1 **Recovering ammonium by treated and untreated zeolitic mixtures: a comprehensive**

2 **experimental and modelling study**

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Highlights:

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14   •   Two zeolitic mixtures with different mineralogy were used for NH_4^+ recovery

15   •   Zeolitic mixtures showed good performance for NH_4^+ removal from solution

16   •   The mineralogical composition of zeolitic mixtures affected NH_4^+ adsorption

17   •   The bimodal-pseudo-first order model well described NH_4^+ adsorption kinetics

18   •   The Langmuir-Sips model provides the best fit for the NH_4^+ adsorption isotherm

19

20 **ABSTRACT**

21 The recovery of ammonium (NH_4^+) from aqueous solutions by zeolite is attractive. In this study, the

22 physical-chemistry of NH_4^+ adsorption process from aqueous solution by two zeolitic mixtures,

23 either treated or not treated with NaCl, was assessed.

24 Results suggested that the zeolitic mixture richer in mordenite and with high specific surface area

25 adsorbed more NH_4^+ than the one richer in clinoptilolite and heulandite showing a lower specific

26 surface area. NaCl treatment increased the amount of NH_4^+ adsorbed by the zeolitic mixtures. The

27 higher amount of NH_4^+ adsorbed by the zeolitic mixtures treated with NaCl was explained by the

28 low/high density water model accounting for cation exchange among the two kosmotropic systems:

29 Na-enriched zeolitic mixtures and NH_4^+-enriched aqueous solution. The adsorption kinetics were

30 best approximated by the bimodal pseudo-first-order model. The two sorption kinetic constants, k_1

31 and k_2 were related to the adsorption (mediated by k_1) and the ion exchange (mediated by k_2)

32 processes. The fitting of NH_4^+ data to Langmuir-Sips model suggested that the NaCl treatment

33 increased the number of active sites only of the zeolitic mixture with the large amount of mordenite.

34 Thus, it is conceivable that modulation of NaCl treatment of zeolitic mixtures can be applied to

35 obtain new materials for water remediation from NH_4^+ contamination.

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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 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 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 NH_4^+ adsorption capacity ranging between 41 and 72 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 mg NH_4^+ g^{-1}, against zeolites with 93% of clinoptilolite that adsorbed up to 25 mg NH_4^+ g^{-1}. However, such a large variability in NH_4^+ adsorbtion has been also found among zeolites with the same mineralogy. Wang and Peng [8] reported that the amount of NH_4^+ adsorbed by clinoptilolite from different origins may range from 3 to 23 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].

65 Also, the treatment to which zeolites undergo prior to any application may affect adsorption

66 capacity. Thushari et al. [10] found that, following the treatment with NaCl, NH_4^+ adsorption by

67 zeolite increased by 25% compared to the untreated one. Recently, also Muscarella et al. [11]

68 revealed that 1 M NaOH treatment of zeolite resulted in a NH_4^+ adsorbing capacity of 18.3 mg g^{-1},

69 whereas an acid treatment with 0.1 M HCl produced zeolite with NH_4^+ adsorption capacity of 22.5

70 mg g^{-1}.

71 In addition, the interactions between the extra framework cations and the framework of zeolite have

72 been studied by using atomistic simulation techniques [12] and no conceptual model of the cation

73 exchange between aqueous solution and zeolite have been proposed.

74 The high variability in adsorbing NH_4^+ showed by zeolite with different mineralogy as related to

75 acid, alkaline or salt treatment stresses the need for further investigation. Moreover, at our best

76 knowledge, no mechanism has been proposed up to now about the exchange between NH_4^+ in

77 aqueous solution and cations adsorbed onto zeolite either treated or not with NaCl. Thus, the aim of

78 the present study is to provide more insights about the ability of zeolite with different mineralogy,

79 either treated or not with NaCl, in exchanging and adsorbing NH_4^+ from aqueous solution.

80 Furthermore, a new conceptual model about the exchange and adsorption processes between NH_4^+

81 in solution and cations adsorbed onto zeolite is proposed.

82

83 **2. MATERIAL AND METHODS**

84 **2.1   Tested zeolite**

85 Two mixtures of natural zeolites (Ø 0.5-1 mm) were used in this study. They are indicated as ZNS

86 and ZNC. Before their chemical and mineralogical characterization, and use, the two zeolitic

87 mixtures were washed trice with distilled water to remove particulate impurities on the surfaces and

88 dried at 105°C for 2 hours [11]. ZSS and ZSC were, respectively, two mixtures obtained by the

89 previous ones after treatment with 1M NaCl for 24 h with a zeolite-to-solution ratio of 1:50 (w/v).

