitrogen reaches the highest value and tends to be stable, and the average removal rate and adsorption capacity are 93.45% and 2.14 mg/g, respectively. Therefore, 1.5 mol/L is the best modification concentration of NaCl.

As can be seen from *Figure 4b*, when the Na_2WO_4 concentration is from 0.01 mol/L to 0.1 mol/L, the ammonia nitrogen removal rate of Na_2WO_4 modified zeolite increases from 83.06% to 88%, and the adsorption capacity increases from 2.1 mg/g to 2.23 mg/g. When the Na_2WO_4 concentration is greater than 0.1 mol/L, the ammonia nitrogen removal rate decreases slightly. Therefore, 0.1 mol/L was selected as the best modification concentration of Na_2WO_4 in this experiment.

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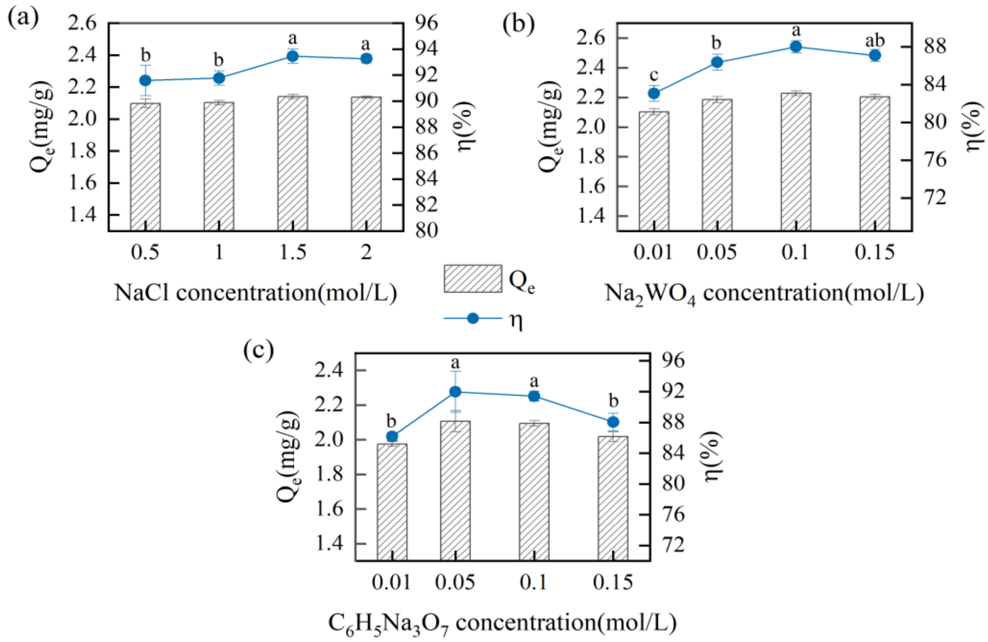

Figure 4. *Effect of modifier concentration on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

As can be seen from *Figure 4c*, when the $C_6H_5Na_3O_7$ concentration is 0.01 mol/L to 0.05 mol/L, the ammonia nitrogen removal rate of $C_6H_5Na_3O_7$ modified zeolite increases from 86.18% to 91.96%, and the adsorption capacity increases from 1.97 mg/g to 2.11 mg/g. When the $C_6H_5Na_3O_7$ concentration is greater than 0.05 mol/L, the ammonia nitrogen removal rate decreases, showing a trend of first increase and then decrease. Therefore, 0.05mol/L was selected as the best modification concentration of $C_6H_5Na_3O_7$ in this experiment.

Effect of modification temperature on adsorption of ammonia nitrogen by zeolites

Figure 5 depicts the adsorption effect of zeolites on ammonia nitrogen after being modified by 1.5 mol/L NaCl, 0.1 mol/L Na_2WO_4 and 0.05mol/L $C_6H_5Na_3O_7$ solutions at different temperatures. *Figure 5* shows that there is a significant difference ($p < 0.05$) in the adsorption of ammonia nitrogen between NaCl modified zeolites and Na_2WO_4 modified zeolites at different modification temperatures. It can be seen from *Figure 5* that there is a positive correlation between temperature and adsorption capacity. When the modified temperature increases from 25°C to 85°C, the average adsorption capacity of NaCl, Na_2WO_4 and $C_6H_5Na_3O_7$ modified zeolites increases from 2.33, 2.19, 2.32 mg/g to 2.54, 2.44, 2.48 mg/g, respectively. When the temperature exceeds 85°C, the adsorption capacity of ammonia nitrogen by three kinds of salt modified zeolites does not increase significantly, so after comprehensive consideration of economic cost and adsorption effect, 85°C was selected as the best modification temperature in this experiment.

