

AREF ALSHAMER<sup>1,2</sup>, HONGPING HE<sup>1</sup>, AMMAR SALMAN DAWOOD<sup>3</sup>, JIANXI ZHU<sup>1</sup>

## SIMULTANEOUS REMOVAL OF $\text{NH}_4^+$ AND $\text{PO}_4^{3-}$ FROM SIMULATED RECLAIMED WATERS BY MODIFIED NATURAL ZEOLITE. PREPARATION, CHARACTERIZATION AND THERMODYNAMICS

Natural zeolite was modified by NaCl,  $\text{AlCl}_3$  and thermal treatment for the removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions. The characteristics of the modified zeolite (AlZ) and its mechanism for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal were studied and compared. The results showed that the surface area and the  $\text{Na}^+$  and  $\text{Al}^{3+}$  content increased whereas the content of  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  decreased after zeolite modification. On natural zeolite when activated with the 1 M NaCl and 10  $\text{cm}^3/\text{g}$  of pillaring dosage, high adsorption efficiencies for the  $\text{NH}_4^+$  (97.80%) and  $\text{PO}_4^{3-}$  (98.60%) were obtained. The results of various analyses indicated that the  $\text{Na}^+$  exchange is the main mechanism for  $\text{NH}_4^+$  removal whereas the adsorption mechanism for  $\text{PO}_4^{3-}$  followed the complexation with Al–OH groups present in the AlZ. In addition, the kinetics study showed that the adsorption of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  followed pseudo-second order model while the adsorption isotherm of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  is consistent with the Langmuir isotherm model. Moreover, the Gibbs free energy change for the simultaneous removal of the ions indicates that  $\text{NH}_4^+$  is adsorbed faster compared to  $\text{PO}_4^{3-}$ . The simultaneous removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  by AlZ adsorbent is cost effective in water treatment at low ion concentrations.

### 1. INTRODUCTION

Eutrophication is a major problem of surface water resulting primarily from  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  pollution [1].  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions are major components of most fertilizers and detergents. More often these chemicals find their way into water bodies either through

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<sup>1</sup>CAS Key Laboratory of Mineralogy and Metallogeny, and Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China, corresponding author H. He, e-mail address: hehp@gig.ac.cn

<sup>2</sup>Geological Survey and Mineral Resources Board, Ministry of Oil and Minerals, Sana'a, Yemen.

<sup>3</sup>College of Engineering, University of Basrah, Basrah, Iraq.

run-off or as direct discharge from industries. When the concentration exceeds the threshold (aquatic environment), eutrophication may result, which threatens the ecosystem [2, 3]. Hypoxia and toxin from algal bloom are the primary characteristics of eutrophication threatening aquatic life [4, 5]. Therefore, removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  from industrial wastewater prior to discharge into surface water is obligatory.

Various methods have been used to remove  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  from water and wastewater, including biological, chemical and physical processes [4]. In fact, finding low-cost and more efficient materials for the adsorption and ion exchange are highly desirable [1, 6]. Adsorption method is an excellent alternative, for it is cheap and allows recycling or re-usage of adsorbent material [5, 7]. Zeolite is an important adsorbent due to its simplicity and high efficiency for the treatment of pollutants [5].

The structures of zeolites are consist of three-dimensional frameworks of aluminosilicates with a porous structure that have valuable physicochemical properties, such as cation exchange, molecular sieving, adsorption and catalysis [8]. The porous nature of this adsorbent and its high internal surface area are favorable properties for adsorption [9–11].

Recently, research efforts have been devoted to zeolite due to its low cost, availability and environmentally friendly properties [8]. In order to improve the adsorption efficiency of natural zeolite, a number of modification processes can be employed. These include chemical processes such as alkali, acid, surfactant, salt treatment and physical processes such as thermal and microwave modification [1, 4, 12].

In this study, Yemeni natural zeolite (Al-Ahyuq zeolite) was selected for the research due to its natural purity [13]. It has been reported in our previous study [13], that the Al-Ahyuq zeolite has the composition of approximately 90–95% of clinoptilolite as the main natural ion-exchanger. Besides, it has 5–10% montmorillonite and amorphous compound contributing to the ion-exchange process. Therefore, the high purity of Al-Ahyuq zeolite deposit and the montmorillonite and amorphous compound contents can contribute to the observed extraordinary adsorption capacity [5]. In addition, it has high Si/Al ratio about 5.1, that gives rise to good selectivity for the  $\text{NH}_4^+$  removal [13]. However, regardless of modified zeolites or natural zeolites, their efficiencies for the simultaneous removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  through one adsorbent material were quite limited, and there are a few reports on the adsorption mechanism [1, 6].

In this study, natural zeolite modified by salts ( $\text{NaCl}$  and  $\text{AlCl}_3$ ) and thermal treatment has been used to treat simulated reclaimed waters and the adsorption mechanism of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  has been investigated.

Thus, the main objective of this research is to prepare Al/zeolite (AlZ) as a low-cost and highly efficient adsorbent material for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  adsorption via  $\text{NaCl}$ ,  $\text{AlCl}_3$  and thermal modification. The mechanism, characteristics, adsorption isotherms, equilibrium and kinetic properties of the new adsorbent were studied and compared. The specific objectives of this paper are as follows: (1) to determine the optimal conditions for the development of modified zeolite to get better results for the simultaneous removal of

$\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions, (2) to study the characteristics of AlZ by conducting scanning electron microscopy (SEM), X-ray diffraction (XRD), X-Ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR) and specific surface area (SSA) analysis to better understand the adsorption mechanism, (3) to find out the effects of contact time, initial concentration, and temperature on  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal by AlZ, (4) to examine isotherms and thermodynamics of the adsorption of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on the modified zeolites.

## SYMBOLS

- $C_0$  – initial concentration,  $\text{mg}/\text{dm}^3$   
 $C_e$  – equilibrium concentration,  $\text{mg}/\text{dm}^3$   
 $V$  – volume of the working solution,  $\text{dm}^3$   
 $M$  – mass of zeolite, g  
 $k_1, k_2$  – constants of adsorption,  $1/\text{min}$ ,  $\text{g}/(\text{mg}\cdot\text{min})$ , respectively  
 $h$  – rate of adsorption,  $\text{mg}/(\text{g}\cdot\text{min})$   
 $K$  – Langmuir constant,  $\text{dm}^3/\text{mg}$   
 $K_F$  – Freundlich adsorbent capacity,  $\text{mg}/\text{g}$ ,  $\text{dm}^3/\text{mg})^{1/n}$   
 $n$  – reaction order  
 $q_t$  – adsorption capacity at time  $t$ ,  $\text{mg}/\text{g}$   
 $q_e$  – adsorption capacity at equilibrium conditions,  $\text{mg}/\text{g}$   
 $q_{\max}$  – maximum adsorption capacity,  $\text{mg}/\text{g}$   
 $K_{id}$  – constant of intraparticle diffusion,  $\text{mg}/(\text{g}\cdot\text{min})^{1/2}$   
 $C$  – thickness of boundary layer,  $\text{mg}/\text{g}$   
 $\Delta G^\circ$  – standard Gibbs energy,  $\text{kJ}/\text{mol}$   
 $\Delta H^\circ$  – standard enthalpy,  $\text{kJ}/\text{mol}$   
 $\Delta S^\circ$  – standard entropy,  $\text{J}/(\text{mol}\cdot\text{K})$   
 $K_0$  – thermodynamic equilibrium constant