90 After NaCl treatment, and prior to all the experiments, ZSS and ZSC have been washed with

91   distilled water in order to remove the excess of sodium. The specific surface area of the two

92   untreated zeolitic mixtures was evaluated by the nitrogen gas adsorption method, using an

93   automated equipment (Nova touch LX1, Quantachrome Instrument, FL, USA), employing

94   multipoint BET isotherm adsorption data fitting.

95   Morphology and elemental composition of treated and untreated zeolite mixtures were examined by

96   scanning electron microscope (SEM) coupled with energy-dispersive X-ray (EDX) analyser

97   (Phenom Pharos and Phenom XL, Phenom-World Thermo Scientific, Waltham, Massachusetts,

98   USA). Powder X-ray diffraction (XRD) data for structure and phase identification of zeolite

99   mixtures were collected by X'PERT PRO, X-ray Diffractometer (Pan Analytical, Malvern, UK).

100   The main functional groups of zeolite mixtures were assessed by ATR-FTIR Spectrometry

101   (Spectrum Two, PerkinElmer). Spectra were collected in the wavenumber range 4000-400 cm^{-1} on

102   samples dried for 2 h at 105 °C and finely ground. The spectra have been elaborate by using Origin

103   (Version 7.5) software program.

104

105   **2.2   Determination of the point of zero charge**

106   The point of zero charge (pH_{pzc}) of the zeolite mixtures was evaluated using the pH drift method

107   according to Nasiruddin et al. [13] as described in Vaičiukynienė et al. [14]. Sodium chloride

108   (0.01M) was used as a background electrolyte. Eight solutions with pH values in a range from 2 to 9

109   were prepared by adjusting the pH adding small amounts of 0.5M HCl or 0.5M NaOH solutions.

110   Then, 1.0 g of zeolitic mixtures were soaked with 40 mL of each solution and left to settle down for

111   24 h at room temperature. The final pH of each solution was measured. The pH_{pzc} of zeolitic

112   mixtures was evaluated; if the initial pH of the solution was equal to the final pH of the solution,

113   then that was considered the pH_{pzc}, and the charge on the surface was zero [14].

114

115   **2.3   Theory: kinetic and isotherm models**

116   The NH_4^+ sorption efficiency of zeolitic mixtures can be evaluated by studying both adsorption

117   kinetics and isotherms. When a kinetic curve is obtained, different models can be applied for the

118   fitting. In particular, the monomodal pseudo-first order model given in eq. (1) is based on the

119   assumption that the adsorption rate depends only on the amount of NH_4^+ placed in contact with the

120   solid porous surface:

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

122   Here, q_t is the amount of NH_4^+ adsorbed on the surface of the porous system at time t, q_e is the

123   equilibrium adsorption capacity (in mg g^{-1}) and k_1 is the pseudo-first order monomodal constant.

124   The latter is directly related to the adsorption rate of the NH_4^+ on the solid surface. The larger is the

125   k_1 value, the faster is the adsorption rate.

126   Otherwise, the bimodal pseudo-first order model is based on the assumption that there is

127   polymodality in the NH_4^+ adsorption, where two pseudo-first order monomodal adsorption patterns

128   exist simultaneously, thereby resulting from different adsorption mechanisms:

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

130   Here, q_t is the amount of NH_4^+ adsorbed on the surface of the porous system at time t, q_{e1} and q_{e2}

131   are the equilibrium adsorption capacities (in mg g^{-1}) at t_1 and t_2, respectively, while k_1 and k_2 are

132   the respective pseudo-first order monomodal kinetic constants. The larger the kinetic constant

133   values, the faster are the adsorption rates mediated by k_1 and k_2.

134   The adsorption isotherms allow to explain solid surface properties such as affinity for the adsorbent

135   and relationship between the amounts of ions exchanged by the porous system and ion

136   concentration at the equilibrium in solution [15]. Moreover, the adsorption isotherms can highlight

137   substantial differences in solid characteristics such as purity, mineral content, and chemical

138   composition.

139 Freundlich and Langmuir isotherm models are usually applied to evaluate NH_4^+ removal from

140 wastewaters by using zeolites [9,16], although some criticisms have been found in the literature

141 [17].