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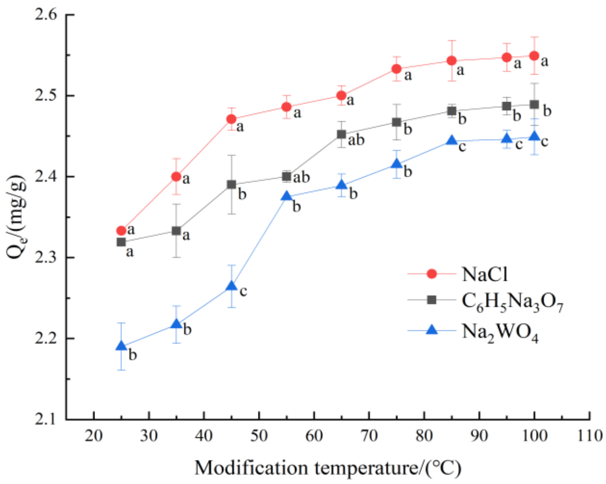

Figure 5. *Effect of modification temperature on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests.* Na_2WO_4 *is sodium tungstate modified zeolite,* $C_6H_5Na_3O_7$ *is sodium citrate modified zeolite, NaCl is sodium chloride modified zeolite. Different lowercase letters represent significant differences between different treatments (*$p < 0.05$*)*

Effect of modification time on adsorption of ammonia nitrogen by zeolites

Figure 6 depicts the adsorption effect of zeolites on ammonia nitrogen after being modified with 1.5 mol/L NaCl, 0.1 mol/L Na_2WO_4 and 0.05mol/L $C_6H_5Na_3O_7$ solutions at 85°C for different times. *Figure 6* shows that there is a significant difference ($p < 0.05$) in the adsorption of ammonia nitrogen between NaCl modified zeolites and Na_2WO_4 modified zeolites at different modification times. With the increase of time, the ion exchange reactions between Na^+ in solution and K^+, Ca^{2+} and Mg^{2+} in zeolites continue to take place. It can be seen from *Figure 6* that the adsorption effect of modified zeolites for ammonia nitrogen increases at first and then stabilizes with the increase of modification time. The adsorption capacity of NaCl modified zeolites for ammonia nitrogen increases rapidly within 1 to 2 hours, and the adsorption capacity increases from 2.3 to 2.38 mg/g. The period from 2 h to 12 h, the adsorption capacity increased slowly to the maximum, from 2.38 to 2.43 mg/g. The average adsorption capacity of Na_2WO_4 and $C_6H_5Na_3O_7$ modified zeolites for ammonia nitrogen increased rapidly from 2.06, 2.17 to 2.24, 2.39 mg/g in 1 h and 12 h, respectively. When the modification time is more than 12 h, the adsorption effect of modified zeolite for ammonia nitrogen reaches the highest value and tends to stabilize gradually. Therefore, the modification time of 12 h was determined as the best preparation condition during the experiment.

Study on the adsorption characteristics of zeolites to ammonia nitrogen

Adsorption kinetic analysis

The effect of different adsorption time on the adsorption of ammonia nitrogen by zeolites before and after modification is shown in *Figure 7*. Under the reaction condition of 30°C, the equilibrium adsorption amount of ammonia nitrogen by zeolite before and after modification was NaCl (2.54 mg/g) > $C_6H_5Na_3O_7$ (2.5 mg/g) > Na_2WO_4 (2.44 mg/g) > natural zeolite (1.58 mg/g). The adsorption capacity of natural

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zeolite was increased by 60.76%, 58.23% and 54.43% by NaCl, $C_6H_5Na_3O_7$ and Na_2WO_4 modification, respectively. Both natural and modified zeolites reach dynamic adsorption equilibrium for ammonia nitrogen at 120 minutes, and the adsorption effect does not increase significantly after 120 minutes. Considering the time cost while ensuring the adsorption effect of zeolite on ammonia nitrogen, this study selected 120 minutes as the optimal adsorption time for natural and modified zeolites. The adsorption effect of NaCl modified zeolites on ammonia nitrogen is better than that of $C_6H_5Na_3O_7$ and Na_2WO_4 modified zeolites. Therefore, the follow-up study of this paper takes NaCl modified zeolite as the primary research object.

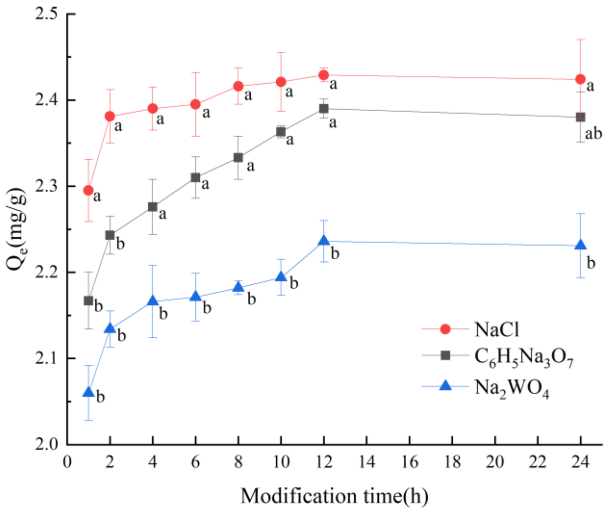

Figure 6. *Effect of modification time on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Na_2WO_4 is sodium tungstate modified zeolite, $C_6H_5Na_3O_7$ is sodium citrate modified zeolite, NaCl is sodium chloride modified zeolite. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

