

## Recovering ammonium by treated and untreated zeolitic mixtures: A comprehensive experimental and modelling study

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### ABSTRACT

The recovery of ammonium ( $\text{NH}_4^+$ ) from aqueous solutions by zeolite is attractive. In this study, the physical-chemistry of  $\text{NH}_4^+$  adsorption process from aqueous solution by two zeolitic mixtures, either treated or not treated with NaCl, was assessed.

Results suggested that the zeolitic mixture richer in mordenite and with high specific surface area adsorbed more  $\text{NH}_4^+$  than the one richer in clinoptilolite and heulandite showing a lower specific surface area. NaCl treatment increased the amount of  $\text{NH}_4^+$  adsorbed by the zeolitic mixtures. The higher amount of  $\text{NH}_4^+$  adsorbed by the zeolitic mixtures treated with NaCl was explained by the low/high density water model accounting for cation exchange among the two kosmotropic systems: Na-enriched zeolitic mixtures and  $\text{NH}_4^+$ -enriched aqueous solution. The adsorption kinetics were best approximated by the bimodal pseudo-first-order model. The two sorption kinetic constants,  $k_1$  and  $k_2$  were related to the adsorption (mediated by  $k_1$ ) and the ion exchange (mediated by  $k_2$ ) processes. The fitting of  $\text{NH}_4^+$  data to Langmuir-Sips model suggested that the NaCl treatment increased the number of active sites only of the zeolitic mixture with the large amount of mordenite. Thus, it is conceivable that modulation of NaCl treatment of zeolitic mixtures can be applied to obtain new materials for water remediation from  $\text{NH}_4^+$  contamination.

### 1. Introduction

Porous materials with an appreciable absorptive capacity are considered an attractive solution for recovering nutrients from treated and not treated wastewaters [1]. Natural zeolites for environmental applications are gaining renewed interest owing to their abundance, ease of extraction, and unique properties, such as cation exchange (CEC) and adsorption (AC) capacities [1–3]. Having high affinity for the adsorption of cations, zeolite is commonly used for the removal of  $\text{NH}_4^+$  from aqueous solutions such as treated and untreated wastewaters [1]. Then, in view of a circular economy approach, N enriched zeolite can be reused as slow-release fertilizers in agriculture [4–6].

The amount of  $\text{NH}_4^+$  adsorbed by zeolite depends, among the others, on mineralogical structure, chemical composition, and chemical treatment [7]. According to the process of formation, it is possible to distinguish among more than 70 types of natural zeolites. The most common zeolite forms are clinoptilolite and mordenite with a  $\text{NH}_4^+$

adsorption capacity ranging between 41 and 72  $\text{mg g}^{-1}$  [1].

By studying 8 different zeolites, Langwaldt et al. [2] revealed that the adsorption capacity depends mainly on the mineralogical composition of zeolites. They found that zeolites containing the largest amount of chabazite (82%) adsorbed 48  $\text{mg NH}_4^+ \text{g}^{-1}$ , against zeolites with 93% of clinoptilolite that adsorbed up to 25  $\text{mg NH}_4^+ \text{g}^{-1}$ . However, such a large variability in  $\text{NH}_4^+$  adsorption has been also found among zeolites with the same mineralogy. Wang and Peng [8] reported that the amount of  $\text{NH}_4^+$  adsorbed by clinoptilolite from different origins may range from 3 to 23  $\text{mg g}^{-1}$ . The latter variability depends on a variety of precursor materials, including volcanic and impact glass, aluminosilicate gels and aluminosilicate minerals, such as other zeolites, smectite, kaolinite, feldspars and feldspatoids. Indeed, such factors may affect surface area and total pore volume as well as the Si/Al ratio. The latter properties are directly correlated with the negative charge of zeolite. In fact, the lower the Si/Al ratio, the larger the amount of the negative charge is [9].

Also, the treatment to which zeolites undergo prior to any

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application may affect adsorption capacity. Thushari et al. [10] found that, following the treatment with NaCl,  $\text{NH}_4^+$  adsorption by zeolite increased by 25% compared to the untreated one. Recently, also Muscarella et al. [11] revealed that 1 M NaOH treatment of zeolite resulted in a  $\text{NH}_4^+$  adsorbing capacity of  $18.3 \text{ mg g}^{-1}$ , whereas an acid treatment with 0.1 M HCl produced zeolite with  $\text{NH}_4^+$  adsorption capacity of  $22.5 \text{ mg g}^{-1}$ .

In addition, the interactions between the extra framework cations and the framework of zeolite have been studied by using atomistic simulation techniques [12] and no conceptual model of the cation exchange between aqueous solution and zeolite have been proposed.

The high variability in adsorbing  $\text{NH}_4^+$  showed by zeolite with different mineralogy as related to acid, alkaline or salt treatment stresses the need for further investigation. Moreover, at our best knowledge, no mechanism has been proposed up to now about the exchange between  $\text{NH}_4^+$  in aqueous solution and cations adsorbed onto zeolite either treated or not with NaCl. Thus, the aim of the present study is to provide more insights about the ability of zeolite with different mineralogy, either treated or not with NaCl, in exchanging and adsorbing  $\text{NH}_4^+$  from aqueous solution. Furthermore, a new conceptual model about the exchange and adsorption processes between  $\text{NH}_4^+$  in solution and cations adsorbed onto zeolite is proposed.

## 2. Material and methods

### 2.1. Tested zeolite

Two mixtures of natural zeolites ( $\phi$  0.5–1 mm) were used in this study. They are indicated as ZNS and ZNC. Before their chemical and mineralogical characterization, and use, the two zeolitic mixtures were washed twice with distilled water to remove particulate impurities on the surfaces and dried at  $105^\circ\text{C}$  for 2 h [11]. ZSS and ZSC were, respectively, two mixtures obtained by the previous ones after treatment with 1 M NaCl for 24 h with a zeolite-to-solution ratio of 1:50 (w/v). After NaCl treatment, and prior to all the experiments, ZSS and ZSC have been washed with distilled water in order to remove the excess of sodium. The specific surface area of the two untreated zeolitic mixtures was evaluated by the nitrogen gas adsorption method, using an automated equipment (Nova touch LX1, Quantachrome Instrument, FL, USA), employing multipoint BET isotherm adsorption data fitting.

Morphology and elemental composition of treated and untreated zeolite mixtures were examined by scanning electron microscope (SEM) coupled with energy-dispersive X-ray (EDX) analyser (Phenom Pharos and Phenom XL, Phenom-World Thermo Scientific, Waltham, Massachusetts, USA). Powder X-ray diffraction (XRD) data for structure and phase identification of zeolite mixtures were collected by X'PERT PRO, X-ray Diffractometer (Pan Analytical, Malvern, UK). The main functional groups of zeolite mixtures were assessed by ATR-FTIR Spectrometry (Spectrum Two, PerkinElmer). Spectra were collected in the wavenumber range  $4000\text{--}400 \text{ cm}^{-1}$  on samples dried for 2 h at  $105^\circ\text{C}$  and finely ground. The spectra have been elaborate by using Origin (Version 7.5) software program.

### 2.2. Determination of the point of zero charge

The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the zeolite mixtures was evaluated using the pH drift method according to Nasiruddin et al. [13] as described in Vaičiukynienė et al. [14]. Sodium chloride (0.01 M) was used as a background electrolyte. Eight solutions with pH values in a range from 2 to 9 were prepared by adjusting the pH adding small amounts of 0.5 M HCl or 0.5 M NaOH solutions. Then, 1.0 g of zeolitic mixtures were soaked with 40 mL of each solution and left to settle down for 24 h at room temperature. The final pH of each solution was measured. The  $\text{pH}_{\text{pzc}}$  of zeolitic mixtures was evaluated; if the initial pH of the solution was equal to the final pH of the solution, then that was considered the  $\text{pH}_{\text{pzc}}$ , and the charge on the surface was zero [14].