142 Freundlich equation is in the form:

143 $$q_e = K_F C^{1/n} \tag{3}$$

144 where q_e is the amount of adsorbate per unit mass of adsorbent, C is NH_4^+ concentration at the

145 equilibrium in solution, K_F is named Freundlich equilibrium constant or distribution factor, and $1/n$

146 is a correction factor related to the number (n) of adsorbing sites on the surface of the porous

147 material [18].

148 According to Moshoeshoe et al. [16], eq. (3) fits experimental data with R^2 values usually > 0.98.

149 However, Canellas [9] revealed that the thermodynamics of NH_4^+ removal from an aqueous

150 solution using natural zeolites of various origins is better described by the Langmuir isotherm given

151 in eq. (4).

152 $$q_e \propto \frac{K_L C}{K_L C + 1} \tag{4}$$

153 Here, q_e and C have the same meaning as in eq. (3), while K_L is the Langmuir equilibrium constant.

154 To account for the non-ideal conditions, eq. (4) can be transformed as in eq. (5):

155 $$q_e \propto \frac{K_L C^n}{K_L C^n + 1} \tag{5}$$

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

157 Eq. (3) assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over

158 the surface and binding sites are not equivalent and/or independent [20]. Eq. (4) is valid for

159 monolayer adsorptions on a surface with a finite number of identical sites. However, equation (5) is

160 a better model, it can be written as in equation (6) (also referred to as Langmuir-SIPS), where three

161 adjustable parameters are accounted for [19,21,22].

162 They are q_{max}, i.e, the maximum amount of adsorbate that is a function of the number of active

163 sites on the zeolite surface, K_L, that is the Langmuir's constant referring to the equilibrium

164      $Z + NH_4^+ \rightleftharpoons ZNH_4$

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

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

167   The advantage of eq. (6) lays in the fact that it contains both Freundlich and Langmuir isotherms. In

168   fact, when $n = 1$ it becomes the Langmuir isotherm reported in eq. (4), while as K_L approaches to

169   0, eq. (6) becomes the Freundlich eq. (3).

170

171   **2.4 NH_4^+ adsorption by zeolitic mixtures**

172   To evaluate NH_4^+ adsorption ability, 1 g of each sample (ZNC, ZSC, ZNS, ZSS) was shaken with

173   100 mL of 20 g NH_4^+ L^{-1} solution on an orbital shaker for 24 h at 80 rpm at 25°C. The

174   concentration of 20 g NH_4^+ L^{-1} was used on the basis of the isotherm study that showed NH_4^+

175   saturation of the samples after 24 h at this concentration. After 24 h, samples were washed three

176   times with 200 mL of distilled water to remove the excess of NH_4^+ and dried in an oven for 2 h at

177   105 °C. NH_4^+ adsorbed by zeolitic mixtures was determined by Kjeldahl distillation with 30 mL of

178   33% (w/v) NaOH solution for six minutes [11]. Amounts of NH_4^+ adsorbed by zeolitic mixtures

179   were analysed by two-way ANOVA (mineralogy and NaCl treatment as factors) followed by Tukey

180   test to assess significant differences at $P < 0.05$ among zeolitic mixtures. The experiment was

181   carried out in triplicate.

182

183   **2.5   Adsorption kinetics**

184   Adsorption kinetics, during 48 h, were assessed by contacting 1 g of each sample (ZNC, ZSC, ZNS,

185   ZSS) with 100 mL of a 50 mg NH_4^+ L^{-1} solution on a horizontal shaker at 80 rpm at 25°C. NH_4^+

186   concentration in solution was determined after 15, 30, 45 minutes, and 1, 2, 4, 8, 24, 48 hours by

187   Berthelot colorimetric method [23]. The NH_4^+ kinetics adsorption data were mathematically

188   analysed according to eqs. 1 and 2, by using Origin (Version 7.5) software program. The

189   experiment was carried out in triplicate.

190

191   **2.6   Equilibrium studies**

192   Data for NH_4^+ adsorption isotherms were obtained by shaking 2 g of each sample (ZNC, ZSC, ZNS,

193   ZSS) with 200 mL of NH_4Cl solution at different concentration (5, 10, 25, 50, 100, 250, 500, 1000,

194   5000, 10000, 20000 mg $NH_4^+ L^{-1}$) on a horizontal shaker at 80 rpm, 25°C for 24 h.