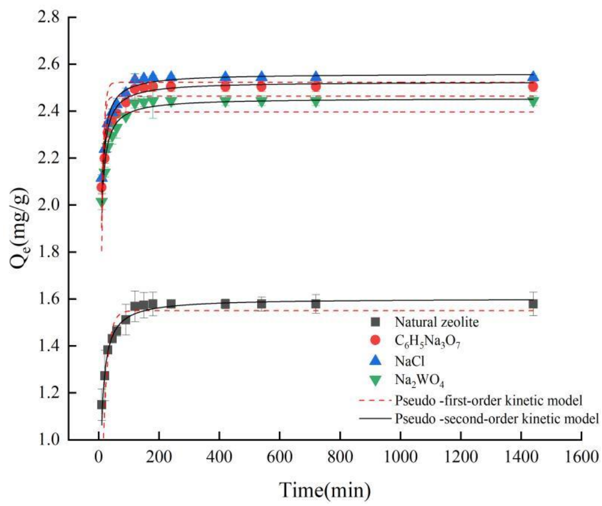

Figure 7. *Adsorption kinetics curve of zeolites before and after modification. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. $C_6H_5Na_3O_7$ is sodium citrate modified zeolite, NaCl is sodium chloride modified zeolite, Na_2WO_4 is sodium tungstate modified zeolite*

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Table 2 shows the kinetic model parameters of zeolites' adsorption of ammonia nitrogen. *Table 2* shows that R^2 (0.975, 0.965, 0.941, 0.960) fitted by the pseudo-second-order model of natural zeolites, NaCl, $C_6H_5Na_3O_7$ and Na_2WO_4 modified zeolites is better than pseudo-first-order model (0.619, 0.665, 0.749, 0.755). The pseudo-second-order kinetic model can better reflect the adsorption behavior of ammonia nitrogen on zeolites. Compared with the theoretical equilibrium adsorption capacity fitted by the pseudo-first-order kinetic model, the pseudo-second-order kinetic model is closer to the actual adsorption capacity obtained by the experiment.

Table 2. *Kinetic model parameters of zeolites adsorption of ammonia nitrogen*

Zeolite	$Q_{e,exp}$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		Q_e	k_1	R^2	Q_e	k_2	R^2
Natural	1.58	1.55	0.066	0.619*	1.60	0.123	0.975**
NaCl	2.54	2.52	0.140	0.665*	2.55	0.156	0.965**
$C_6H_5Na_3O_7$	2.50	2.46	0.154	0.749*	2.52	0.150	0.941**
Na_2WO_4	2.44	2.40	0.140	0.755*	2.45	0.155	0.960**

Note: R^2 stands for correlation coefficients, **indicates statistical significance at $p \leq 0.01$, and *indicates statistical significance at $p \leq 0.05$. Natural is natural zeolite. NaCl is sodium chloride modified zeolite, $C_6H_5Na_3O_7$ is sodium citrate modified zeolite, Na_2WO_4 is sodium tungstate modified zeolite

Adsorption isothermal thermodynamic analysis

In order to understand the adsorption characteristics and mechanism of NaCl modified zeolites for ammonia nitrogen, the adsorption experiments of ammonia nitrogen with initial concentration of 10, 30, 50, 70, 90 and 100 mg/L were carried out at 15°C, 25°C and 35°C. The results are shown in *Figure 8*. At three different temperatures, with the increase of initial concentration, the adsorption rate of natural and NaCl modified zeolites for ammonia nitrogen decreased gradually, while the adsorption capacity of ammonia nitrogen increased gradually, and the adsorption capacity of NaCl modified zeolites for ammonia nitrogen was higher than that of natural zeolites. When the initial concentration of ammonia nitrogen is 100 mg/L at 25°C, the adsorption capacities of natural and NaCl modified zeolites are 2.70 mg/g and 5.17 mg/g, respectively.

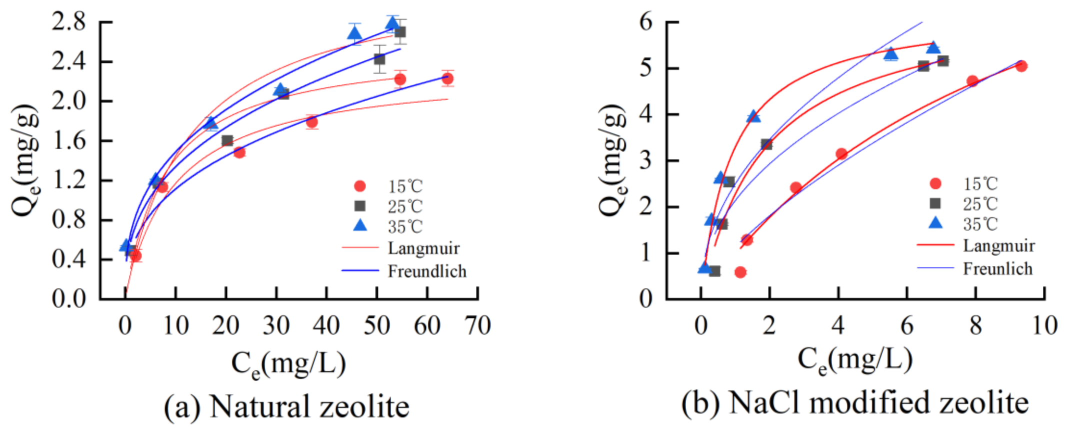

Figure 8. *Isothermal adsorption curve of zeolites before and after modification. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests*