### 2.3. Theory: kinetic and isotherm models

The  $\text{NH}_4^+$  sorption efficiency of zeolitic mixtures can be evaluated by studying both adsorption kinetics and isotherms. When a kinetic curve is obtained, different models can be applied for the fitting. In particular, the monomodal pseudo-first order model given in eq. (1) is based on the assumption that the adsorption rate depends only on the amount of  $\text{NH}_4^+$  placed in contact with the solid porous surface:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

Here,  $q_t$  is the amount of  $\text{NH}_4^+$  adsorbed on the surface of the porous system at time  $t$ ,  $q_e$  is the equilibrium adsorption capacity (in  $\text{mg g}^{-1}$ ) and  $k_1$  is the pseudo-first order monomodal constant. The latter is directly related to the adsorption rate of the  $\text{NH}_4^+$  on the solid surface. The larger is the  $k_1$  value, the faster is the adsorption rate.

Otherwise, the bimodal pseudo-first order model is based on the assumption that there is polymodality in the  $\text{NH}_4^+$  adsorption, where two pseudo-first order monomodal adsorption patterns exist simultaneously, thereby resulting from different adsorption mechanisms:

$$q_t = q_{e1}(1 - e^{-k_1 t}) + q_{e2}(1 - e^{-k_2 t}) \quad (2)$$

Here,  $q_t$  is the amount of  $\text{NH}_4^+$  adsorbed on the surface of the porous system at time  $t$ ,  $q_{e1}$  and  $q_{e2}$  are the equilibrium adsorption capacities (in  $\text{mg g}^{-1}$ ) at  $t_1$  and  $t_2$ , respectively, while  $k_1$  and  $k_2$  are the respective pseudo-first order monomodal kinetic constants. The larger the kinetic constant values, the faster are the adsorption rates mediated by  $k_1$  and  $k_2$ .

The adsorption isotherms allow to explain solid surface properties such as affinity for the adsorbent and relationship between the amounts of ions exchanged by the porous system and ion concentration at the equilibrium in solution [15]. Moreover, the adsorption isotherms can highlight substantial differences in solid characteristics such as purity, mineral content, and chemical composition.

Freundlich and Langmuir isotherm models are usually applied to evaluate  $\text{NH}_4^+$  removal from wastewaters by using zeolites [9,16], although some criticisms have been found in the literature [17].

Freundlich equation is in the form:

$$q_e = K_F C^{1/n} \quad (3)$$

where  $q_e$  is the amount of adsorbate per unit mass of adsorbent,  $C$  is  $\text{NH}_4^+$  concentration at the equilibrium in solution,  $K_F$  is named Freundlich equilibrium constant or distribution factor, and  $1/n$  is a correction factor related to the number ( $n$ ) of adsorbing sites on the surface of the porous material [18].

According to Moshoeshoe et al. [16], eq. (3) fits experimental data with  $R^2$  values usually  $>0.98$ . However, Canellas [9] revealed that the thermodynamics of  $\text{NH}_4^+$  removal from an aqueous solution using natural zeolites of various origins is better described by the Langmuir isotherm given in eq. (4).

$$q_e \propto \frac{K_L C}{K_L C + 1} \quad (4)$$

Here,  $q_e$  and  $C$  have the same meaning as in eq. (3), while  $K_L$  is the Langmuir equilibrium constant. To account for the non-ideal conditions, eq. (4) can be transformed as in eq. (5):

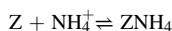
$$q_e \propto \frac{K_L C^n}{K_L C^n + 1} \quad (5)$$

where  $n$  is an empirical parameter related to the effects of the adsorbate concentration [19].

Eq. (3) assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and binding sites are not equivalent and/or independent [20]. Eq. (4) is valid for monolayer

adsorptions on a surface with a finite number of identical sites. However, equation (5) is a better model, it can be written as in equation (6) (also referred to as Langmuir-SIPS), where three adjustable parameters are accounted for [19,21,22].

They are  $q_{max}$ , i.e., the maximum amount of adsorbate that is a function of the number of active sites on the zeolite surface,  $K_L$ , that is the Langmuir's constant referring to the equilibrium



with  $Z$  = zeolite. In eq. (6) the meaning of the parameter  $n$  is the same as reported for eq. (5).

$$q_e = \frac{q_{max} K_L C^n}{K_L C^n + 1} \quad (6)$$

The advantage of eq. (6) lays in the fact that it contains both Freundlich and Langmuir isotherms. In fact, when  $n = 1$  it becomes the Langmuir isotherm reported in eq. (4), while as  $K_L$  approaches to 0, eq. (6) becomes the Freundlich eq. (3).

#### 2.4. $\text{NH}_4^+$ adsorption by zeolitic mixtures

To evaluate  $\text{NH}_4^+$  adsorption ability, 1 g of each sample (ZNC, ZSC, ZNS, ZSS) was shaken with 100 mL of 20 g  $\text{NH}_4^+ \text{L}^{-1}$  solution on an orbital shaker for 24 h at 80 rpm at 25 °C. The concentration of 20 g  $\text{NH}_4^+ \text{L}^{-1}$  was used on the basis of the isotherm study that showed  $\text{NH}_4^+$  saturation of the samples after 24 h at this concentration. After 24 h, samples were washed three times with 200 mL of distilled water to remove the excess of  $\text{NH}_4^+$  and dried in an oven for 2 h at 105 °C.  $\text{NH}_4^+$  adsorbed by zeolitic mixtures was determined by Kjeldahl distillation with 30 mL of 33% (w/v) NaOH solution for 6 min [11]. Amounts of  $\text{NH}_4^+$  adsorbed by zeolitic mixtures were analysed by two-way ANOVA (mineralogy and NaCl treatment as factors) followed by Tukey test to assess significant differences at  $P < 0.05$  among zeolitic mixtures. The experiment was carried out in triplicate.

#### 2.5. Adsorption kinetics

Adsorption kinetics, during 48 h, were assessed by contacting 1 g of each sample (ZNC, ZSC, ZNS, ZSS) with 100 mL of a 50 mg  $\text{NH}_4^+ \text{L}^{-1}$  solution on a horizontal shaker at 80 rpm at 25 °C.  $\text{NH}_4^+$  concentration in solution was determined after 15, 30, 45 min, and 1, 2, 4, 8, 24, 48 h by Berthelot colorimetric method [23]. The  $\text{NH}_4^+$  kinetics adsorption data were mathematically analysed according to eqs. (1) and (2), by using Origin (Version 7.5) software program. The experiment was carried out in triplicate.

#### 2.6. Equilibrium studies

Data for  $\text{NH}_4^+$  adsorption isotherms were obtained by shaking 2 g of each sample (ZNC, ZSC, ZNS, ZSS) with 200 mL of  $\text{NH}_4\text{Cl}$  solution at different concentration (5, 10, 25, 50, 100, 250, 500, 1000, 5000, 10000, 20000 mg  $\text{NH}_4^+ \text{L}^{-1}$ ) on a horizontal shaker at 80 rpm, 25 °C for 24 h.

The  $\text{NH}_4^+$  adsorbed on zeolitic mixtures, determined by Berthelot colorimetric method, was fitted to the Freundlich, Langmuir and Langmuir-Sips equation. All the isotherms were calculated by using non-linear regression with Origin (Version 7.5) software program. The experiment was carried out in triplicate.

### 3. Results and discussion

#### 3.1. XRD, SEM-EDX and FT-IR characterization of the zeolitic mixtures

The specific surface area of the two untreated zeolitic mixtures was  $40 \pm 2 \text{ g m}^{-2}$  for ZNS and  $47 \pm 2 \text{ g m}^{-2}$  for ZNC. XRD analyses revealed

that ZNS was a mixture of heulandite, mordenite, clinoptilolite and stellerite, whereas ZNC was made only by heulandite and mordenite (Table 1). Moreover, the XRD spectra (not reported here) showed also that the NaCl treatment had no impact on the mineralogical composition of the zeolitic mixtures.

