

The effect of ammonia activation on the desalination potential of natural zeolite

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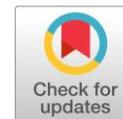
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Abstract

Despite the abundance of water bodies on Earth, there is a limited amount of potable water. Therefore, the desalination process is of great interest. Adsorption of the main contaminants of saline water (Na^+ , K^+ , Cl^- ions) is an alternative process of desalination. In the present work, a sorbent based on natural zeolite (NZ) modified with ammonium chloride (NH_4Cl) is obtained and the effect of modification on the removal of Na^+ and K^+ ions from saline water is studied. According to the Brunauer-Emmett-Teller (BET) analysis, the modification of zeolite with NH_4Cl leads to an increase in its surface area (7.85 to 8.09 m^2/g). According to the results of the cation exchange capacity (CEC) determination, the modification leads to a decrease in total CEC of zeolite (431.67 ± 29.01 to 300.88 ± 31.86 meq/100 g). According to the obtained results, ammonia modification enhances the adsorption ability of NZ to extract Na^+ and K^+ ions from saline water. The extraction degree (E) of Na^+ ions by $\text{NH}_4\text{-Z}$ increases from 7.93 ± 1.63 to $10.44 \pm 1.52\%$, while for K^+ ions it increases about 2 times (27.69 ± 2.45 to $56.46 \pm 3.71\%$). These results indicate that the ammonia-modified NZ can potentially be used as a desalination agent for the removal of Na^+ and K^+ ions from saline water.

Keywords

natural zeolite
ammonia activation
desalination
sodium adsorption
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Key findings

- Modification of zeolite with NH_4Cl leads to an increase in its surface area, enhancing its adsorption capabilities.
- The modified zeolite, $\text{NH}_4\text{-Z}$, shows higher selectivity for Na^+ and K^+ ions, resulting in increased extraction percentages.
- NH_4Cl modification alters zeolite's cation-exchange capacity, favoring enhanced Na^+ and K^+ ion adsorption for desalination.

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1. Introduction

Water is one of the main vital human needs. It is one of the most abundant substances on Earth. But despite its abundance, there is only a limited amount of potable water available for human use. The scarcity of fresh water affects people's daily lives as well as agriculture, food processing, the economy, and other aspects of life [1]. As the population grows, the need for water becomes an urgent problem. According to recent investigations, 40% population of the Earth is already facing water shortages. These data are estimated to grow up to 60% by 2025 [2]. Vari-

ous methods, such as disinfection, aeration, distillation, coagulation, etc., have been used to obtain fresh water [3]. These methods are aimed at removing contaminants from wastewater, such as inorganic and organic impurities, microbes, heavy metal ions, and radiological contaminants. Despite the availability of different wastewater purification techniques, they work better in combination by creating multi-stage purification. However, this method tends to be time and energy consuming.

Saline water desalination is an alternative solution to the problem of freshwater scarcity. Desalination is the process of reducing the salinity of saline water [4, 5]. Ac-

cording to the World Health Organization (WHO), the salinity limit for drinking water is 500 ppm [5]. Currently, many countries provide fresh water to their the population by by desalting saline water reserves [6, 7].

The desalination process was invented in the 18th century. Since then, different desalination methods have been developed. They are reverse osmosis (RO), thermal desalination, multistage flash desalination (MSF), multi-effect distillation (MED), electrodialysis, and nanofiltration (NF) [8–12]. However, the commercialized desalination methods have several drawbacks, such as the high cost of desalination plants for developing countries that are currently experiencing drinking water storage and high energy consumption [13]. Therefore, the existing methods still need to be improved.

Adsorption is an alternative approach to solving the problem of freshwater scarcity. It is of interest due to its simplicity and effectiveness. Adsorption does not require energy consumption [14, 15]. The main contaminants of saline water are Na^+ , K^+ , and Cl^- ions, which determine the salinity level of the water. The adsorption of these ions by adsorbent enables freshwater production. However, the use of the adsorption process by any adsorbent for desalination is a relatively new approach. The main challenge here is to develop an effective adsorbent that provides a high adsorption value for the removal of Na^+ , K^+ , Cl^- ions.

Aluminosilicate raw materials (zeolites, clays, etc.) are quite effective and widespread materials, with high sorption activity towards various substances and relatively low cost [14]. Zeolites are well-known for their adsorption and ion exchange properties, especially towards various heavy metals and organic compounds [15, 16]. Various investigations regarding saline water desalination by zeolites have been carried out. Zeolites, especially clinoptilolite, have high cation selectivity and cation exchange capacity (CEC), as well as they are non-toxic and low-cost. All these properties make zeolites suitable for the adsorption of Na^+ , K^+ , Cl^- ions, thus desalinating saline water [17, 18]. The use of zeolites in the desalination process is one of the promising ways to solve freshwater scarcity.