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In order to further explain the adsorption characteristics of NaCl modified zeolites for ammonia nitrogen, the isothermal adsorption process of ammonia nitrogen adsorption on zeolites before and after modification was fitted and compared by Langmuir and Freundlich models, and the fitting results are shown in *Table 3*. It can be seen from *Table 3* that the adsorption isotherm correlation coefficient R^2 of natural zeolite Freundlich (0.947 ~ 0.984) is higher than that fitted by Langmuir model (0.897 ~ 0.953), which indicates that the adsorption of ammonia nitrogen by natural zeolite is multimolecular layer adsorption, while the adsorption isotherm correlation coefficient R^2 of NaCl modified zeolite Langmuir is higher than that fitted by Freundlich model (0.947 ~ 0.976). This shows that the modified zeolite adsorbs ammonia nitrogen mainly by monolayer adsorption. According to the theory of Freundlich model, 1/n indicates the adsorption intensity: if 1/n is between 0.1 and 0.5, it shows that the adsorption of zeolite to ammonia nitrogen is favorable; if 1/n is greater than 2, it means that the adsorption of zeolite to ammonia nitrogen is disadvantageous. According to the Langmuir model theory, we can see whether the zeolite can effectively adsorb ammonia nitrogen through the separation factor R_L value: if the R_L value is between 0 and 1, it shows that the zeolite adsorption of ammonia nitrogen is favorable; if the R_L value is greater than 1, it indicates that the zeolite adsorption of ammonia nitrogen is disadvantageous; if the R_L value is equal to 1, it shows that the adsorption of zeolite to ammonia nitrogen is linear. If the R_L value is equal to 0, it shows that the adsorption of ammonia nitrogen by zeolite is irreversible (Zhao et al., 2010). It can be calculated from *Table 3* that the 1/n of natural zeolite is 0.36 ~ 0.38, and the R_L of NaCl-modified zeolite is 0.02 ~ 0.16, indicating that both natural and NaCl modified zeolites are favorable for the adsorption of ammonia nitrogen. In Langmuir and Freundlich equations, K_L and K_F are positive, meaning that the adsorption of ammonia nitrogen by natural and NaCl modified zeolites can be carried out spontaneously at room temperature (Ates et al., 2016). The higher the K_L value, the stronger the ability of the corresponding adsorbents to adsorb pollutants. In this paper, the adsorption effect of NaCl modified zeolites for ammonia nitrogen is better than that of natural zeolites, which is consistent with the fitting results. Therefore, the Freundlich model can better fit the adsorption process of ammonia nitrogen on natural zeolites, and the Langmuir model can better fit the adsorption process of ammonia nitrogen on NaCl modified zeolites (Liu et al., 2021).

Table 3. *Fitting result of adsorption isotherms*

zeolite	T/ °C	Langmuir model			Freundlich model		
		Q_m/ (mg/g)	k_L/ (L/mg)	R^2	k_F/ (L/mg)	n	R^2
Natural	15	2.33	0.100	0.897**	0.464	2.634	0.947**
	25	2.56	0.124	0.953**	0.563	2.663	0.984**
	35	3.31	0.078	0.891**	0.642	2.744	0.982**
NaCl	15	6.27	0.203	0.984**	1.127	1.466	0.967**
	25	8.68	0.542	0.990**	2.146	2.202	0.976**
	35	10.42	1.105	0.992**	2.497	2.126	0.947**

Note: R^2 stands for correlation coefficients, **indicates statistical significance at p≤0.01, and *indicates statistical significance at p≤0.05. Natural is natural zeolite. NaCl is sodium chloride modified zeolite

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Table 4 shows the thermodynamic parameters of zeolite adsorption of ammonia nitrogen. The ΔG of zeolites before and after modification is adverse and decreases with the increase in temperature, indicating the spontaneous nature of the adsorption process, and the adsorption effect is better at higher temperature. The enthalpy changes of natural and NaCl modified zeolites for adsorption of ammonia nitrogen are 9.4936, 36.8240 and 11.8770 kJ/mol, ΔH is greater than 0, indicating that the adsorption process is endothermic. The ΔS values of natural and NaCl modified zeolites for ammonia nitrogen are 0.1039, 0.2044 and 0.1152 kJ/mol/K, ΔS is greater than 0, indicating that the adsorption process is irreversible. To sum up, the adsorption of ammonia nitrogen by natural and NaCl modified zeolites is a spontaneous, endothermic, and disordered process.