The SEM images suggested that NaCl treatment significantly affected surface properties of treated zeolitic mixtures (Fig. 1). Indeed, the latter were more regular, close-grained and with well-defined edges compared to the untreated ones which showed disordered crystal orientation (Fig. 1). Such changes were similar to those reported by Thushari et al. [10] for NaCl treated zeolite.

Elemental analysis performed by SEM-EDX revealed that, following the treatment with NaCl, oxygen, silicon, and aluminium decreased, while Na increased (Fig. S1). The increase of NaCl was also confirmed by the presence of non-homogeneously distributed NaCl on the surfaces of treated zeolitic mixtures. However, the Si/Al, Si/O and Al/O ratios were not affected by NaCl treatment, thus suggesting no alteration in the lattice structure of the two zeolitic mixtures (Table 2).

All the zeolitic mixtures showed similar FTIR spectra (Fig. 2). In particular, in the range 500–420  $\text{cm}^{-1}$ , bending of the bonds between tetrahedral (Si, Al) and octahedral species (Al, Fe, Mg) have been observed; the intervals 720–650  $\text{cm}^{-1}$ , and 1250–950  $\text{cm}^{-1}$  were due to symmetrical and asymmetrical stretching typical of the internal tetrahedra linkages [24]. Other bands were in the range 650–500  $\text{cm}^{-1}$  (double ring), 420–300  $\text{cm}^{-1}$  (pore opening), 820–750  $\text{cm}^{-1}$  (symmetrical stretching) and 1150–1050  $\text{cm}^{-1}$  (asymmetrical stretching), typical of external tetrahedra linkages (Fig. 2). Indeed, according to Byrappa and Kumar [24] the infrared spectrum useful for the characterization of the structural features of zeolite frameworks is in the region of 1500–400  $\text{cm}^{-1}$ .

#### 3.2. $\text{pH}_{\text{pzc}}$ of zeolitic mixtures

The  $\text{pH}_{\text{pzc}}$  determined according to the pH drift method, ranged from 5.5 to 6.5. It was lower in ZNC and ZSC as compared to ZNS and ZSS. Moreover, it was not affected by NaCl treatment (Fig. 3). Therefore, ZNC and ZSC surfaces show negative charges at pH values lower than that of ZNS and ZSS. Based on such results, it can be argued that ZNC and ZSC should have greater potential for removing ammonium ions from aqueous solution than ZNS and ZSS. However, considering that the pHs of all tested zeolitic mixtures were lower than 5.5, we can conclude that there is no effect of  $\text{pH}_{\text{pzc}}$  on zeolite  $\text{NH}_4^+$  ion removal from the solution.

#### 3.3. $\text{NH}_4^+$ adsorption by zeolitic mixtures

The amount of  $\text{NH}_4^+$  adsorbed by the two zeolitic mixtures ranged from  $29.3 \pm 0.2$  to  $35.0 \pm 0.4 \text{ mg g}^{-1}$  (Fig. 4). Regardless of the treatment for their activation, ZNC and ZSC adsorbed more  $\text{NH}_4^+$  than ZNS and ZSS. The higher amount of  $\text{NH}_4^+$  adsorbed by ZNC and ZSC compared to ZNS and ZSS can be ascribed to concomitant factors such as the higher specific surface area of ZNC compared to ZNS and to the higher mordenite content, that has been demonstrated to have higher cation exchange capacity [2]. Indeed, Chen et al. [25] have found that mordenite shows higher specific surface area as compared to clinoptilolite and heulandite. Also, mordenite crystal structure may contribute to higher  $\text{NH}_4^+$  adsorption compared to clinoptilolite and heulandite due to the presence of larger pores and cavities [26].

The amount of  $\text{NH}_4^+$  adsorbed by the tested zeolitic mixtures was

**Table 1**  
Mineralogical composition of tested zeolites.

ZEOLITE	HEULANDITE	MORDENITE	CLINOPTILOLITE	STELLERITE
SAMPLE				
ZNS	47%	20%	17%	16%
ZNC	53%	47%	–	–

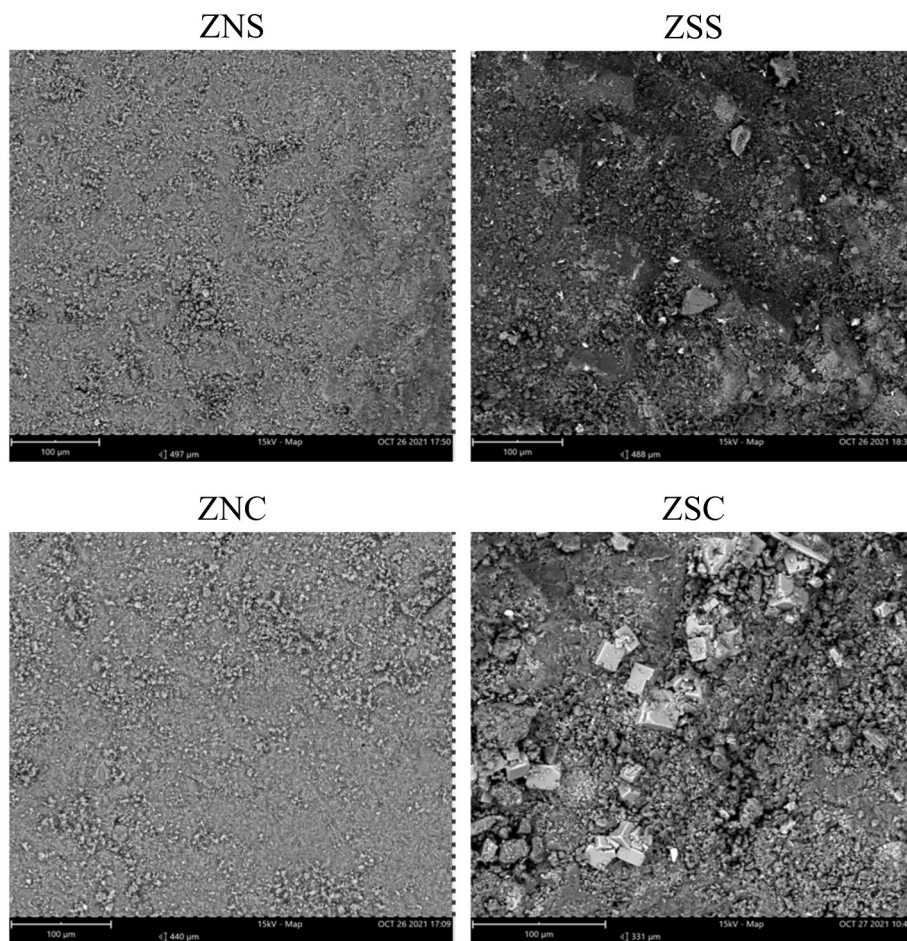


Fig. 1. SEM-EDX SEM images of untreated (ZNS and ZNS) treated (ZSS and ZSC) zeolites.

Table 2

Elemental composition (%) of the tested zeolites.