195   The NH_4^+ adsorbed on zeolitic mixtures, determined by Berthelot colorimetric method, was fitted to

196   the Freundlich, Langmuir and Langmuir-Sips equation. All the isotherms were calculated by using

197   non-linear regression with Origin (Version 7.5) software program. The experiment was carried out

198   in triplicate.

199

200   **3. RESULTS AND DISCUSSION**

201   **3.1   XRD, SEM-EDX and FT-IR characterization of the zeolitic mixtures**

202   The specific surface area of the two untreated zeolitic mixtures was 40 ± 2 g m^{-2} for ZNS and 47 ± 2 g

203   m^{-2} for ZNC. XRD analyses revealed that ZNS was a mixture of heulandite, mordenite,

204   clinoptilolite and stellerite, whereas ZNC was made only by heulandite and mordenite (Table 1).

205   Moreover, the XRD spectra (not reported here) showed also that the NaCl treatment had no impact

206   on the mineralogical composition of the zeolitic mixtures.

207   The SEM images suggested that NaCl treatment significantly affected surface properties of treated

208   zeolitic mixtures (Fig. 1). Indeed, the latter were more regular, close-grained and with well-defined

209   edges compared to the untreated ones which showed disordered crystal orientation (Fig. 1). Such

210   changes were similar to those reported by Thushari et al. [10] for NaCl treated zeolite.

211   Elemental analysis performed by SEM-EDX revealed that, following the treatment with NaCl,

212   oxygen, silicon, and aluminium decreased, while Na increased (Fig. S1). The increase of NaCl was

213   also confirmed by the presence of non-homogeneously distributed NaCl on the surfaces of treated

214   zeolitic mixtures. However, the Si/Al, Si/O and Al/O ratios were not affected by NaCl treatment,

215   thus suggesting no alteration in the lattice structure of the two zeolitic mixtures (Table 2).

216   All the zeolitic mixtures showed similar FTIR spectra (Fig. 2). In particular, in the range 500-420

217   cm^{-1}, bending of the bonds between tetrahedral (Si, Al) and octahedral species (Al, Fe, Mg) have

218   been observed; the intervals 720-650 cm^{-1}, and 1250-950 cm^{-1} were due to symmetrical and

219   asymmetrical stretching typical of the internal tetrahedra linkages [24]. Other bands were in the

220   range 650-500 cm^{-1} (double ring), 420-300 cm^{-1} (pore opening), 820-750 cm^{-1} (symmetrical

221   stretching) and 1150-1050 cm^{-1} (asymmetrical stretching), typical of external tetrahedra linkages

222   (Fig. 2). Indeed, according to Byrappa and Kumar [24] the infrared spectrum useful for the

223   characterization of the structural features of zeolite frameworks is in the region of 1500-400 cm^{-1}.

224

225   **3.2 pH_{pzc} of zeolitic mixtures**

226   The pH_{pzc} determined according to the pH drift method, ranged from 5.5 to 6.5. It was lower in

227   ZNC and ZSC as compared to ZNS and ZSS. Moreover, it was not affected by NaCl treatment (Fig.

228   3). Therefore, ZNC and ZSC surfaces show negative charges at pH values lower than that of ZNS

229   and ZSS. Based on such results, it can be argued that ZNC and ZSC should have greater potential

230   for removing ammonium ions from aqueous solution than ZNS and ZSS. However, considering that

231   the pHs of all tested zeolitic mixtures were lower than 5.5, we can conclude that there is no effect of

232   pH_{pzc} on zeolite NH_4^+ ion removal from the solution.

233

234   **3.3 NH_4^+ adsorption by zeolitic mixtures**

235   The amount of NH_4^+ adsorbed by the two zeolitic mixtures ranged from 29.3 ± 0.2 to 35.0 ± 0.4 mg

236   g^{-1} (Fig. 4). Regardless of the treatment for their activation, ZNC and ZSC adsorbed more NH_4^+

237   than ZNS and ZSS. The higher amount of NH_4^+ adsorbed by ZNC and ZSC compared to ZNS and

238   ZSS can be ascribed to concomitant factors such as the higher specific surface area of ZNC

239 compared to ZNS and to the higher mordenite content, that has been demonstrated to have higher

240 cation exchange capacity [2]. Indeed, Chen et al. [25] have found that mordenite shows higher

241 specific surface area as compared to clinoptilolite and heulandite. Also, modernite crystal structure

242 may contribute to higher NH_4^+ adsorption compared to clinoptilolite and heulandite due to the

243 presence of larger pores and cavities [26].