Table 4. *Thermodynamic parameters of adsorption of ammonia nitrogen by zeolites*

Zeolite	**T/°C**	**ΔG/ (kJ/mol)**	**ΔH/ (kJ/mol)**	**ΔS/ (kJ/mol/K)**
Natural	15 25 35	-11.16 -11.71 -15.9	3.53	252.42
NaCl	15 25 35	-12.09 -15.59 -17.94	2.83	255.92

Note: Natural is natural zeolite. NaCl is sodium chloride modified zeolite

Effect of particle size on adsorption of ammonia nitrogen by zeolites

As shown in *Figure 9*, during the process of changing the particle size of natural zeolite from 20-40 mesh to above 120 mesh, the adsorption capacity and removal rate of ammonia nitrogen by zeolite gradually increase, showing a trend of first rapid increase and then slow increase overall.

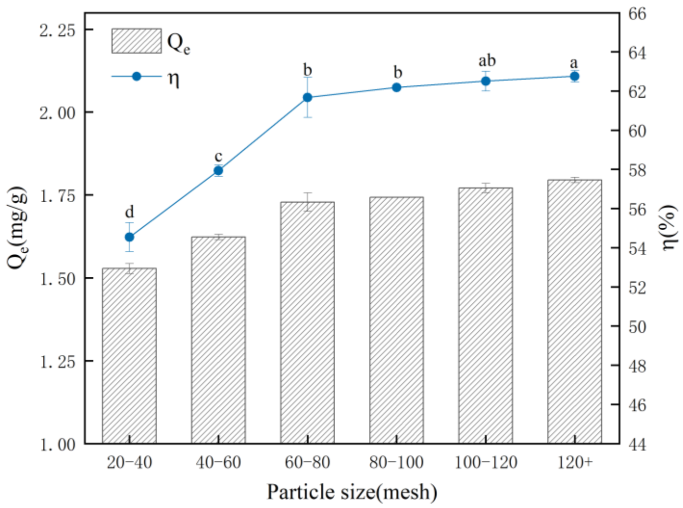

Figure 9. *Effect of different particle sizes on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

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Among them, the removal rates of ammonia nitrogen by zeolite with 60-80, 80-100, 100-120, and above 120 mesh are 57.03%, 57.6%, 58.74%, and 59.7%, respectively. The increase in adsorption effect is insignificant, and zeolite with 80 mesh or above is too delicate and not in granular form, resulting in significant losses during pretreatment and cleaning in the early stage. Therefore, based on the comprehensive adsorption effect and economic cost, subsequent studies will use natural zeolite with a mesh size of 60-80 as the raw material.

Effect of background liquid pH on adsorption of ammonia nitrogen by zeolites

The effect of different pH on the adsorption of ammonia nitrogen by zeolites is shown in *Figure 10*. With the gradual increase of pH, the adsorption capacity of natural and NaCl modified zeolites for ammonia nitrogen increased slowly and then decreased sharply. When pH was 7.0, the adsorption capacity reached the maximum, and the adsorption capacities of natural and NaCl modified zeolites were 1.67 mg/g and 2.68 mg/g, respectively. Therefore, the best pH value is 7 in this study.

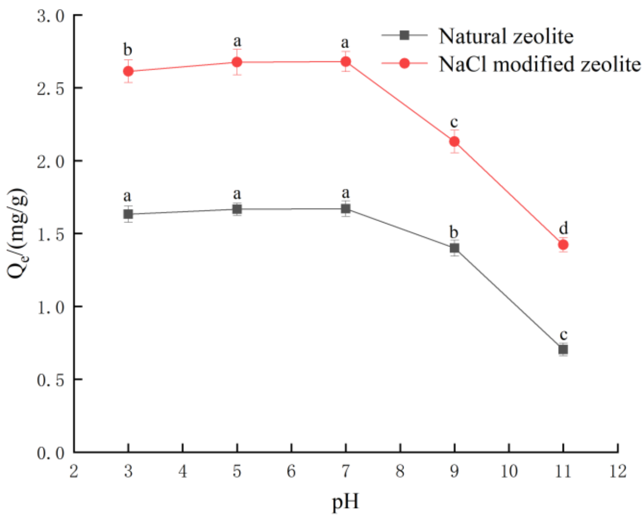

Figure 10. *Effect of different pH on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Different lowercase letters represent significant differences between natural and NaCl modified zeolites in different pH treatments ($p < 0.05$)*

Effect of temperature on adsorption of ammonia nitrogen by zeolites

The effect of different temperatures on the adsorption of ammonia nitrogen by zeolites is shown in *Figure 11*. With the increase in adsorption temperature, the adsorption capacity of zeolite to ammonia nitrogen also increases. However, when the temperature rises to 30°C, the effect of growing adsorption capacity gradually becomes flat. At the same time, in practical engineering, increasing temperature will significantly increase the operating cost and shorten the service life of the equipment. Therefore, considering the economic cost and adsorption effect, the best adsorption temperature selected in this study is 30°C.