Element (%)	ZNS	ZSS	ZNC	ZSC
Oxygen	70.6 ± 1.2	69.5 ± 4.3	72.7 ± 0.6	72.3 ± 2.2
Silicon	16.9 ± 0.7	15.5 ± 1.2	14.6 ± 0.5	13.8 ± 2.4
Aluminium	4.1 ± 0.2	3.7 ± 0.2	3.9 ± 0.1	3.7 ± 0.54
Iron	0.5 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.3
Calcium	2.5 ± 0.1	0.8 ± 0.5	2.6 ± 0.1	0.6 ± 0.2
Magnesium	0.9 ± 0.0	0.4 ± 0.1	0.9 ± 0.1	0.4 ± 0.3
Sodium	0.8 ± 0.1	7.3 ± 3.3	1.8 ± 0.1	6.6 ± 2.2
Potassium	1.5 ± 0.3	0.9 ± 0.1	1.5 ± 0.1	0.4 ± 0.1
Si/Al	4.2 ± 0.2	4.2 ± 0.2	3.8 ± 0.1	3.7 ± 0.2
Si/O	0.24 ± 0.01	0.22 ± 0.01	0.20 ± 0.01	0.19 ± 0.04
Al/O	0.06 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.01

larger than that reported by Lin et al. [27], i.e., 17 mg  $\text{NH}_4^+$   $\text{g}^{-1}$ . Although these authors used clinoptilolite with a diameter range like that of the zeolites used in this study (0.8–1.43 mm), they applied a  $\text{NH}_4^+$  solution for zeolite saturation with a concentration of 990 mg  $\text{NH}_4^+$   $\text{L}^{-1}$  which was much lower than that used here (i.e., 20 g  $\text{L}^{-1}$ ). This difference can explain the discrepancy between our data and those from Lin et al. [27].

After NaCl treatment, larger  $\text{Na}^+$  but lower  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content was observed in the treated zeolitic mixtures rather than in the untreated ones. This indicates that the  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions on the exchange surfaces of the untreated zeolitic mixtures were replaced by  $\text{Na}^+$  after sodium chloride treatment.

The amount of  $\text{NH}_4^+$  adsorbed by NaCl treated zeolitic mixtures increased as compared to the untreated zeolitic mixtures. However, such

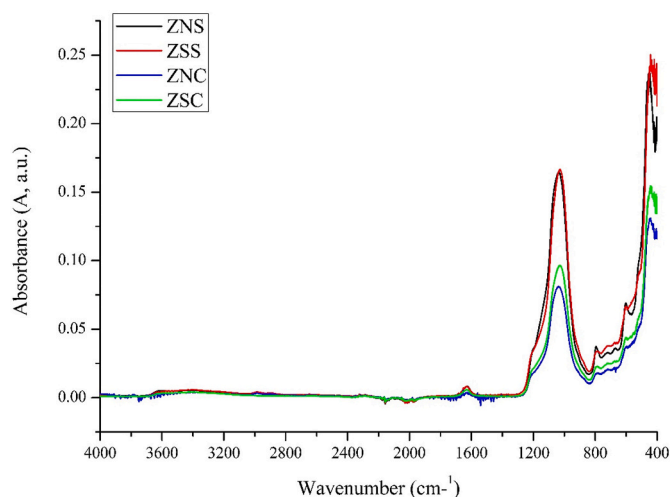


Fig. 2. FT-IR spectra of tested zeolites within the 4000-400  $\text{cm}^{-1}$  wavenumber.

an increase was similar among zeolitic mixtures, thus suggesting no mineralogy effect following NaCl treatment.

These results agreed with previous research on zeolites [10,28,29]. Recently, Thushari et al. [10] suggested that one of the reasons for increased  $\text{NH}_4^+$  adsorption by NaCl treated zeolites could be the differences in exchange efficiency of cations associated with their charge. For example, mordenite revealed a selectivity sequence of  $\text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$  [15,30], thus suggesting that monovalent cations

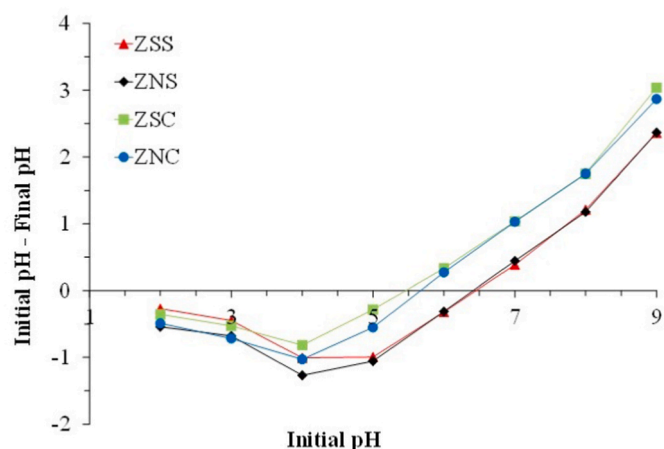


Fig. 3. Determination of zero point charge of zeolitic mixtures according pH drift method.

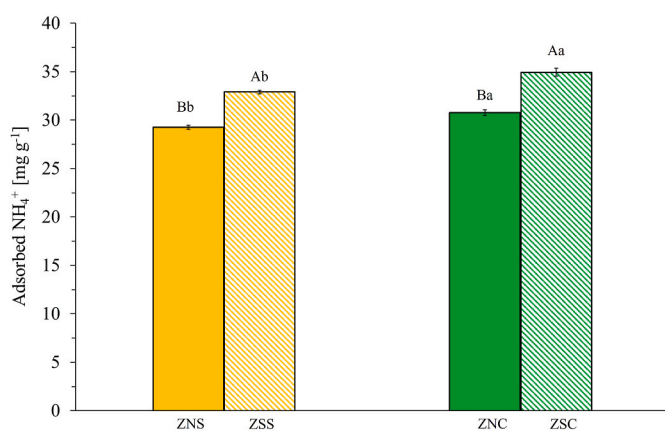


Fig. 4. Amount of  $\text{NH}_4^+$  adsorbed by the tested zeolites during 24 h from a mono-component solution with an initial concentration of  $20,000 \text{ mg NH}_4^+ \text{ L}^{-1}$ . Values are mean  $\pm$  standard deviation of three replicates.

are preferentially adsorbed than the divalent ones. Thushari et al. [10] explained the high  $\text{NH}_4^+$  by NaCl treated zeolite as it follows: 1) following the NaCl treatment, monovalent  $\text{Na}^+$  replace  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  transforming zeolite into a unified valency structure and facilitating the exchange; 2) the replacement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Na}^+$  increases surface area and pore volume of NaCl treated zeolites, thereby increasing their adsorption capacity. The large  $\text{NH}_4^+$  amount adsorbed by the NaCl treated zeolites could be explained, speculatively, by using the low-density/high-density water model set up by Conte and Schmdit [31] based on what observed by Dhopatkar et al. [32]. This model was elaborated to explain the dynamics of nutrients in soils. Namely, on the one hand, a pseudo-ice thin layer is formed on the  $\text{Na}^+$ -functionalised zeolitic mixtures surface (that is, zeolitic mixtures surface is a kosmotrope). On the other hand, due to the high charge density, the  $20 \text{ g NH}_4^+ \text{ L}^{-1}$  solution acts as a kosmotrope, thus leading water molecules to the formation of another pseudo-ice structure (Fig. 5). Due to the pseudo-ice behaviour, we can argue that low-density water (LDW) micro-domains are present in both aforementioned systems. As water molecules move away from the kosmotropic environment, high-density water (HDW) microdomains can be accounted for. In other words, chaotropic environments are detectable when the transition from LDW to HDW is achieved.

Due to the density gradient, water molecules included in the HDW domain move towards the LDW one in order to obtain water density homogeneity. However, water molecules do not move alone. They all

take part to the hydration shell of the ions present in the system. Consequently, both the sodium ions on the zeolitic mixtures surface and the  $\text{NH}_4^+$  ions in the high concentrated solution move towards the HDW part of the system. Therefore, negative charged surface zeolite sites are available for  $\text{NH}_4^+$  to be adsorbed.

The hypothesised mechanism cannot be applied to the not NaCl treated zeolitic mixtures where the hydrogens of the hydroxyl groups of the zeolite are covalently bound to the oxygens. Therefore, a larger amount of  $\text{NH}_4^+$  can be adsorbed on the NaCl treated zeolitic mixtures compared to the untreated ones.