## 2. MATERIALS AND METHODS

*Materials and chemicals.* Natural zeolite (NZ) samples were collected from Al-Ahyuq area in Taiz province, Yemen. All analytical grade chemicals and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

*Preparation of Al/zeolite samples.* Natural zeolite (NZ) was pulverized and passed through a  $74\ \mu\text{m}$  sieve and then dried in an oven at  $100\ ^\circ\text{C}$  for 24 h. The activation of natural zeolite (NZ) by NaCl for optimum performance is based on our previous work [13]. NZ was saturated with sodium ions of 1 M sodium chloride solution and zeolite/solution ratio was maintained as  $1\ \text{g}/10\ \text{cm}^3$ . The suspension was stirred in a conical flask ( $500\ \text{cm}^3$ ) using a magnetic stirrer water bath at a rate of 120 rpm and  $80\ ^\circ\text{C}$  for 1 h. Subsequently the suspension was filtered and washed with distilled water. The wet activated material was dried at  $70\ ^\circ\text{C}$  in an oven for 24 h and then used in batch Al/zeolite modified experiments.

*Al-modified zeolite.* The first stage of the equilibrium study focused on the improved adsorption capacity which could be achieved through aluminum-modified zeolite. The method used for Al/zeolite modified was similar to that described by Tian et al. [8]. To study the optimum aluminum chloride concentrations required for the modification of Yemen's natural zeolite, the aluminum-modified zeolite samples were prepared in four different loadings by 5, 10, 15 and 20 cm<sup>3</sup> pillaring solution/g zeolite.

Under stirring, 150 cm<sup>3</sup> of a 1 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution was added drop wise to 250 cm<sup>3</sup> of 0.5 M AlCl<sub>3</sub>·6H<sub>2</sub>O at 60 °C to obtain the molar ratio [OH<sup>-</sup>]/[Al<sup>3+</sup>] = 2.4. The prepared solution was stirred for another 2 h and aged overnight at room temperature. Under vigorous stirring, a weighed quantity of zeolite was dispersed into the prepared pillaring solution to obtain 5, 10, 15 and 20 cm<sup>3</sup>/g at 60 °C. The mixture was stirred continuously for 5 h at the same temperature and then was cooled to room temperature. After 24 h, it was separated by filtration and then washed four times with distilled water. The solid was oven-dried at 90 °C for 24 h. The dried product (AlZ) was used in batch adsorption experiments at an initial ammonium and phosphate concentration of 20 mg NH<sub>4</sub><sup>+</sup>/dm<sup>3</sup> and 5 mg PO<sub>4</sub><sup>3-</sup>/dm<sup>3</sup>, respectively, at pH = 6 and 35 °C and 24 h stirring time. The best amount of pillaring solution for the modification of zeolite was selected as the corresponding to the highest NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> removal. Figure 1 illustrated the synthesis process of zeolite and its particles after the implementation of chemical modification.

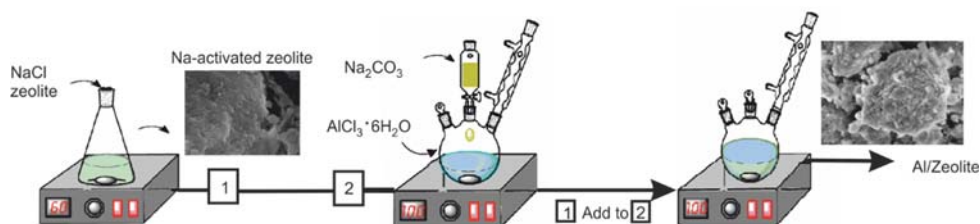


Fig. 1. Schematic illustration of the synthesis process of zeolite (Na and Al forms of zeolite) and SEM image of natural zeolite surface after the implementation of chemical modification

*Analysis and characterization methods.* The AlZ was characterized by the XRD, SEM, EDS, XRF and specific surface area (SSA). Identification of mineral species in the zeolite samples was carried out by XRD pattern using a German D8-FOCOS X-ray diffractometer with Cu-K $\alpha$  ( $\lambda = 0.154$  nm) radiation operating at 40 kV and 40 mA and a step width of 0.05°. Semi-quantitative weight percentages of samples were calculated by using mineral intensity factors.

The morphology and surface element composition of the AlZ and NZ were performed using an electron microscope, operating at an accelerating voltage of 15 kV for photomicrographs with an energy dispersion X-ray (EDS) (Japanese Netherlands FESEM Quanta SU8010). The samples were initially placed in a vacuum chamber for coating with a thin layer (few nm) of gold.

The surface and porous properties of NZ and AlZ were evaluated by the nitrogen gas adsorption method, with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size distribution were performed by the  $\text{N}_2$  adsorption at  $77\text{ K}$  with an automatic volumetric sorption analyzer (ASAP2020, TSI, USA).

X-ray fluorescence spectroscopy (XRF) was used to identify the chemical composition of the samples (Netherlands, Panalytical B.V. AXIOSmAX). The IR absorption measurements were carried out using a Fourier transform IR (FTIR) spectrophotometer (China, 370-DTGS-AVATAR FT-IR). The FTIR spectra in the wavenumbers range from  $400$  to  $4000\text{ cm}^{-1}$  were obtained with the KBr pellet technique.

The  $\text{PO}_4^{3-}$  ion concentration in solution was determined by molybdenum blue phosphorus method using a UV-Vis spectrophotometer at  $700\text{ nm}$  (UV-723, Jinghur, China). The  $\text{NH}_4^+$  ion concentration in solution was determined by the Nessler's method carried out with a UV-Vis spectrophotometer at  $420\text{ nm}$  (UV-723, Jinghur, China). Quality control testing included experiments with blanks and duplicates. pH 6 was selected to simulate the removal of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ .

*Ammonium and phosphate batch adsorption studies.* The stock solution was obtained by dissolving accurately weighed sample of  $\text{NH}_4\text{Cl}$  (AR, 99.5%) and  $\text{KH}_2\text{PO}_4$  (AR, 99.5%). The stock solution was further diluted with distilled water to get the desired concentrations of experimental working solution. Batch adsorption kinetic experiments were performed at the initial concentration of ammonium ( $20\text{ mg}/\text{dm}^3$ ) and phosphate ( $5\text{ mg}/\text{dm}^3$ ) according to reclaimed water as prepared by Huo et al. [1].

The optimum time required for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  to attain equilibrium was determined. Weighted amounts of NZ and AlZ adsorbents ( $0.5\text{ g}$ ) were placed in the  $250\text{ cm}^3$  Erlenmeyer flasks, then  $50\text{ cm}^3$  of  $20\text{ mg NH}_4^+/\text{dm}^3$  and  $5\text{ mg PO}_4^{3-}/\text{dm}^3$  solutions were added to each flask and the flasks were placed in a temperature controlled orbital shaker. The samples were agitated for  $10\text{--}150\text{ min}$  at a fixed pH = 6 and  $35\text{ }^\circ\text{C}$ .