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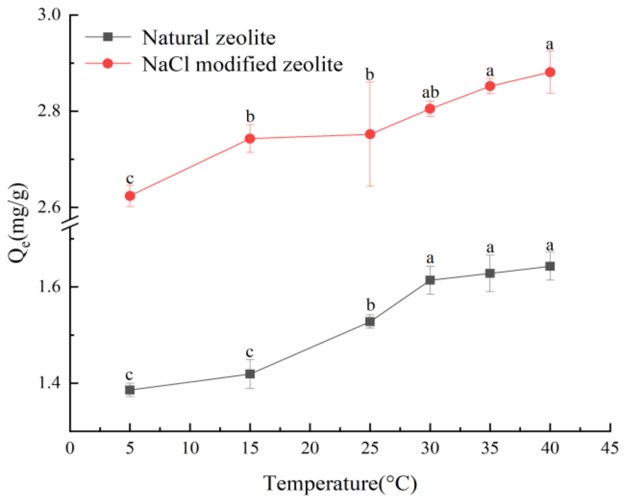

***Figure 11.** Effect of different temperature on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Different lowercase letters represent significant differences between natural and NaCl modified zeolites in different temperature treatments ($p < 0.05$)*

Effect of dosage on adsorption of ammonia nitrogen by zeolites

As shown in *Figure 12*, as can be seen from the above figure, when the dosage increases from 2 g/L to 20 g/L, the ammonia nitrogen removal rate of natural zeolite increases from 16.29% to 69.16%, while the ammonia nitrogen removal rate of NaCl modified zeolite increases from 43.35% to 99.32%. With the increase in dosage, the removal rate of ammonia nitrogen by natural and NaCl modified zeolites grew initially and then gradually stabilized while the adsorption capacity decreased. Appropriately increasing the dosage not only improves the removal rate but also increases the cost. To sum up, after all-round consideration, the unified selection of the dosage is 10 g/L. When the dosage is 10 g/L, the removal rate of ammonia nitrogen by natural zeolite is 54.89%, while the removal rate of ammonia nitrogen by NaCl modified zeolite is 90.39%.

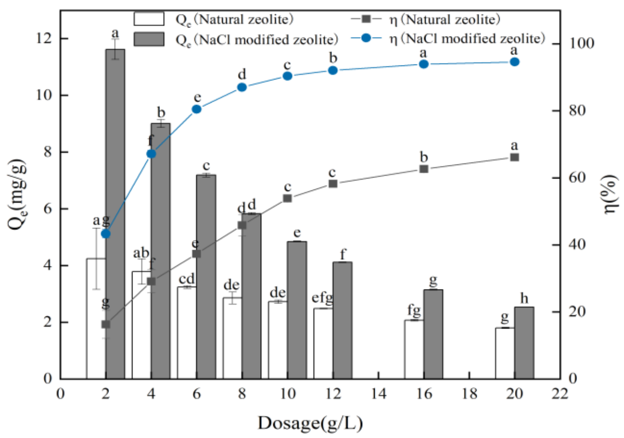

***Figure 12.** Effect of different dosages on adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. Different lowercase letters represent the significant differences between natural and NaCl modified zeolites in different dosage treatments ($p < 0.05$)*

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Effect of ion type and ion concentration on the adsorption of ammonia nitrogen by zeolites

In this study, three common cations, K^+, Mg^{2+} and Al^{3+}, were selected to investigate cations' effect on ammonia nitrogen adsorption by zeolites. The result is shown in *Figure 13*. From the point of view of ion types, the impact of different types of ions on zeolites is closely related to their ion radius and valence. *Figure 13* shows that there is a significant difference ($p < 0.05$) in the effect of different types of interfering ions on the adsorption of ammonia nitrogen by natural and NaCl modified zeolites. The inhibition order of the three cations' adsorption capacity is $Al^{3+} > Mg^{2+} > K^+$. Compared with the addition of K^+ solution, the addition of Mg^{2+} background electrolyte solution reduced the adsorption capacity of natural and NaCl modified zeolites by 12.15% and 9.17%, while the addition of Al^{3+} background electrolyte solution reduced the adsorption capacity of natural and NaCl modified zeolites by 80.05% and 78.37%. It can be seen that the higher the ion valence, the more unfavorable the adsorption of ammonia nitrogen by zeolites.

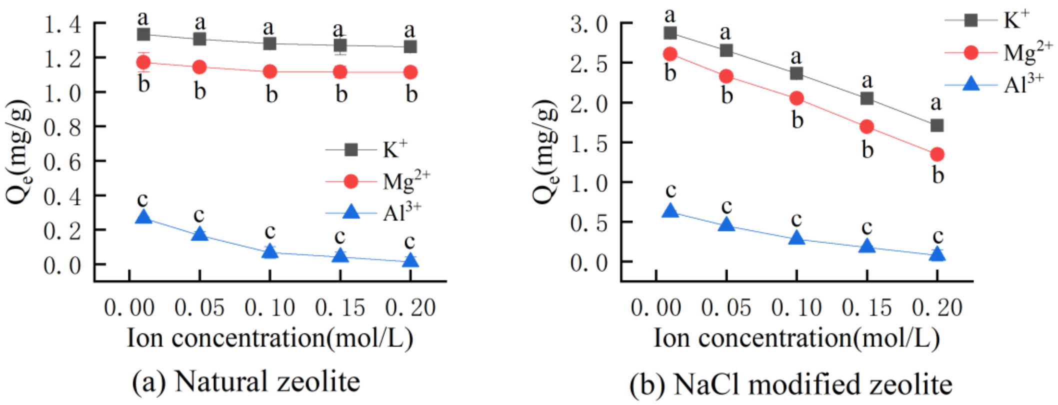

Figure 13. *Effects of different ion types on the adsorption of ammonia nitrogen by zeolites. Note: The error bar in the figure refers to the standard deviation of the data of three repeated tests. K^+ is potassium chloride solution, Mg^{2+} is magnesium chloride solution, and Al^{3+} is aluminum chloride solution. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