#### 3.4. $\text{NH}_4^+$ monomodal and bimodal pseudo-first order adsorption kinetic models

Adsorption of  $\text{NH}_4^+$  by zeolitic mixtures was studied at various time intervals (Fig. 6A and B). The amount of  $\text{NH}_4^+$  adsorbed by the different zeolitic mixtures after 48 h of incubation was in the order  $\text{ZSS} > \text{ZNS}$ , and  $\text{ZSC} > \text{ZNC}$  (Fig. 6A and B).  $\text{NH}_4^+$  adsorption rate by zeolitic mixtures was fast at the beginning of the incubation and then it slowed down (Fig. 6A and B). After 2 h, zeolitic mixtures adsorbed about 80% of  $\text{NH}_4^+$  from the solution. The aforementioned results fall within the range observed by Alshameri et al. [33] and Kotoulas et al. [34]. Those authors analysed clinoptilolite with a grain size similar to that used in the present study (i.e., 0.71–1.0 mm), and found that around 80% of  $\text{NH}_4^+$  was removed from mono-component solution between one and 6 h of incubation.

NaCl treatment had no effect on  $\text{NH}_4^+$  adsorption rate by ZSC, whereas it improved that of the ZSS (Fig. 6A and B). Indeed, ZSS adsorbed more  $\text{NH}_4^+$  and saturated faster than ZNS. Such a behaviour remains unsolved. It might be ascribed to the different mineralogy of the tested zeolitic mixtures. In fact, ZNS contains less morденite and more clinoptilolite and stellerite as compared to ZNC (Table 1). Indeed, it could either be related to a different binding strength of the  $-\text{OH}$  hydroxyl groups, which is closely linked to the different framework, or to the different exposure in the framework of the  $-\text{OH}$  groups on the surface, which may or may not facilitate  $\text{NH}_4^+$  binding.

The kinetics of  $\text{NH}_4^+$  adsorption by the zeolitic mixtures was mathematically analysed by the application of non-linear model reported in eqs. (1) and (2).

The bimodal first-order kinetic model returned the highest  $R^2$  and the lowest  $\chi^2$  values than the monomodal first-order kinetic model, thus suggesting a better fitting of the experimental data than the former model (Table 3). Indeed, although the monomodal first order kinetic model returned also significant high  $R^2$  values, the fitting curve was not able to include some of the experimental points (see sharp-bend in Fig. 6A). Conversely, the bimodal model well fitted all the experimental points (Fig. 6B). Based on such results, the sorption process can be described as two simultaneous pseudo first-order reactions where the two sorption constants ( $k_1$  and  $k_2$ ), calculated according to eqs. (1) and (2), suggest two different  $\text{NH}_4^+$  sorption mechanisms [35] both based on the number of active sites present in the solid systems. Based on such findings, we can argue that  $k_1$  is related to the adsorption process of  $\text{NH}_4^+$  on the zeolitic mixtures surface, whereas  $k_2$  to the ion exchange process between  $\text{NH}_4^+$  in solution and cations placed on the zeolitic mixture surface [36]. In fact, both untreated zeolitic mixtures revealed the similar  $k_1$  and  $k_2$  values, being in all cases  $k_1 > k_2$ . After the NaCl treatment the kinetic constant remained similar among the treated zeolitic mixtures, but  $k_2 > k_1$ . Such speculation derives from the following deductions: before the NaCl treatment, both monovalent and divalent cations are adsorbed on the zeolitic mixtures, with divalent cations stronger adsorbed than the monovalent ones due to the high charge per unit of surface. In such a case, the adsorption process of  $\text{NH}_4^+$  is favoured over the ion exchange process. After the NaCl treatment, both monovalent and divalent cations adsorbed on the zeolitic mixtures are substituted by  $\text{Na}^+$ . In the latter case,  $\text{NH}_4^+$  easily may substitute  $\text{Na}^+$  by ion exchange process. Indeed, it is conceivable that a faster

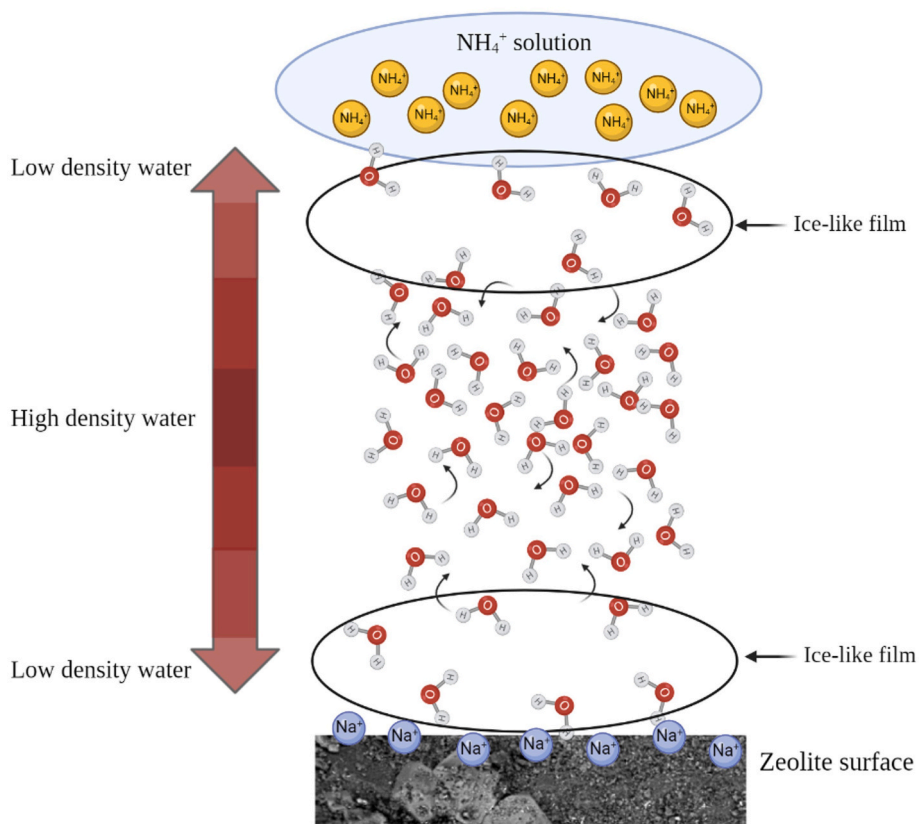


Fig. 5. A model of the exchange between  $\text{NH}_4^+$  solution and cations on zeolite surface. The exchange is driven by the water density gradient occurring between the two different surface (Modified by Conte & Schmidt, 2017).

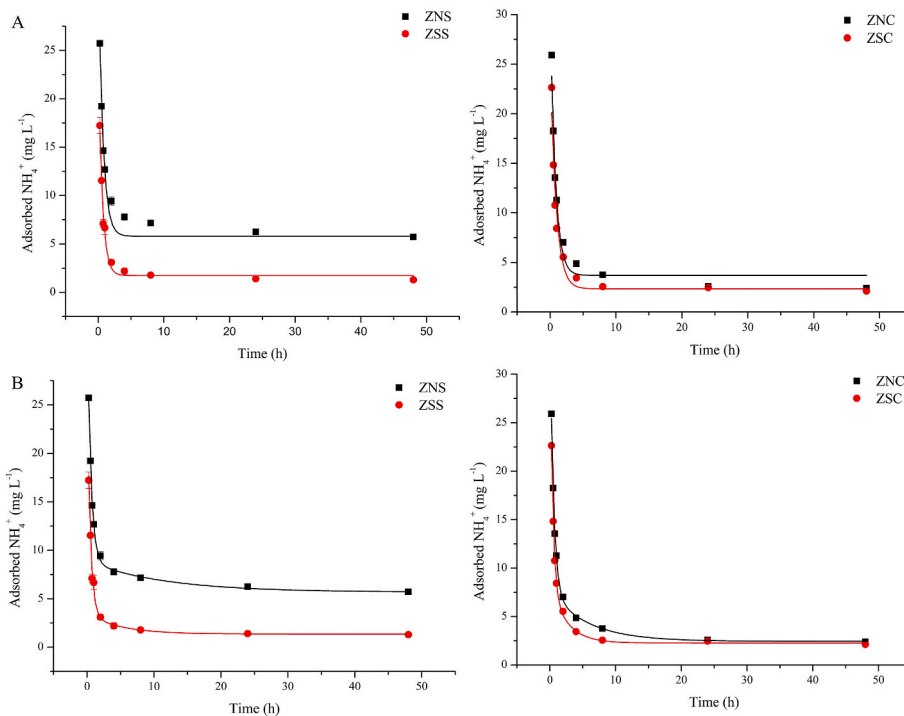


Fig. 6. Monomodal (A) and bimodal (B) pseudo-first order  $\text{NH}_4^+$  adsorption kinetics by zeolites during 48 h from a mono-component solution with an initial concentration of  $50 \text{ mg NH}_4^+ \text{ L}^{-1}$ . Values are mean  $\pm$  standard deviation of three replicates.