The effects of initial  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentration on their removal efficiency in the batch adsorption experiments were evaluated by varying the concentrations in the range of  $5\text{--}160\text{ mg}/\text{dm}^3$  at pH = 6, AlZ dosage of  $0.5\text{ g}/50\text{ cm}^3$  and  $35\text{ }^\circ\text{C}$  for 2 h.  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  adsorption isotherms for  $15, 25$  and  $35\text{ }^\circ\text{C}$  were studied by varying the initial concentration of ammonium and phosphate ( $10\text{--}160\text{ mg}/\text{dm}^3$ ) at pH = 6 with AlZ dosage of  $0.5\text{ g}/50\text{ cm}^3$  for 2 h.

The removal efficiencies (for zeolites (NZ and AlZ) and the equilibrium adsorption capacities ( $q_e$ ) were calculated by using the following equations:

$$\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. EFFECT OF Al/ZEOLITE ON $\text{NH}_4^+$ AND $\text{PO}_4^{3-}$ REMOVAL

The optimization of water and wastewater purification processes requires cost effective materials with high pollutant-removal efficiency. Therefore, the optimum conditions of the activated and pillaring solution loading on the natural zeolite were investigated. As shown in Fig. 2, the modification of natural zeolite by NaCl and  $\text{AlCl}_3$  and thermal treatment showed significantly enhanced removal of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ .

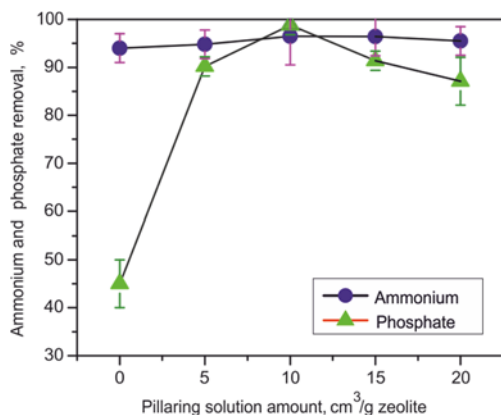


Fig. 2. Effect of aluminum-modified zeolite on the ammonium and phosphate removal at  $35^\circ\text{C}$ ;  $[\text{NH}_4^+]$   $20 \text{ mg}/\text{dm}^3$ ,  $[\text{PO}_4^{3-}]$   $5 \text{ mg}/\text{dm}^3$  AlZ dosage  $0.5 \text{ g}/50 \text{ cm}^3$ , and pH 6)

The  $\text{PO}_4^{3-}$  removal increased by increasing pillaring solution dosage and the highest  $\text{PO}_4^{3-}$  removal (98.60 %) was obtained at the pillaring dosage of  $10 \text{ cm}^3/\text{g}$ . Thereafter, the  $\text{PO}_4^{3-}$  removal decreased with increasing the pillaring dosage. Hence, further addition of pillaring solution is not desirable for the removal of  $\text{PO}_4^{3-}$ . The high loading of aluminum in activated zeolite was not necessarily favored for the adsorption as the inner surface area may not be available for the active adsorption sites for phosphate ions due to the blockage of pores. Therefore, a pillaring dosage of  $10 \text{ cm}^3/\text{g}$  for the AlZ was selected for further experiments. On the other hand, the pillaring solution loading zeolite showed slightly significant effect on the  $\text{NH}_4^+$  removal (Fig. 2). This observation suggests that the high  $\text{NH}_4^+$  removal was due to Na-zeolite (Na-Z) rather than to the pillaring solution indicated by the higher sodium oxide present in the modified zeolite (Table 1). Higher  $\text{NH}_4^+$  removal efficiency means higher  $\text{Na}^+$  content [4, 14]. Thus, it can be confirmed that the main removal mechanism of  $\text{NH}_4^+$  by the AlZ is the  $\text{Na}^+$  exchange reaction.

It was also found that after reaction, the equilibrium pH of each filtered solution was generally higher than that before reaction likely due to the release of  $\text{OH}^-$  ions from

the sorbent into the solution. This specifies that there are aluminum groups present on the AlZ surface and reactive sites for the  $\text{PO}_4^{3-}$  adsorption.

Table 1

Composition of the natural zeolite (NZ), sodium activated zeolite (Na-Z) and Al/zeolite (AlZ) [wt. %]

Oxide	NZ	Na-Z	AlZ
$\text{SiO}_2$	69.88	72.98	72.56
$\text{Al}_2\text{O}_3$	11.78	11.79	14.23
$\text{Fe}_2\text{O}_3$	2.44	2.49	2.05
$\text{TiO}_2$	0.24	0.23	0.20
$\text{MgO}$	0.16	0.06	0.06
$\text{Na}_2\text{O}$	1.08	3.58	3.87
$\text{CaO}$	2.38	0.92	0.34
$\text{K}_2\text{O}$	3.68	2.94	2.07
$\text{P}_2\text{O}_5$	0.01	0.01	0.01
$\text{MnO}$	0.04	0.05	0.03

Accordingly, the modified zeolite showed higher  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal efficiency from the model solution. In this study, the removals of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  using modified zeolite may involve two reaction mechanisms:  $\text{Na}^+$  ions in NaCl solution were exchanged in natural zeolite and the  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were replaced by  $\text{Na}^+$  ions during the NaCl activation as shown in the Table 1. The ionic radius of  $\text{Na}^+$  ion is smaller than those of  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , therefore the effective aperture and exchange capacity of the modified zeolite increased [4]. This increased the  $\text{NH}_4^+$  removal efficiency of the modified zeolite.

Table 2

Maximum  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal on various adsorbents

Adsorbent	Removal [%]		Reference
	$\text{NH}_4^+$	$\text{PO}_4^{3-}$	
Al-modified Zeolite (AlZ)	97.80	98.60	Present study
Zeolite synthesized from fly ash (Mg-ZFA)	43–58	<5	[15]
Modified zeolite combined with struvite crystallization	82.00	98.00	[6]
Modified clinoptilolite (NaCl, $\text{FeCl}_3$ and thermal)	98.46	99.80	[1]
Magnesium ammonium phosphate (MAP) crystallization	13.00	90.00	[16]

Hydrous aluminum oxide was formed on the surface of AlZ by  $\text{AlCl}_3$  and thermal treatment.  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  complexation with  $\text{OH}^-$  groups of the hydrous aluminum oxide in the water sample. Thus, hydrous aluminum oxide in the AlZ contributed mainly towards  $\text{PO}_4^{3-}$  removal. At an initial  $\text{NH}_4^+$  concentration of  $20 \text{ mg/dm}^3$ , the  $\text{NH}_4^+$  removal by

natural zeolite was 50.28%, while at the initial  $\text{PO}_4^{3-}$  concentration of  $5 \text{ mg/dm}^3$ , the  $\text{PO}_4^{3-}$  removal by the natural zeolite was 12.20%. By the addition of  $10 \text{ cm}^3/\text{g}$  zeolite of pillaring solution after zeolite activated by NaCl, the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal by the AIZ increased to 97.80 and 98.60 %, respectively (Fig. 2).