Various works have been done to further enhance the adsorption properties of aluminosilicate and other raw materials for desalination purposes. Ahmed S. Alsaman et al. used HCl acid pretreatment in the preparation of composite silica-gel [19]. In another study, Alsaman et al. used acid pretreatment to enhance the adsorption properties of bentonite [20]. Moreover, Guo et al. investigated the use of zeolite modified with NaCl to remove K^+ ions from seawater and brackish water [21]. Acid treatment was also found to be effective for the use of natural zeolite in adsorption processes [22, 23]. This study is aimed at describing the physicochemical characteristics of the natural zeolite (NZ) and modified NZ of the Shankanai deposit (Almaty region, Kazakhstan). The key novelty of this study is the modification of NZ using NH_4Cl to enhance its effectiveness in removing Na^+ and K^+ ions from saline water.

2. Experimental

The following materials and reagents were used for the experiments: zeolite of Shankanai deposit (Almaty origin), NH_4Cl , AgNO_3 , NaCl , KCl .

2.1. Natural zeolite modification

Modified zeolite was obtained by treating dried and ground NZ with 1 M NH_4Cl solution at a ratio of 1:5 for 24 hours and rinsing it with distilled water until the excess Cl^- ions were removed. The presence of Cl^- ions was checked by qualitative analysis with 0.1 M AgNO_3 solution.

2.2. Sample characterization

The morphology of NZ and $\text{NH}_4\text{-Z}$ was studied, and the elemental analysis was performed using a scanning electron microscope (SEM) (Quanta 3D 200i Dual system, FEI, USA) equipped with energy dispersive X-ray spectroscopy (EDX). The specific surface area of the zeolite samples was determined by the Brunauer-Emmett-Teller (BET) method. Fourier-transform infrared spectroscopy (FTIR) analysis was performed to identify the chemical bonds present in the zeolite samples.

2.3. Cation-exchange capacity determination

For the determination of the cation-exchange capacity (CEC) of the samples, the standard method with NH_4Cl was applied [24]. Zeolite samples were mixed with a 1 M NH_4Cl solution in a ratio of 1:100 and stirred for 24 h on a laboratory shaker (Lauda, Germany). The suspensions were then centrifuged using a Z 306 Hermle Universal Centrifuge (Labnet, USA). The CEC was calculated as the sum of the concentrations of released Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions which were calculated using the following formula:

$$M_{\text{meq}/100\text{ g}} = C_{\text{ppm}}(\text{eq. wt} \cdot 10), \quad (1)$$

where $M_{\text{meq}/100\text{ g}}$ is the concentration of released cation expressed in meq/100 g; C_{ppm} is the concentration of released cation expressed in ppm; *eq.wt.* is the equivalent weight of the released cation.

2.4. Adsorption study

The ability of the obtained sorbents to absorb Na^+ and K^+ ions was studied at room temperature. For this purpose, the separate solutions containing Na^+ and K^+ ions with a concentration of 100 mg/L were prepared. 0.1 g of the sorbent was placed in a measuring beaker, filled with 10 mL of the solution, and stirred on the laboratory shaker at room temperature (25 ± 5) °C for 24 hours. Then the solution was filtered, and the adsorption value and extraction degree were calculated.

The adsorption value was calculated using the following formula:

$$A = \frac{c_0 - c_{\text{eq}}}{m} \cdot V, \quad (2)$$

where c_0 and c_{eq} are initial and equilibrium concentrations of the sorbate, mcg/cm³; V is a volume of the sorbate solu-

tion, L ; m is a sample mass, g.

Extraction degree of the ions was calculated as follows:

$$E = \frac{c_0 - c_{eq}}{c_0} * 100 \% \quad (3)$$

The initial and equilibrium concentrations of ions were determined by laboratory ionometer "I-160MI" (Measuring equipment, Russia).

3. Results and Discussion

3.1. SEM

The SEM images of zeolite samples are presented in Figure 1. It can be seen from the SEM micrographs that after modifying NZ with NH_4Cl the material becomes looser and a slight increase in the porosity of the surface of the particles is observed.

3.2. Elemental analysis

The results of the elemental analysis of the zeolite samples are presented in Table 1. All the samples contain mainly O, Si, and Al followed by minor amounts of Na, Mg, K, Ca, and Fe. Treatment of natural zeolite with 1 M NH_4Cl leads to a slight increase in the amount of sodium, magnesium, potassium and iron. The changes in the content of elements after modification could be because ammonium ions have a higher affinity for the zeolite's framework compared to sodium and potassium ions. The selectivity of ammonium ions for those ions could possibly enable the $\text{NH}_4\text{-Z}$ to remove these ions from saline water by ion exchange.