From the point of view of ion concentration, different ion concentration has a great influence on the adsorption of ammonia nitrogen by zeolite before and after modification. With the increase in ion concentration, the adsorption capacity of zeolite before and after modification showed a significant downward trend. When the K^+ concentration increased from 0.01mol/L to 0.20 mol/L, the adsorption capacity of natural and NaCl modified zeolites for ammonia nitrogen decreased by 5.40% and 40.44% respectively; with the increase of Mg^{2+} concentration, the adsorption capacity of natural and NaCl modified zeolites decreased by 4.95% and 48.35%; with the rise of Al^{3+} concentration, the adsorption capacity of natural and NaCl modified zeolites decreased by 95.74% and 87.60%.

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Discussion

Characterization of zeolites

We found that salt solution could remove water and inorganic impurities from zeolite pores, exchange cations in zeolite with cations in salt solution, increase porosity, change natural zeolites' original surface structure, and make the surface become loose and porous. This structure was more favorable for the adsorption of ammonia nitrogen by zeolites. The results of this study indicate that the NaCl solution had a more prominent effect on zeolite modification, possibly due to the more significant change in zeolite surface and pores caused by inorganic salts compared to organic salts. After adsorbing ammonia nitrogen, the effect of zeolite on aluminum removal was substantial, and the silicon-aluminum ratio increased. The adsorption of ammonia nitrogen by zeolite may primarily be an ion exchange reaction.

Selection of optimal modification conditions

Because the relative atomic mass of Na^+ was small, it could exchange ions with K^+, Ca^{2+} and Mg^{2+} with larger radii in zeolites, increased the pore size and improved the adsorption capacity of zeolites, the adsorption effect of zeolite on ammonia nitrogen was constantly growing with the increase of NaCl concentration. Yu (2021) found that the modification effect of zeolite was the best when the concentration of NaCl was 1.5 mol/L, which was consistent with the experimental results in this paper. 0.1 mol/L was selected as the optimal modification concentration for Na_2WO_4 in this experiment. Since no scholar has studied the best modification conditions of Na_2WO_4 modified zeolite, this study provides a new treatment idea for natural zeolite and provides reference for other scholars. Lin et al. (2015) also showed that the modification effect of zeolite was the best when the concentration of $C_6H_5Na_3O_7$ was 0.05mol/L, which was similar to our results in this paper.

High temperature may be more able to alter the internal structure of zeolites, and this result was approved by Tongxi et al. (2010). They studied the effect of modification temperature on the adsorption of ammonia nitrogen by zeolite. The results showed that the adsorption capacity increased gradually with the increase of modification temperature, which was consistent with the results of this experiment.

The longer the modification time, the more the contact time between the zeolite and the modifier, which increased the ion exchange time and then increased the porosity of the zeolite. Liu et al. (2022) pointed out that with the increase in modification time, the adsorption capacity of NaCl modified zeolite gradually increased at first and then stabilized, which was consistent with the results of this study.

Effect of modified zeolite on adsorption characteristics of ammonia nitrogen

The results of the adsorption kinetics study showed that the three modified zeolites also had a fast adsorption rate. The adsorption amount of ammonia nitrogen increased rapidly within 60 minutes and increased slowly at 60-120 minutes. After 120 min, the ammonia nitrogen adsorption was stable and reached the adsorption equilibrium. This was because with the increase of adsorption time, the adsorption of ammonia nitrogen by zeolite gradually got saturation, occupied most of the adsorption sites on the surface of zeolites, and fewer adsorption sites were available later. Hence, the adsorption slowed down obviously, showing the characteristics of “fast adsorption and slow equilibrium”, which was consistent with the natural zeolite adsorption of ammonia

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nitrogen (Song et al., 2022). The adsorption of ammonia nitrogen by natural and modified zeolites was more consistent with the pseudo-second-order kinetic model, which indicated that the adsorption of ammonia nitrogen by zeolite was a compound effect of multiple mechanisms, including relatively fast physical adsorption and relatively slow chemical adsorption process (Plazinski et al., 2009). Zeolite modified by tungstate could improve the adsorption capacity of zeolite to ammonia nitrogen. Other interested scholars can use tungstate modified zeolite in other pollution fields for a better adsorption effect.

The results of adsorption isothermal thermodynamics showed that with the increase of the initial concentration of ammonia nitrogen, the adsorption capacity of natural and modified zeolites for ammonia nitrogen also increased. When the initial concentration of ammonia nitrogen was 100 mg/L at 25°C, the adsorption capacity of modified zeolites for ammonia nitrogen was 1.92 times that of natural zeolites. This was because modified zeolites had more adsorption sites, thus increasing the adsorption capacity of zeolites for ammonia nitrogen. The adsorption of ammonia nitrogen by natural and modified zeolites was a spontaneous, endothermic, and disordered process. The adsorption capacity increased with the increase in temperature. This increase may be due to the increased mobility of ions in the solution, increasing the diffusion rate of NH_4^+ (Masoodi et al., 2021).