**Table 3**

Parameter values obtained from the application of pseudo-first order kinetic models to the tested zeolites. Values are mean  $\pm$  standard deviation of three replicates.

Monomodal pseudo-first order	R <sup>2</sup>	$\chi^2$	Offset	q <sub>e1</sub>	q <sub>e2</sub>	k <sub>1</sub>	k <sub>2</sub>
ZNS	0.998	22.3	5.8 $\pm$ 0.1	28 $\pm$ 1	-	1.5 $\pm$ 0.2	-
ZSS	0.990	3.2	1.7 $\pm$ 0.2	23 $\pm$ 3	-	1.7 $\pm$ 0.2	-
ZNC	0.961	1373.8	3.7 $\pm$ 0.2	28 $\pm$ 5	-	1.3 $\pm$ 0.3	-
ZSC	0.907	780.5	2.3 $\pm$ 0.1	24 $\pm$ 5	-	1.1 $\pm$ 0.3	-
Bimodal pseudo-first order	R <sup>2</sup>	$\chi^2$	Offset	q <sub>e1</sub>	q <sub>e2</sub>	k <sub>1</sub>	k <sub>2</sub>
ZNS	0.999	1.3	5.7 $\pm$ 0.1	27.6 $\pm$ 0.5	3.2 $\pm$ 0.6	1.9 $\pm$ 0.1	0.09 $\pm$ 0.03
ZSS	0.996	1.3	1.3 $\pm$ 0.2	2.1 $\pm$ 0.8	25 $\pm$ 3	0.2 $\pm$ 0.1	2.2 $\pm$ 0.3
ZNC	0.997	82.2	2.4 $\pm$ 0.2	29 $\pm$ 1	5.2 $\pm$ 0.7	1.9 $\pm$ 0.2	0.17 $\pm$ 0.03
ZSC	0.965	295.3	2.3 $\pm$ 0.1	6 $\pm$ 5	28 $\pm$ 7	0.4 $\pm$ 0.2	2.6 $\pm$ 1.2

replacement mechanism of Na<sup>+</sup> with NH<sub>4</sub><sup>+</sup> occurs (k<sub>2</sub>>k<sub>1</sub>), compared to a slower one (k<sub>1</sub>>k<sub>2</sub>) when NH<sub>4</sub><sup>+</sup> exchanges with all the other cations among which the divalent ones (Ca<sup>2+</sup> and Mg<sup>2+</sup>; Fig. 7). Considering that k<sub>1</sub> is greater than k<sub>2</sub> for zeolitic mixtures not treated with NaCl and that the opposite occurs following the treatment with NaCl, we may hypothesize that k<sub>1</sub> is an expression of the adsorption process whereas k<sub>2</sub>

of the ion exchange one. Thus, such results also suggested that the treatment with NaCl improved the rate of NH<sub>4</sub><sup>+</sup> sorption and that such improvement does not depend on zeolitic mixtures mineralogy.

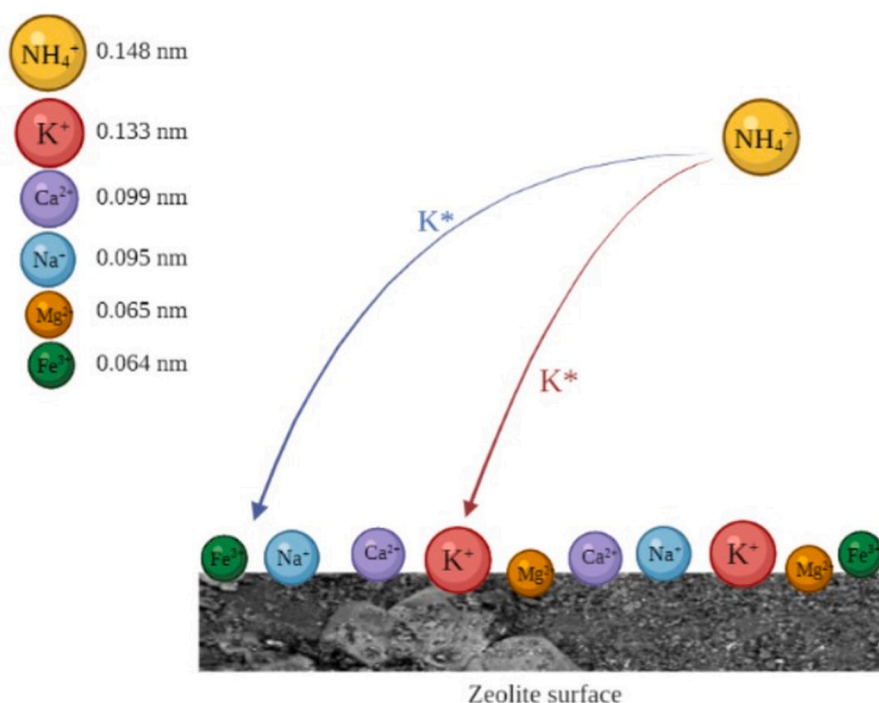
### 3.5. The isotherms evaluation

Isotherms models that describe the physical-chemical sorption process are important for the interpretation and prediction of sorption data [15,22]. Thus, for the effective use of a natural zeolite as an ion exchanger, different isotherm models have been used to accurately describe the NH<sub>4</sub><sup>+</sup> sorption equilibrium. In addition, isotherms models are needed to describe the equilibrium relationship between the amounts of ions adsorbed by zeolite and their equilibrium concentration in the solution. The fitting goodness of the different isotherm models tested in this study (eqs. (3), (4) and (6)) was evaluated on the basis of R<sup>2</sup> and  $\chi^2$  values. Based on such values, sorption of NH<sub>4</sub><sup>+</sup> by zeolitic mixtures was significantly consistent with all models, with a preference for the model described by eq. (6) that showed the highest R<sup>2</sup> and the lowest  $\chi^2$  values, respectively (Table 4; Fig. 8A and B).

The parameters calculated through the non-linear method by applying eq. (6) to NH<sub>4</sub><sup>+</sup> adsorbed on ZNS and ZSS suggested that the treatment with NaCl increased the number of active sites (lower value of the “n” parameter) leading to higher NH<sub>4</sub><sup>+</sup> adsorption (higher value of q<sub>max</sub>). Such results agree with data obtained from static experiment where NH<sub>4</sub><sup>+</sup> adsorbed by ZSS was higher than that adsorbed by ZNS (Fig. 4).

Also, the equilibrium constant, K<sub>L</sub>, calculated by eq. (6), suggested higher affinity of ZSS for NH<sub>4</sub><sup>+</sup>. Indeed, ZSS showed higher K<sub>L</sub> value compared to ZNS suggesting the shift of the equilibrium Z + NH<sub>4</sub><sup>+</sup>  $\rightleftharpoons$  (Z-NH<sub>4</sub>) towards the associated phase (Z-NH<sub>4</sub>).