3.3. BET

BET analysis allows us to define the specific surface area of the studied materials. Table 2 represents the the specific surface area values of the initial and modified zeolite. Treatment with 1 M NH_4Cl slightly increases the surface area of NZ from 7.85 to 8.09 m^2/g , making it favorable for adsorption processes.

3.4. FTIR spectroscopy

The spectra of NZ and $\text{NH}_4\text{-Z}$ are shown in Figure 2. The FTIR spectrum of NZ shows prominent peaks at 1025.40 cm^{-1} , 1633.35 cm^{-1} , and 3444.88 cm^{-1} . In the IR spectrum of NZ, a strong band at 1025.40 cm^{-1} corresponds to the stretching vibrations of Si-O-Si and Si-O-Al bonds. The peak at 1633.35 cm^{-1} and 3444.88 cm^{-1} indicates the vibrations of present water and OH-groups in the structure of NZ, suggesting the presence of moisture in the zeolite structure. After the modification, a peak at 761.19 cm^{-1} appears on the spectrum. The peak at 761.19 cm^{-1} in the

spectrum of $\text{NH}_4\text{-Z}$ may be related to the potential change in the tetrahedral structure of zeolite.

3.5. CEC

The adsorption capacity of zeolites is usually explained by their ion-exchange properties. Therefore, an investigation of the CEC of zeolite samples is done. The results of CEC are presented in Table 3. From the CEC results of NZ, it can be seen that the zeolite contains more calcium ions than the other exchange cations. The second abundant element is sodium. This could be explained by the fact that sodium ions react more easily than magnesium in the ion-exchange processes. In the case of NH_4Cl modification, the release of magnesium and calcium ions decreased significantly, while the sodium and potassium content only slightly decreased, making the total CEC to decrease.

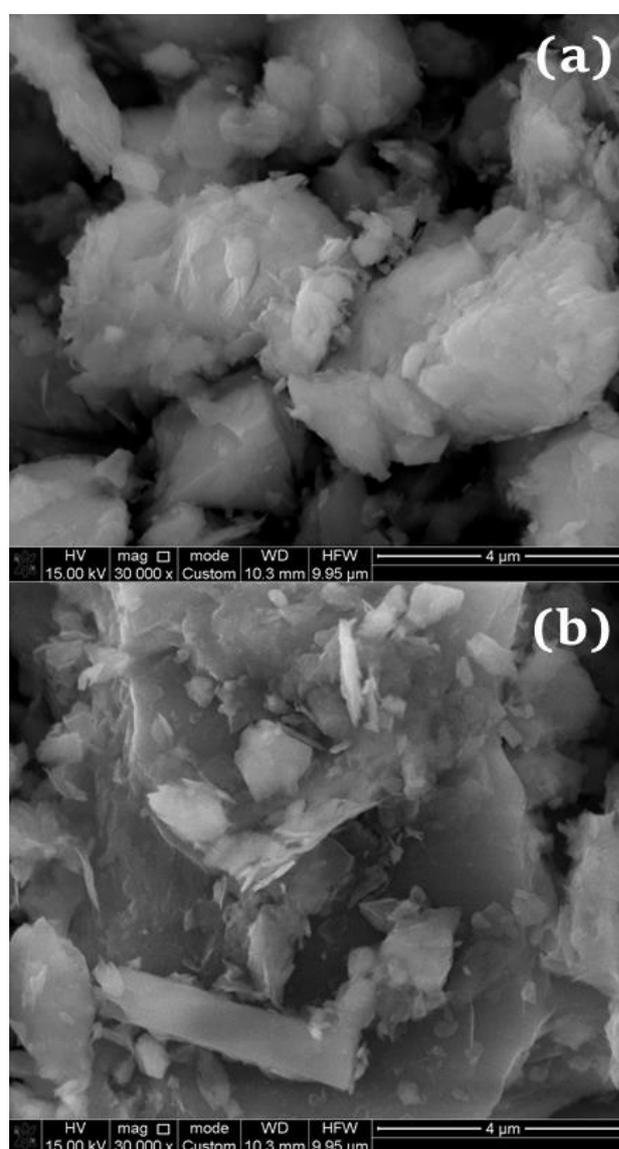


Figure 1 SEM images of NZ (a) and $\text{NH}_4\text{-Z}$ (b).

Table 1 Results of the elemental analysis of the samples.