These results were compared with those for other adsorbents for the simultaneous removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  reported in the literature (Table 2). It is evident that, the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal by the AIZ composite is higher than the previously reported by modified or synthesized mineral adsorbents [6, 15, 16] and similar for the modified clinoptilolite [1].

### 3.2. ADSORBENT CHARACTERISTICS AND PROPOSED $\text{NH}_4^+$ AND $\text{PO}_4^{3-}$ REMOVAL MECHANISM ON AIZ

The XRD pattern of NZ (Fig. 3a) reveals that the NZ is composed of 90% clinoptilolite (as the main natural ion-exchanger present in the used sample) and 10% montmorillonite [13].

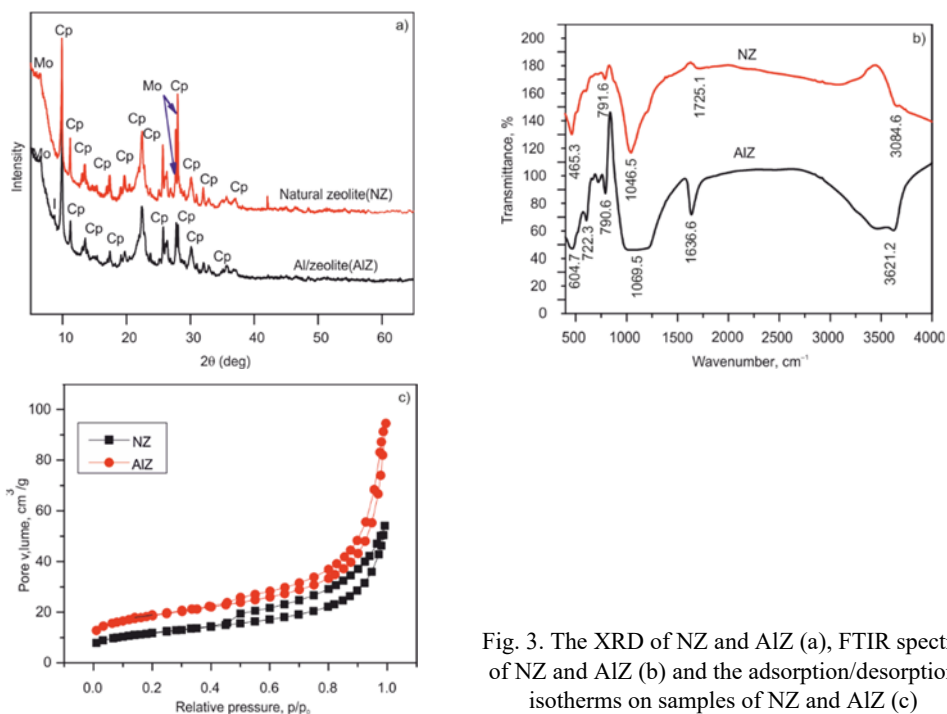


Fig. 3. The XRD of NZ and AIZ (a), FTIR spectra of NZ and AIZ (b) and the adsorption/desorption isotherms on samples of NZ and AIZ (c)

Comparison of the NZ XRD pattern with the AIZ (Fig. 3a) reveals that the intensities of some diffraction peaks of Al/zeolite decreased as well as the peak of illite corresponding to  $2\theta \approx 8.7^\circ$  ( $d = 1.0155 \text{ nm}$ ) appeared. This indicates that the surface of zeolite was covered with amorphous aluminum. The main peak positions of natural zeolite



(Fig. 3a) remain unaffected, indicating good thermal stability of natural zeolite [5]. The FTIR spectra (Fig. 3b) of NZ and Al/zeolite ( $400\text{--}4000\text{ cm}^{-1}$ ) show strong vibration bands from  $466\text{ cm}^{-1}$  to  $791\text{ cm}^{-1}$ . In both IR spectra, they appear due to vibrations of T–O bonds (between aluminum silicates and oxygen) independent of the degree of crystallization of the samples. The peak at  $1046.5\text{ cm}^{-1}$  can be assigned to Si(Al)–O bond in the tetrahedral structure of Si(Al) $\text{O}_4$  present in natural zeolite and broadened due to the introduction of the OH groups of the pillars after modification [17]. The frequency shifted to higher value ( $1069.5\text{ cm}^{-1}$ ) due to the presence of aluminum oxocations in the samples. The peaks in the region  $3150\text{--}3750\text{ cm}^{-1}$  are due to the presence of zeolitic water. These peaks are key indicators of the desorption behavior of the zeolites. A broad peak appearing at  $3084.6\text{ cm}^{-1}$  is a feature of bonded OH and oxygen atoms and its intensity increases after aluminum loading. The peak at  $1725.1\text{ cm}^{-1}$  is the usual bending vibration of water molecule and it decreases to  $1636.6\text{ cm}^{-1}$  after modification. This change can be attributed to the decrease in water content present in the samples due to the heating required for the modified formation process. Therefore, It can be concluded that  $\text{Al}_2\text{O}_3$  was covered by the amorphous or crystallized Al on the surface of the adsorbent [18].

The comparison of chemical components of NZ, Na-Z and AlZ (Table 1) shows the increased content of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in the natural zeolite from 1.08 and 11.78 wt.% to 3.38 and 14.22 wt. %, respectively, after modification. Meanwhile, CaO, MgO and  $\text{K}_2\text{O}$  decreased due to their replacement by  $\text{Na}^+$  ions. Upon modification ( $\text{NaCl}$ ,  $\text{AlCl}_3$  and thermal treatment) of natural zeolite, the adsorption process was further enhanced. This means that the main removal mechanism of  $\text{NH}_4^+$  by the zeolites is the  $\text{Na}^+$  exchange reaction whereas, the hydrous aluminum oxide in the AlZ the main phosphate removal mechanism. Thus, it can be concluded that sodium and aluminum oxide contributed mainly to the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal in the modified zeolite.

The adsorption/desorption isotherms (Fig. 3c) recorded on samples of NZ and AlZ reveal a characteristic hysteresis loops, associated with capillary condensation in the mesopores. The final parts of adsorption isotherms are not horizontal over a range of  $p/p_0$ . The BET specific surface area, total pore volume, and average pore diameter of the NZ are  $35.85\text{ m}^2/\text{g}$ ,  $0.04\text{ cm}^3/\text{g}$  and  $7.89\text{ }\mu\text{m}$ , respectively. However, the BET analysis (obtained after zeolite modification) revealed that the AlZ has a higher BET-specific surface area of  $65.11\text{ m}^2/\text{g}$  with a pore volume of  $0.10\text{ cm}^3/\text{g}$  and an average pore diameter of  $6.33\text{ }\mu\text{m}$ . The increase in the surface area after modification results from distribution of Al throughout the natural zeolite matrix. This suggests that Al/zeolite provide high specific surface area therefore facilitates more effective adsorption.