The higher affinity of ZSS for NH<sub>4</sub><sup>+</sup> can be attributed to the greater ability of ZSS to form H-bonds or ionic linkages with NH<sub>4</sub><sup>+</sup>. The formation of H-bonds between zeolite and NH<sub>4</sub><sup>+</sup> can be accepted by assuming that the isomorphous substitution of Al<sup>3+</sup> with Si<sup>4+</sup> results in insufficient positive charges in the crystal lattice [37]. On the one hand, the existence of excessive net negative charges means that some O atoms in the structure exist in unbound form. Therefore, the bound and unbound O atoms are considered as independent sites on which the -H in NH<sub>4</sub><sup>+</sup> can

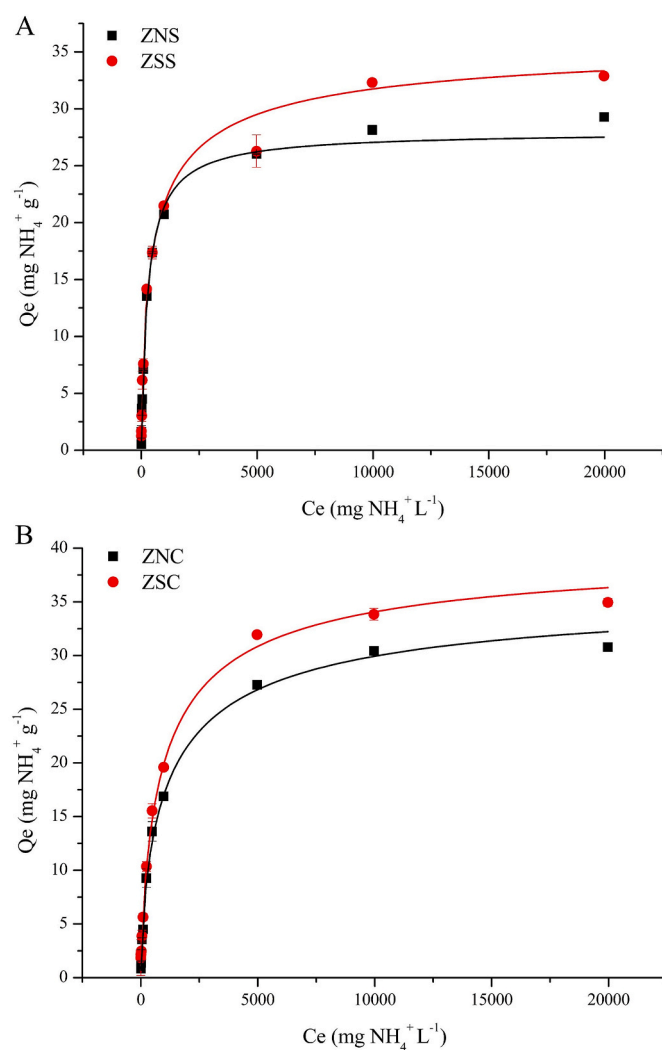


**Fig. 7.** Polymodality of cation substitution on the surface of zeolites by NH<sub>4</sub><sup>+</sup> in relation to cations size.

**Table 4**

Parameter values obtained from the application of Freundlich, Langmuir and Langmuir-Sips isotherm models to the tested zeolites. Values are mean  $\pm$  standard deviation of three replicates.

Freundlich					
	R <sup>2</sup>	$\chi^2$	K <sub>F</sub> (mg L <sup>-1</sup> )	n	
ZNS	0.925	614.6	2.8 $\pm$ 0.7	3.8 $\pm$ 0.4	
ZSS	0.903	567.6	4.0 $\pm$ 0.9	4.3 $\pm$ 0.6	
ZNC	0.948	150.6	4.6 $\pm$ 0.5	3.1 $\pm$ 0.3	
ZSC	0.916	139.5	2.6 $\pm$ 0.7	3.6 $\pm$ 0.4	
Langmuir					
	R <sup>2</sup>	$\chi^2$	K <sub>L</sub> (mg L <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )	
ZNS	0.997	23.2	0.003 $\pm$ 0.2	27.6 $\pm$ 0.3	
ZSS	0.987	75.5	0.0019 $\pm$ 0.0003	32.8 $\pm$ 1.4	
ZNC	0.987	35.6	0.0012 $\pm$ 0.0002	32.3 $\pm$ 1.3	
ZSC	0.988	19.13	0.0015 $\pm$ 0.0002	36.4 $\pm$ 1.2	
Langmuir Sips					
	R <sup>2</sup>	$\chi^2$	K <sub>L</sub> (mg L <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )	n
ZNS	0.997	22.3	0.005 $\pm$ 0.001	28.0 $\pm$ 0.5	0.93 $\pm$ 0.05
ZSS	0.998	7.8	0.015 $\pm$ 0.002	36.5 $\pm$ 0.8	0.66 $\pm$ 0.03
ZNC	0.998	6.1	0.007 $\pm$ 0.001	36.7 $\pm$ 1.2	0.71 $\pm$ 0.03
ZSC	0.995	7.6	0.006 $\pm$ 0.002	40.3 $\pm$ 1.6	0.74 $\pm$ 0.05



**Fig. 8.** The Langmuir Sips isotherms of tested zeolites. Values are mean  $\pm$  standard deviation of three replicates.

bind [37,38]. On the other hand, ionic bonding is conceivable since the zeolite and the adsorbate have different charge densities.

With regard to the ZNC and ZSC, the parameters calculated by applying eq. (6) to  $\text{NH}_4^+$  adsorbed data confirmed the absence of NaCl treatment effect on adsorption capacity of zeolitic mixtures. Indeed, the n and  $K_L$  parameters did not show significant differences among ZNC and ZSC; only  $q_{\text{max}}$  was of 3.6 mg of  $\text{NH}_4^+$  per g of zeolite higher in ZSC compared to ZNC (Fig. 8B).

#### 4. Conclusion

The specific surface area as well as the mineralogical composition of zeolitic mixtures affected their ability in adsorbing  $\text{NH}_4^+$  from a mono-component solution: high presence of mordenite enhanced such an ability. The treatment with NaCl increased the amount of  $\text{NH}_4^+$  adsorbed by the two zeolitic mixtures similarly in static adsorption experiment, thus suggesting no dependence of NaCl treatment from the mineralogical composition. The high amount of  $\text{NH}_4^+$  adsorbed on NaCl treated zeolitic mixtures can be explained using the low density/high density water model firstly proposed for nutrient adsorption by soil. The bimodal pseudo-first-order model explained better than the other tested models the adsorption kinetics of  $\text{NH}_4^+$  on zeolitic mixtures. Furthermore, it suggested two different mechanisms of  $\text{NH}_4^+$  adsorption depending on the size of the cations and on the number of positive charges. Indeed, the two sorption constants,  $k_1$  and  $k_2$ , calculated by the bimodal pseudo-first-order model, may be linked to the adsorption (the former) and ion exchange (the latter) processes. The NaCl treatment affected the rate of  $\text{NH}_4^+$  adsorption of zeolitic mixtures. The Langmuir-Sips model provided the best fit to the equilibrium data. The parameters obtained by applying such model suggested that treatment with NaCl increased the number of active sites of zeolitic mixtures with the low amount of mordenite.

#### CRedit authorship contribution statement

**Sofia Maria Muscarella:** Writing – original draft, Methodology, Formal analysis, Data curation. **Vito Armando Laudicina:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Beatriz Cano:** Writing – review & editing, Investigation, Data curation. **Luigi Badaluco:** Writing – review & editing, Conceptualization. **Pellegrino Conte:** Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Giorgio Mannina:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Giorgio Mannina reports financial support was provided by European Union.

#### Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2023.112434>.