Sample	C, wt.%	O, wt.%	Na, wt.%	Mg, wt.%	Al, wt.%	Si, wt.%	K, wt.%	Ca, wt.%	Fe, wt.%
NZ	3.13	44.97	2.53	2.23	10.18	27.51	1.02	2.99	4.78
$\text{NH}_4\text{-Z}$	3.16	39.83	3.63	2.44	10.22	25.89	1.66	1.66	10.73

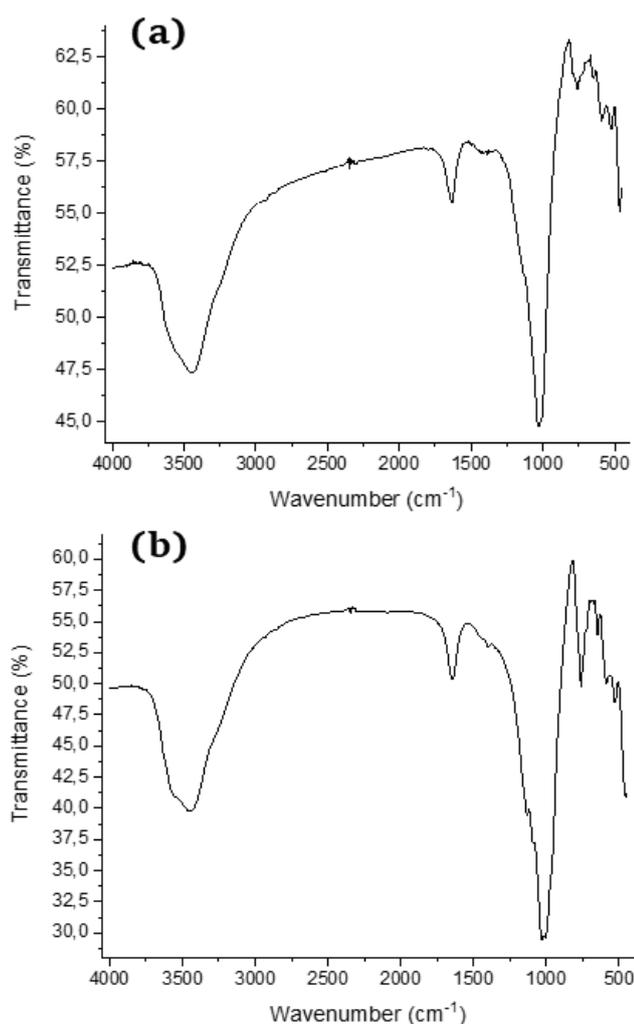


Figure 2 FTIR spectra of (a) NZ and (b) NH₄-Z.

Table 2 Specific surface area of sorbents.

Sorbent	Surface area, m ² /g
NZ	7.85
NH ₄ -Z	8.09

3.6. Adsorption of Na⁺ and K⁺ ions

The adsorption capacity of the zeolite samples towards Na⁺ and K⁺ ions were investigated. The results of the study are presented in Table 4 below. From the data in the table, it can be concluded that the modification of NZ with NH₄Cl enhances its adsorption capacities, increasing the extraction degree of Na⁺ ions from 7.93 to 10.44 % and increasing the removal of K⁺ 2 times. Clearly, the modified zeolite has demonstrated a higher affinity for K⁺ ions compared to Na⁺ ions. This finding is significant and suggests that the obtained adsorbents could be promising materials for application in the desalination of potash brine-impacted groundwater.

Table 3 CEC of zeolite samples (meq/100 g).

Sample	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Total
NZ	152.94±9.34	15.19±1.57	32.91±3.61	230.62±14.49	431.67±29.01
NH ₄ -Z	152.09±21.71	13.85±0.85	7.74±0.59	127.20±8.72	300.88±31.86

Table 4 Adsorption of Na⁺ and K⁺ ions by zeolite samples.

Sample	E(Na ⁺), %	E(K ⁺), %
NZ	7.93±1.63	27.69±2.45
NH ₄ -Z	10.44±1.52	56.46±3.71

4. Limitations

The modified zeolite shows a significant change in the extraction of potassium ions. However, there is no notable change in the extraction of sodium ions. Using the two-step modification (ammonia and acid activation) of NZ could possibly solve this problem.

5. Conclusions

In the present work, the physicochemical properties of natural and modified zeolites were studied. The modification of zeolite leads to an increase in its surface area, making it favorable for adsorption processes, but decreases its CEC. The removal of Na⁺ and K⁺ ions by NZ and NH₄-Z shows that the modification of zeolite enables more high extraction of ions to be achieved. From the study results it can be concluded that zeolite modified with NH₄Cl can be used as potential sorbents for Na⁺ and K⁺ ions from saline water.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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