The surface conditions of the natural and modified zeolite were investigated by the SEM analysis as shown in Fig. 4. The SEM micrograph shows that NZ has a smooth surface (Fig. 4a). Upon modification of NZ, the surface became rough (Fig. 4c), indicating that  $\text{Al}_2\text{O}_3$  present as clusters attached to the zeolite matrix. Figure 4c also shows pores and cavities resulting in an increased specific surface area of the modified zeolite.

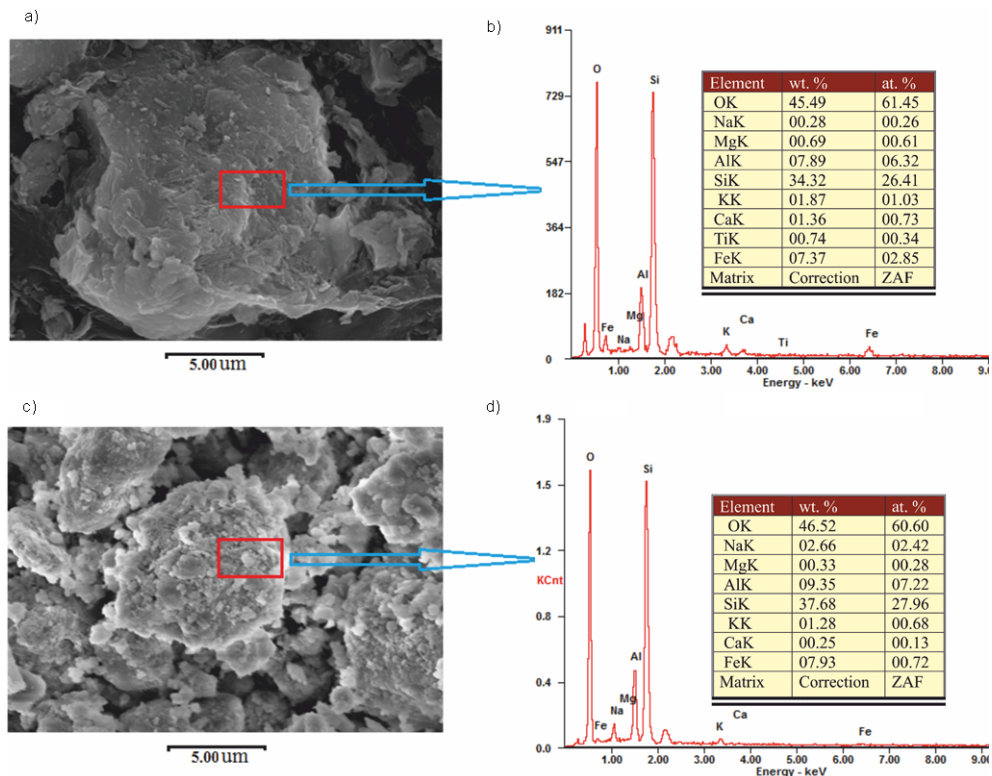


Fig. 4. SEM and EDS analyses of zeolite grain of natural zeolite (NZ) (a, b) and Al/zeolite (AlZ) (c, d)

The EDS spectrum of NZ and AlZ (Fig. 4b, d) revealed that the  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ , and  $\text{Mg}^{2+}$  ion contents in the structure of NZ decreased after modification while the contents of  $\text{Na}^{+}$  and  $\text{Al}^{3+}$  increased from 0.028 and 7.89 wt. % to 2.66 and 9.35 wt. %, respectively. These findings are consistent with the results obtained from the XRF (Table 1). This is the reason why the efficiency for the simultaneous removal of  $\text{NH}_4^{+}$  and  $\text{PO}_4^{3-}$  increased sharply.

### 3.3. ADSORPTION KINETICS OF $\text{NH}_4^{+}$ AND $\text{PO}_4^{3-}$ ON NATURAL AND MODIFIED ZEOLITE

As shown in Figure 5,  $\text{NH}_4^{+}$  and  $\text{PO}_4^{3-}$  ions were removed by AlZ within 70 min in 97.80% and 98.60%, respectively while 50.28% of  $\text{NH}_4^{+}$  and 12.20% of  $\text{PO}_4^{3-}$  were removed by the NZ in 120 min. This indicates that the adsorption of  $\text{NH}_4^{+}$  and  $\text{PO}_4^{3-}$  by AlZ is faster than the NZ. Further increase in contact time did not significantly affect the removal percentage.

The rapid removal of  $\text{NH}_4^{+}$  and  $\text{PO}_4^{3-}$  by AlZ shows additional evidence that the modification increases the number of active surface sites available for the sorption of  $\text{NH}_4^{+}$  and

$\text{PO}_4^{3-}$  ions. Likewise, removal rate and equilibrium time of AlZ is faster and shorter than for reported modified zeolites [1, 15, 19] and other adsorbents such as *Microalgae chlorella*, *Festuca arundinacea Schreb.* and *zoysia* [20], which require several hours to reach adsorption equilibrium. It has been widely accepted that fast adsorption kinetics plays an important role in the efficiency and field-deployment of the adsorbents [5].

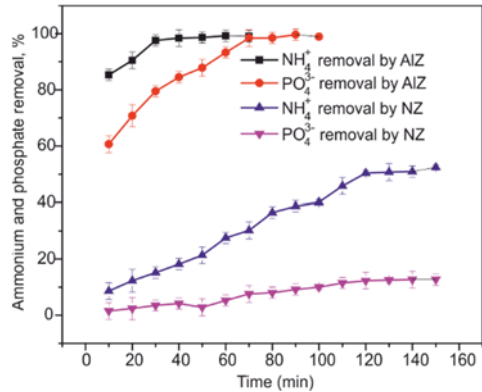


Fig. 5. Influence of contact time on ammonium and phosphate removal efficiency onto NZ and AlZ ( $0.5 \text{ g}/50 \text{ cm}^3$ ) at  $35 \text{ }^\circ\text{C}$ ;  $[\text{NH}_4^+]$   $20 \text{ mg}/\text{dm}^3$ ,  $[\text{PO}_4^{3-}]$   $5 \text{ mg}/\text{dm}^3$  and pH 6)

Rapid and efficient removal of ammonium and phosphate suggests that AlZ can be considered as a suitable adsorbent at low ion concentration of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  in eutrophic waters and wastewater treatment facilities. Three kinetic models were used in order to investigate the adsorption process of contaminants onto the adsorbents. Pseudo-first order, pseudo-second order and the intraparticle diffusion-based Weber–Morris model were used to fit the experimental data and can be summarized as follows for boundary conditions of  $q_e = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t_e$ :

- pseudo-first order

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

- pseudo-second order

$$h = k_2 q_e^2 \quad (4)$$

- Weber–Morris

$$q_t = K_{id} t^{1/2} + C \quad (5)$$

The adsorption kinetics experiments of the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  (Fig. 6) revealed that the pseudo-second order model is the best for describing the kinetics of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  adsorbed on AlZ as indicated by higher  $R^2$  values (Table 3). The pseudo-second order model indicates that chemisorption prevails in the adsorption process. The difference in

the concentration of the adsorbate at equilibrium ( $q_e$ ) and at time  $t$  ( $q_t$ ) is the key driving force for the adsorption, and yet the adsorption capacity is proportional to the number of active sites on the adsorbent surface. The adsorbate transport from the solution to the surface of the adsorbent occurs in several steps. This phenomenon may be controlled by one or more steps such as film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or else a combination of more than one step through the adsorption process. The diffusion of ammonium and phosphate ions from aqueous phase is much faster than the surface and intraparticle diffusion processes because the adsorption was performed under shaking conditions.