## References

- [1] S. Chowdhury, N. Khan, G.H. Kim, J. Harris, P. Longhurst, N.S. Bolan, in: M.N. V. Prasad, K. Shih (Eds.), *Environmental Materials and Waste*, Academic Press, 2016, pp. 569–589.
- [2] J. Langwaldt, *Separ. Sci. Technol.* 43 (2008) 2166–2182, <https://doi.org/10.1080/01496390802063937>.
- [3] J. Volavšek, O. Pliekhov, O. Pliekhova, G. Mali, N.Z. Logar, *Nanomat* 12 (2022) 1–13, <https://doi.org/10.3390/nano12081352>.
- [4] G. Mannina, L. Badalucco, L. Barbara, A. Cosenza, D. Di Trapani, V.A. Laudicina, S. M. Muscarella, D. Presti, *Water (Switzerland)* 14 (2022) 156, <https://doi.org/10.3390/w14020156>.
- [5] T.D. Saliu, N.A. Oladoja, *Environ. Chem. Lett.* 19 (2021) 2299–2316, <https://doi.org/10.1007/s10311-020-01159-7>.
- [6] X. You, C. Valderrama, J.L. Cortina, *Sci. Total Environ.* 656 (2019) 902–909, <https://doi.org/10.1016/j.scitotenv.2018.11.420>.
- [7] M.L. Nguyen, C.C. Tanner, *NZJAR (N. Z. J. Agric. Res.)* 41 (1998) 427–446, <https://doi.org/10.1080/00288233.1998.9513328>.
- [8] S. Wang, Y. Peng, *Chem. Eng. J.* 156 (2010) 11–24, <https://doi.org/10.1016/j.cej.2009.10.029>.
- [9] J. Canellas, *Sch. Water, Environ. Energy Res. Degree, Cranf. Univ.*, 2018.
- [10] D. Thushari, N. Wijesinghe, K.B. Dassanayake, S.G. Sommer, G.Y. Jayasinghe, P. J. Scales, D. Chen, *J. Environ. Sci. Health* 51 (2016) 614–625, <https://doi.org/10.1080/10934529.2016.1159861>.
- [11] S.M. Muscarella, L. Badalucco, B. Cano, V.A. Laudicina, G. Mannina, *Bioresour. Technol.* 341 (2021), 125812, <https://doi.org/10.1016/j.biortech.2021.125812>.
- [12] Y.M. Channon, C.R.A. Catlow, R.A. Jackson, S.L. Owens, *Microporous Mesoporous Mater.* 24 (1998) 153–161, [https://doi.org/10.1016/S1387-1811\(98\)00155-3](https://doi.org/10.1016/S1387-1811(98)00155-3).
- [13] M.N. Khan, A. Sarwar, *Surf. Rev. Lett.* 14 (2007) 461–469, <https://doi.org/10.1142/S0218625X07009517>.
- [14] D. Vaičiukynienė, A. Mikėlionienė, A. Baltušnikas, A. Kantautas, A. Radzevičius, *Sci. Rep.* 10 (2020) 1–11, <https://doi.org/10.1038/s41598-019-55906-0>.
- [15] M. Sarioglu, *Separ. Purif. Technol.* 41 (2005) 1–11, <https://doi.org/10.1016/j.seppur.2004.03.008>.
- [16] M. Moshoeshoe, M. Silas Nadiye-Tabbiruka, V. Obuseng, *Am. J. Mater. Sci.* 7 (2017) 196–221, <https://doi.org/10.5923/j.materials.20170705.12>.
- [17] N.Z. Misak, *React. Funct. Polym.* 43 (2000) 153–164, [https://doi.org/10.1016/S1381-5148\(99\)00046-2](https://doi.org/10.1016/S1381-5148(99)00046-2).
- [18] D. Sparks, *Environmental Soil Chemistry*, second ed., Academic Press, Oxford, 2003.
- [19] P. Conte, R. Bertani, P. Sgarbossa, P. Bambina, H.-P. Schmidt, R. Raga, G. Lo Papa, D.F. Chillura Martino, P. Lo Meo, *Agronomy* 11 (2021) 615, <https://doi.org/10.3390/agronomy11040615>.
- [20] N. Widiastuti, H. Wu, H.M. Ang, D. Zhang, *Desalination* 277 (2011) 15–23, <https://doi.org/10.1016/j.desal.2011.03.030>.
- [21] M. Belhachemi, F. Addoun, *Appl. Water Sci.* 1 (2011) 111–117, <https://doi.org/10.1007/s13201-011-0014-1>.
- [22] R. Malekian, J. Abedi-Koupai, S.S. Eslamian, S.F. Mousavi, K.C. Abbaspour, M. Afyuni, *Appl. Clay Sci.* 51 (2011) 323–329, <https://doi.org/10.1016/j.clay.2010.12.020>.
- [23] R.L. Mulvaney, in: D.L. Sparks (Ed.), *Methods of Soil Analysis. Part 3-Chemical Methods*, 1996, pp. 1123–1184. Madison.
- [24] K. Byrappa, B.V.S. Kumar, *Asian J. Chem.* 19 (2007) 4933–4935. ISSN 0970-7077.
- [25] H.F. Chen, Y.J. Lin, B.H. Chen, I. Yoshiyuki, S.Y.H. Liou, R.T. Minerals 8 (2018) 499, <https://doi.org/10.3390/min8110499>.
- [26] O.Y. Korkuna, T.Y. Vrublevska, *Stud. Surf. Sci. Catal.* 158 (2005) 1035–1042, [https://doi.org/10.1016/s0167-2991\(05\)80445-8](https://doi.org/10.1016/s0167-2991(05)80445-8).
- [27] L. Lin, Z. Lei, L. Wang, X. Liu, Y. Zhang, C. Wan, D.J. Lee, J.H. Tay, *Separ. Purif. Technol.* 103 (2013) 15–20, <https://doi.org/10.1016/j.seppur.2012.10.005>.
- [28] N.A. Booker, E.L. Cooney, A.J. Priestley, *Water Sci. Technol.* 34 (1996) 17–24, <https://doi.org/10.2166/wst.1996.0167>.
- [29] S. Komarowski, Q. Yu, *Environ. Technol.* 18 (1997) 1085–1097, <https://doi.org/10.1080/09593331808616628>.
- [30] D.L. Bish, D.W. Ming, *Natural zeolites : occurrences, properties, applications*, *Rev. Mineral. Geochem.* 45 (2001) 207–210, <https://doi.org/10.2138/rmg.2001.45.0>.
- [31] P. Conte, H.-P. Schmidt, *EMagRes*, vol. 6, John Wiley & Sons, Ltd, 2017, pp. 453–464, <https://doi.org/10.1002/9780470034590.emrstm1535>.
- [32] N. Dhopatkar, A.P. Defante, A. Dhinojwala, *Sci. Adv.* 2 (2016), e1600763, <https://doi.org/10.1126/sciadv.1600763>.
- [33] A. Alshameri, C. Yan, Y. Al-Ani, A.S. Dawood, A. Ibrahim, C. Zhou, H. Wang, *J. Taiwan Inst. Chem. Eng.* 45 (2014) 554–564, <https://doi.org/10.1016/j.jtice.2013.05.008>.
- [34] A. Kotoulas, D. Agathou, I.E. Triantaphyllidou, T.I. Tatoulis, C.S. Akrotas, A. G. Tekerlekopoulou, D.V. Vayenas, *Water (Switzerland)* 11 (2019) 136, <https://doi.org/10.3390/w11010136>.
- [35] R.A. Griffin, J.J. Jurinak, *Soil Sci. Soc. Am. J.* 38 (1974) 75–79, <https://doi.org/10.2136/sssaj1974.03615995003800010026x>.
- [36] S.E. Jørgensen, S.E. Jørgensen, in: M.J. Gromiec (Ed.), *Adsorption and Ion Exchange*, Math. Submodels Water Qual. Syst., Elsevier, 1989, pp. 65–81.
- [37] P. Liu, Y. Liu, A. Zhang, Z. Liu, X. Liu, L. Yang, *Water (Switzerland)* 14 (2022) 2413, <https://doi.org/10.3390/w14152413>.
- [38] G. Gilli, P. Gilli, M. Khosravi, V. Murthy, I.D.R. Mackinnon, *J. Mol. Struct.* 552 (2019) 1–17, <https://doi.org/10.3390/molecules24203652>.