With the decrease in zeolite particle size, the adsorption capacity of zeolite to ammonia nitrogen increased. This may be due to the smaller the particle size and the larger the specific surface area in contact with the solution. Eljamal et al. (2022) found that both acidic and alkaline environments could reduce the adsorption capacity of zeolite to ammonia nitrogen. This result was because when the pH value was less than 7, the existence of H^+ would inhibit the hydrolysis of NH_4^+ in aqueous solution, which was beneficial to the adsorption of ammonia nitrogen. Still, if the pH was too low, a large number of H^+ would exist and compete with NH_4^+ for the adsorption site on zeolite, resulting in the decrease of the NH_4^+ adsorption effect; when the pH value was more significant than 7 due to the existence of OH^- in aqueous solution, the concentration of NH_4^+ would be reduced, which was also not conducive to zeolite adsorption of ammonia nitrogen. Ma et al. (2022) concluded that the removal rate of RhB by CTMAB modified zeolite increased with temperature. The increase of temperature enhanced the molecular Brownian motion, which made the movement of the NH_4^+ molecule in the solution more intense and improved the contact efficiency between the molecules and the adsorption sites. With the increase of zeolite dosage, NH_4^+ was gradually adsorbed and the removal rate increased, but due to the rise of zeolite dosage, the average adsorption capacity decreased. Wang et al. (2022) found that the absorption of enrofloxacin onto the biochars negatively correlated with the concentration of Ca^{2+} in the background solution. The reason may be that the competitive ability of cations increased with the increase of the number of positive charges, which showed that they would compete with ammonia nitrogen for more negative charge adsorption sites, thus affected the zeolite adsorption of ammonia nitrogen in the form of ion exchange. As the ion concentration increased, the zeolite adsorption sites occupied by the ions increased, resulting in a significant decrease in adsorption. This result was approved by Fu et al. (2020). They pointed out that the effect of ionic strength on the adsorption of ammonia nitrogen by modified zeolites was that the adsorption capacity of ammonia nitrogen decreased with the increase of the concentration of coexisting ions, and cations had a competitive effect on the adsorption process.

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Adsorption mechanism

The adsorption mechanism of salt modified zeolite to ammonia nitrogen was mainly pore filling, electrostatic attraction, and ion exchange. From the SEM diagram of zeolites, it could be seen that there were many pores on the modified zeolite surface. The more pores, the more adsorption sites for ammonia nitrogen. From the adsorption kinetics, it could be seen that the adsorption process of ammonia nitrogen was a simple pore filling action. With the increase of adsorption time, the adsorption of ammonia nitrogen by zeolite gradually reached saturation and occupied most of the adsorption sites on the surface of zeolites. As a result, fewer adsorption sites were available later, and the adsorption slowed down obviously. From the effect of the initial pH value of the solution on the adsorption capacity, it could be seen that the electrification of ammonia nitrogen and zeolite surface ions was also different with different pH. The adsorption capacity was small when ammonia nitrogen and zeolite surface ions were repulsed by static electricity. On the contrary, it was large, and this process was electrostatic gravitation. From the XRD diagram, it could be seen that the dealumination effect of zeolites was obvious after the adsorption of ammonia nitrogen, and the ratio of silicon to aluminum increased. This process was ion exchange.

Conclusion

Compared with natural zeolite, the adsorption effects of NaCl, Na_2WO_4 and $C_6H_5Na_3O_7$ solution modified zeolites for ammonia nitrogen were significantly improved. The optimal modifier concentrations were 1.5 mol/L, 0.1 mol/L, and 0.05 mol/L, respectively; the best modification temperature was 85°C; and the best modification time was 12 hours. Among them, NaCl modified zeolite had the best adsorption effect, with a removal rate of 90.39%. Combined with characterization analysis, it could be seen that the sodium zeolite characteristic peak of the modified zeolite was more significant. The formation of sodium zeolite was conducive to removing ammonia nitrogen, thereby enhancing the adsorption capacity of natural zeolite for ammonia nitrogen. The adsorption of ammonia nitrogen on zeolite before and after modification was more consistent with the pseudo-second-order kinetic model. The fitting results of isothermal adsorption showed that the Freundlich model could better fit the adsorption process of natural zeolites for ammonia nitrogen, and the Langmuir model could better fit the adsorption process of ammonia nitrogen on NaCl modified zeolites. The adsorption was spontaneous, endothermic, and disordered. Under the conditions of particle size 60-80 mesh, pH 7, temperature 30°C, zeolite dosage 10 g/L, and adsorption of wastewater with an initial nitrogen concentration of 50 mg/L, the removal rate of ammonia nitrogen by zeolite modification was 1.65 times higher than that of unmodified zeolite. In summary, salt solution modified natural zeolite was an environmentally friendly and effective method for adsorbing ammonia nitrogen in wastewater.

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