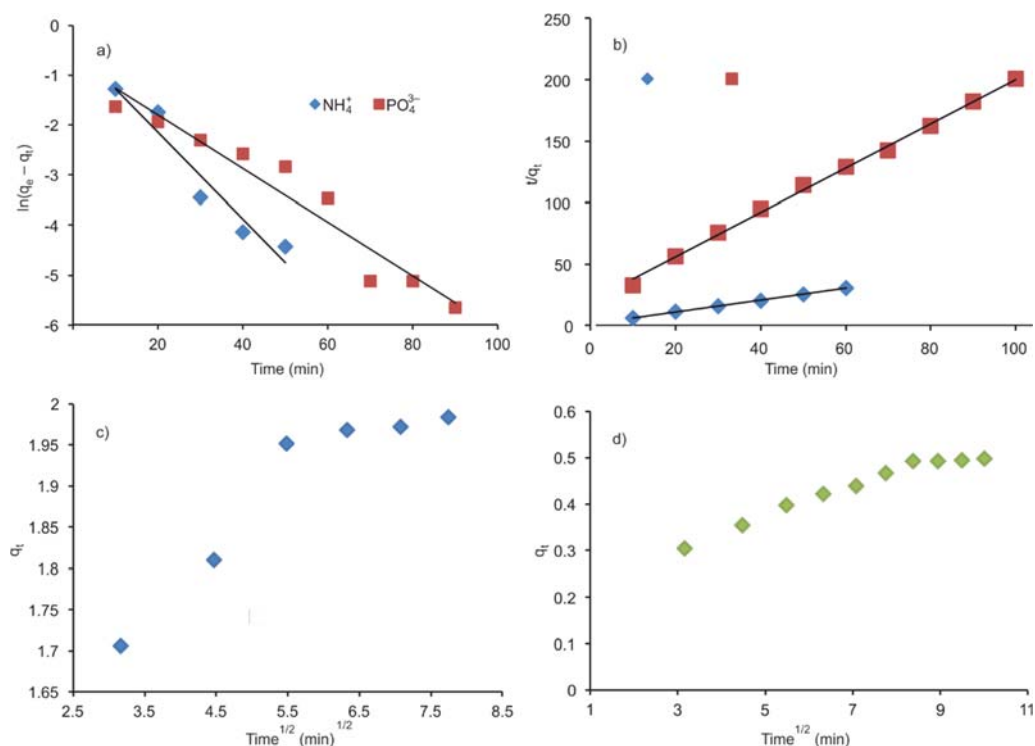


Fig. 6. Pseudo-first order (a), pseudo-second order (b), and intraparticle diffusion for ammonium (c) and phosphate (d) removal

To reveal the relative contribution of surface and intraparticle diffusion to the kinetic process, the kinetic adsorption data were further fitted with the Weber–Morris model using Eq. (5). Intraparticle diffusion is assumed to be the sole rate-controlling step if the regression of  $q_t$  versus  $t^{1/2}$  is linear and the plot passes through the origin. The fitting results show that the regression was linear but the plot did not pass through the origin ( $C \neq 0$ ).

Therefore, the adsorption kinetics of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions on zeolite was regulated by both the surface and particle diffusion process. The removal of ammonium and phosphate by the AlZ involves two stages (Fig. 6c, d). The first stage was suggested to be attributed to the instantaneous occupation of most available surface sites by external surface adsorption. As the external surface of the adsorbent reached saturation,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions entered the inner portion of the AlZ. This is followed by the second stage in which  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions diffuse into the AlZ and other interactions may take place. Table 3 presents the results of fitting experimental data to the pseudo-first, pseudo-second order, and intraparticle diffusion models.

Table 3

Kinetic parameters for ammonium and phosphate adsorption onto AlZ for various kinetic models

Kinetic model	Parameters		
	Pseudo-first order	$K_1$ [ $\text{min}^{-1}$ ]	$q_e$ [ $\text{mg/g}$ ]
ammonium	0.0867	0.6675	0.9363
phosphate	0.0535	0.4833	0.9328
Pseudo-second order	$h$ [ $\text{mg}/(\text{g}\cdot\text{min})$ ]	$q_e$ [ $\text{mg/g}$ ]	$R^2$
ammonium	0.9466	2.0614	0.9996
phosphate	0.0511	0.5533	0.9975
Intraparticle diffusion	$K_{id}$ [ $\text{mg}/(\text{g}\cdot\text{min}^{1/2})$ ]	$C$ [ $\text{mg/g}$ ]	$R^2$
ammonium	0.1816	0.2278	0.9862
phosphate	0.3317	1.3348	0.9252

The coefficient of determination  $R^2$  (Table 3) decreases in the following order: pseudo-second order > intraparticle diffusion > pseudo-first order model under all experimental conditions, which indicates that the pseudo-second order model is the most suitable to describe the adsorption kinetics of the ammonium and phosphate on modified zeolite. pH of a solution plays a major role on the adsorption capacity of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . According to our previous study [5, 13] and literature data [1, 3], the adsorption of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  onto the zeolite occurred near neutral character of the solution. Therefore, pH 6 was selected to simulate the removal of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ .

### 3.4. $\text{NH}_4^+$ AND $\text{PO}_4^{3-}$ ISOTHERMS

Figure 7 shows the effect of adsorbate concentration on the removal efficiency of various initial concentrations of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on the AlZ. The AlZ displays much greater adsorption efficiency at low concentrations of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . These results indicate that the main adsorption mechanism for the  $\text{PO}_4^{3-}$  ions could be attributed to the adsorption among the oxides and oxyacids of aluminum contained in AlZ. Whereas the

$\text{NH}_4^+$  exchange generally increased upon increasing contents of exchangeable ions ( $\text{Na}^+$ ) present in the AlZ. Remarkably, it was observed that relatively high removal efficiency for both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  could be obtained at low ion concentrations. This suggests a favorable adsorption for the simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal at low ion concentrations.

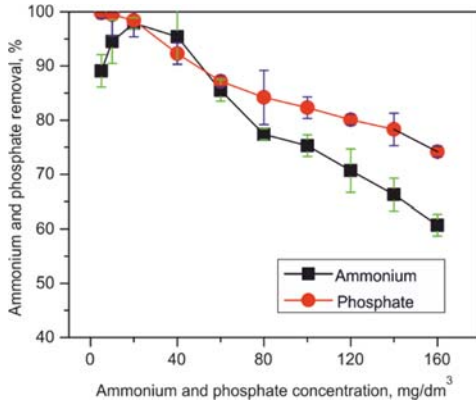


Fig. 7. Dependence of ammonium and phosphate removal efficiency on AlZ on the initial  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentration; dosage of  $0.5 \text{ g}/50 \text{ cm}^3$ , contact time 2 h at  $35^\circ \text{C}$  and pH 6)

Two main isotherm models, Langmuir model (LM) and Freundlich model (FM) were used to describe the experimental results of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  adsorption:

LM is based on the assumption that each active site can only hold one adsorbate molecule. The linear form of LM is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Kq_{\max}} + \frac{1}{q_{\max}} C_e \quad (6)$$

The FM assumes heterogeneity of the surface adsorption occurring at sites with different energy of adsorption. It is described by the following equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

The linear plot of the Langmuir isotherm of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  (Fig. 8a) shows that the values of  $q_{\max}$  and  $K$  can be calculated from the slope and the intercept of the plot using Eq. (6), the calculated values are given in Table 4. It could be seen that the appropriateness of the simple Langmuir equation for the present isotherm data indicates that the Langmuir equation is able to describe properly the isotherm of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on Al/zeolite ( $R^2 > 0.95$ ).

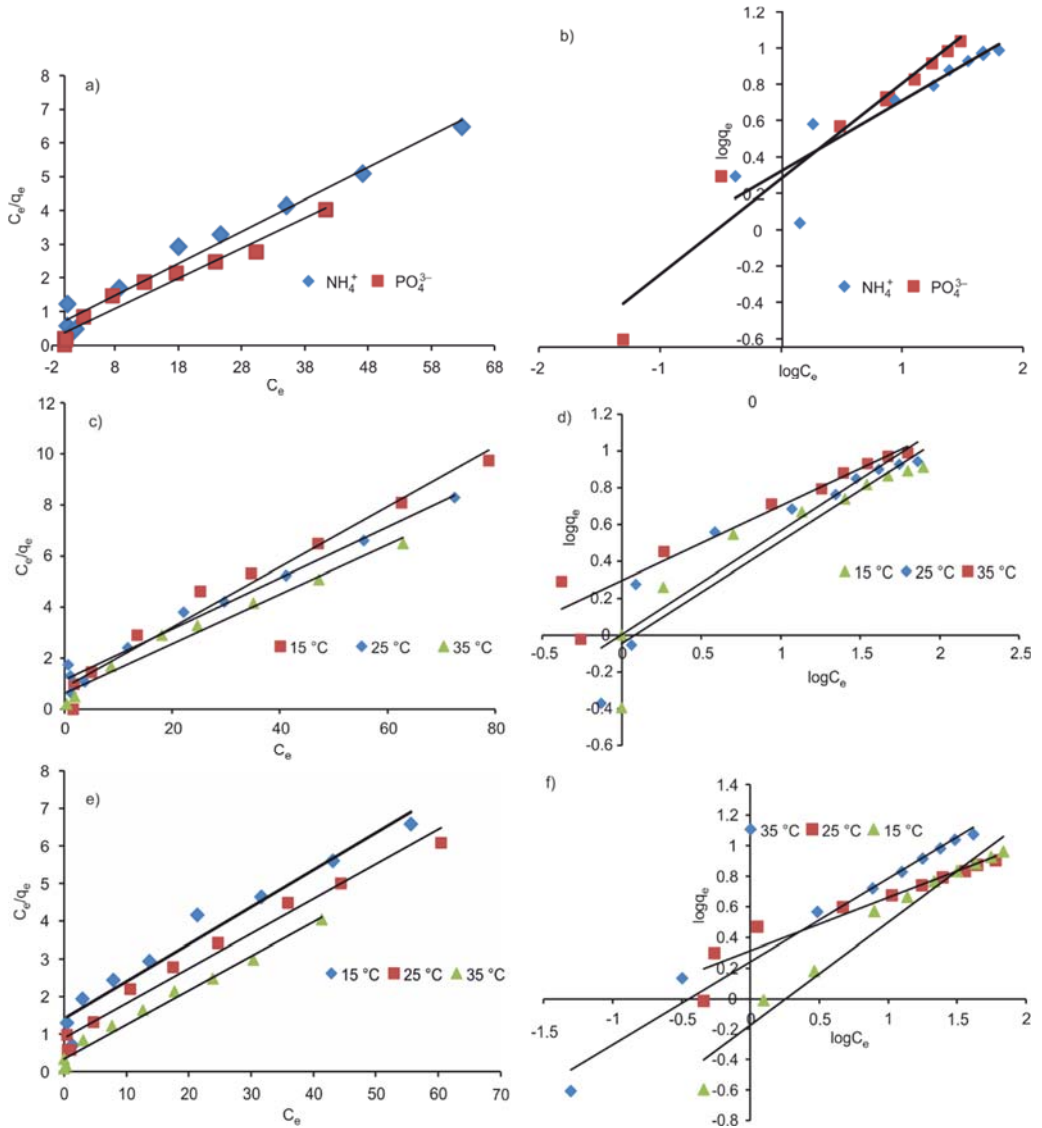


Fig. 8. The linearized Langmuir (a), Freundlich (b) for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  at 35 °C and Langmuir (c, e), Freundlich (d, f) adsorption isotherms of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  at various temperatures on AlZ

As shown in Table 4, at 35 °C the Langmuir parameters  $q_{\text{max}}$  for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on Al/zeolite are 10.31 and 11.00 mg/g, respectively. These values are much higher than those obtained for natural zeolite as reported in our pervious study (8.29 mg/g of  $\text{NH}_4^+$  [13] and 1.30 mg/g of  $\text{PO}_4^{3-}$  [5]). The linear Freundlich adsorption isotherm of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  and the Freundlich parameters (Fig. 8b) are summarized in Table 4.

Table 4

Parameters for equilibrium isotherm models  
for ammonium and phosphate adsorption on AlZ at various temperatures

Langmuir model	Parameters		
	$q_{\max}$ [mg/g]	$K$ [dm <sup>3</sup> /mg]	$R^2$
Ammonium			
15 °C	8.5106	0.136	0.9744
25 °C	10.020	0.088	0.9806
35 °C	10.309	0.155	0.976
Phosphate			
15 °C	10.1419	0.069	0.9567
25 °C	10.8453	0.103	0.9773
35 °C	11.0011	0.0260	0.9822
Freundlich model	Parameters		
	$K_F$ [mg/g]/[mg/dm <sup>3</sup> ] <sup>1/n</sup>	1/n	$R^2$
Ammonium			
15 °C	1.048	0.5536	0.8783
25 °C	1.001	0.562	0.8805
35 °C	1.341	0.4054	0.9256
Phosphate			
15 °C	0.840	0.6724	0.9598
25 °C	1.266	0.3483	0.9058
35 °C	1.373	0.5446	0.9783

It was observed that the LM of Al/zeolite for the PO<sub>4</sub><sup>3-</sup> provides more consistent fit to the data ( $R^2 = 0.906$ – $0.942$ ) when compared with the FM for the ( $R^2 = 0.878$ – $0.925$ ). Similar values of  $1/n$  (lower than 1) have been reported for the NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> removal using natural and modified zeolites from different countries. This suggests that the adsorption conditions are favorable [21]. Similarly, the experimental data for the NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> are best fitted by the LM when compared with the FM as evident from higher  $R^2$  (Table 4).

### 3.5. THERMODYNAMIC STUDY

It was observed that the adsorption capacity of the Al/zeolite towards NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> ions increases upon increasing temperature (Fig. 9).  $q_e$  increases sharply at low equilibrium concentrations, whereas at higher values of  $C_e$ , the increase of  $q_e$  is less evident. The adsorbate concentration gradient is a driving force for the intraparticle transport, which enhances the diffusion of the adsorbate ions to the surface sites for the ultimate attachment. The increase in adsorption capacity of modified zeolite at higher temperatures may be caused by the increase of pore size and activation of the adsorbent surface [22]. A similar trend has been reported for other absorbents [23, 24]. The results indicate



that the rate of the adsorption process is slow and the temperature at 35 °C is preferred to improve the adsorption rate.

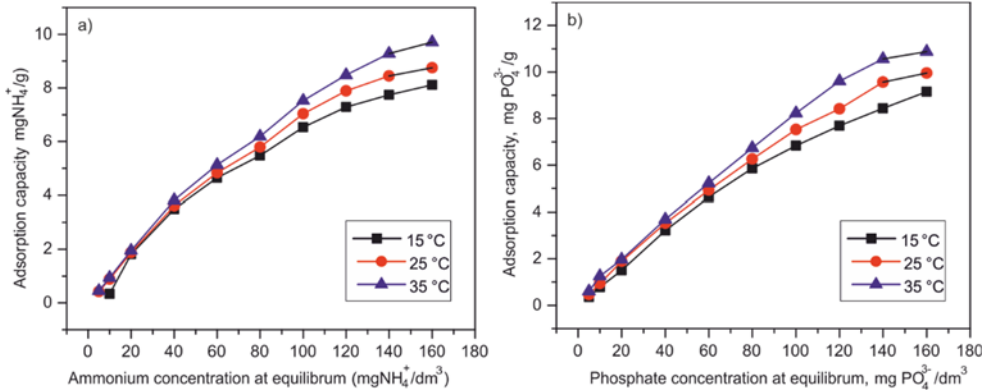


Fig. 9. Adsorption capacity towards  $\text{NH}_4^+$  (a) and  $\text{PO}_4^{3-}$  (b) onto AlZ in dependence of their initial concentration at various temperatures

Adsorption isotherm (for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) at various temperatures on Al/zeolite (Fig. 8c–f) and the LM and FM parameters (Table 4) show that the increase in adsorption capacity can be evaluated by comparing the values of parameters and coefficient of determination ( $R^2$ ). A comparison of the coefficient of determination reflects that LM yields better fit than that of the FM for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ .

The  $q_{\text{max}}$  increased from 8.51 to 10.31 mg/g for the  $\text{NH}_4^+$  while it increased from 10.14 to 11.00 mg/g for the  $\text{PO}_4^{3-}$  when the temperature increased (from 15 to 35 °C). These results were compared with those for previously reported adsorbents (Table 5). The AlZ adsorption towards  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  was higher than that reported for modified minerals [1, 2, 25] and lower than that for mesoporous MgO-loaded diatomite composite [3].

The thermodynamic functions can be determined from the thermodynamic equilibrium constant,  $K_0$  (or the thermodynamic distribution coefficient). The standard Gibbs energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ), for the adsorption of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on Al/zeolite were calculated using the following equations:

$$K_0 = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G^\circ = -RT \ln K_0 \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

$$\ln K_0 = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

The values of  $K_0$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are summarized in Table 6. The results show that the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  adsorption process on AlZ is non-spontaneous in nature as indicated by the positive value of the  $\Delta G^\circ$  for both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ .

Table 5

Adsorption capacities [mg/g] of various adsorbents for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$

Adsorbent	$\text{NH}_4^+$	$\text{PO}_4^{3-}$	Reference
Al-modified zeolite (AlZ)	10.31	11.00	Present study
Natural calcium-rich attapulgite-based versatile adsorbent	2.02	3.32	[2]
A hydrated aluminum oxide modified natural zeolite	30.00	7.00	[25]
Modified clinoptilolite (NaCl, $\text{FeCl}_3$ and thermal)	3.33	0.87	[1]
Mesoporous MgO-loaded diatomite composite	77.05	160.94	[3]

The decrease in  $\Delta G^\circ$  with the increase in temperature shows an increase in the effectiveness of sorption at higher temperatures [23]. Positive changes in the standard enthalpy  $\Delta H^\circ$  (29.001 kJ/mol for  $\text{PO}_4^{3-}$  and 17.077 kJ/mol for  $\text{NH}_4^+$ ) suggest that the sorption is an endothermic process at 15–35 °C. The positive value of  $\Delta S^\circ$  for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  means an increase in randomness at the solid–solution interface during the adsorption process. This value corresponds to an increase in the degree of freedom of the adsorbed species.

Table 6

Thermodynamic parameters for ammonium and phosphate adsorption at various temperatures

Adsorbate	$T$ [K]	$K_0$	$\Delta G^\circ$ [kJ/mol]	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [kJ/(mol·K)]
Ammonium	288	0.123714	4.98	17.077	0.042
	298	0.151889	4.56		
	308	0.196736	3.96		
Phosphate	288	0.151889	4.52	29.001	0.085
	298	0.199685	3.67		
	308	0.334496	2.82		

For all the temperatures,  $|\Delta G^\circ \text{NH}_4^+| > |\Delta G^\circ \text{PO}_4^{3-}|$ , indicating that in simultaneous removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  onto AlZ,  $\text{NH}_4^+$  adsorption is preferred when compared to the  $\text{PO}_4^{3-}$ .

#### 4. CONCLUSIONS

Natural zeolite (NZ) has been modified by NaCl,  $\text{AlCl}_3$  and thermal treatment and applied for simultaneous removal of nutrients from reclaimed water. It showed an excellent performance for the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal. More than 97% of the nutrients could be removed from solution within 70 min, which indicates that the removal rate of

AlZ is higher than that of NZ and previously reported modified minerals. The adsorption capacity of NZ increased from 8.29 to 10.31 mg/g for the  $\text{NH}_4^+$  and from 1.30 to 11.00 mg/g for  $\text{PO}_4^{3-}$  after zeolite modification. The surface area and the  $\text{Na}^+$  and  $\text{Al}^{3+}$  content increased while the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content decreased after zeolite modification. XRD, XRF, SEM-EDS, FTIR and SSA studies confirmed that the main removal mechanism of  $\text{NH}_4^+$  is based on  $\text{Na}^+$  ion exchange whereas phosphate adsorption mainly followed the surface complexation mechanism, the surface hydroxyl groups playing the key role.

The pseudo-second order kinetic model agreed very well with data for the adsorption of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on AlZ, and the adsorption isotherm complied with the Langmuir isotherm equilibrium model. In addition, the thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) reveal the endothermic nature of the process and 35 °C is the optimum temperature for the maximum removal of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  on the AlZ. Based on these results, simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal onto the AlZ adsorbent may reduce the cost of water treatment at low ion concentrations.

#### ACKNOWLEDGMENTS

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