244 The amount of NH_4^+ adsorbed by the tested zeolitic mixtures was larger than that reported by Lin et

245 al. [27], i.e., 17 mg NH_4^+ g^{-1}. Although these authors used clinoptilolite with a diameter range like

246 that of the zeolites used in this study (0.8-1.43 mm), they applied a NH_4^+ solution for zeolite

247 saturation with a concentration of 990 mg NH_4^+ L^{-1} which was much lower than that used here (i.e.,

248 20 g L^{-1}). This difference can explain the discrepancy between our data and those from Lin et al.

249 [27].

250 After NaCl treatment, larger Na^+ but lower K^+, Ca^{2+} and Mg^{2+} content was observed in the treated

251 zeolitic mixtures rather than in the untreated ones. This indicates that the K^+, Ca^{2+} and Mg^{2+} ions on

252 the exchange surfaces of the untreated zeolitic mixtures were replaced by Na^+ after sodium chloride

253 treatment.

254 The amount of NH_4^+ adsorbed by NaCl treated zeolitic mixtures increased as compared to the

255 untreated zeolitic mixtures. However, such an increase was similar among zeolitic mixtures, thus

256 suggesting no mineralogy effect following NaCl treatment.

257 These results agreed with previous research on zeolites [10,28,29]. Recently, Thushari et al. [10]

258 suggested that one of the reasons for increased NH_4^+ adsorption by NaCl treated zeolites could be

259 the differences in exchange efficiency of cations associated with their charge. For example,

260 mordenite revealed a selectivity sequence of $K^+ > NH_4^+ > Ba^{2+} > Na^+ > Ca^{2+} > Mg^{2+}$ [15,30], thus

261 suggesting that monovalent cations are preferentially adsorbed than the divalent ones. Thushari et

262 al. [10] explained the high NH_4^+ by NaCl treated zeolite as it follows: 1) following the NaCl

263 treatment, monovalent Na^+ replace Mg^{2+} and Ca^{2+} transforming zeolite into a unified valency

264 structure and facilitating the exchange; 2) the replacement of Ca^{2+} and Mg^{2+} with Na^+ increases

265 surface area and pore volume of NaCl treated zeolites, thereby increasing their adsorption capacity.

266 The large NH_4^+ amount adsorbed by the NaCl treated zeolites could be explained, speculatively, by

267 using the low-density/high-density water model set up by Conte and Schmdit [31] based on what

268 observed by Dhopatkar et al. [32]. This model was elaborated to explain the dynamics of nutrients

269 in soils. Namely, on the one hand, a pseudo-ice thin layer is formed on the Na^+-functionalised

270 zeolitic mixtures surface (that is, zeolitic mixtures surface is a kosmotrope). On the other hand, due

271 to the high charge density, the 20 g NH_4^+ L^{-1} solution acts as a kosmotrope, thus leading water

272 molecules to the formation of another pseudo-ice structure (Fig. 5). Due to the pseudo-ice

273 behaviour, we can argue that low-density water (LDW) micro-domains are present in both

274 aforementioned systems. As water molecules move away from the kosmotropic environment, high-

275 density water (HDW) microdomains can be accounted for. In other words, chaotropic environments

276 are detectable when the transition from LDW to HDW is achieved.

277 Due to the density gradient, water molecules included in the HDW domain move towards the LDW

278 one in order to obtain water density homogeneity. However, water molecules do not move alone.

279 They all take part to the hydration shell of the ions present in the system. Consequently, both the

280 sodium ions on the zeolitic mixtures surface and the NH_4^+ ions in the high concentrated solution

281 move towards the HDW part of the system. Therefore, negative charged surface zeolite sites are

282 available for NH_4^+ to be adsorbed.

283 The hypothesised mechanism cannot be applied to the not NaCl treated zeolitic mixtures where the

284 hydrogens of the hydroxyl groups of the zeolite are covalently bound to the oxygens. Therefore, a

285 larger amount of NH_4^+ can be adsorbed on the NaCl treated zeolitic mixtures compared to the

286 untreated ones.

287

288 **3.4 NH_4^+ monomodal and bimodal pseudo-first order adsorption kinetic models**

289 Adsorption of NH_4^+ by zeolitic mixtures was studied at various time intervals (Figs. 6A and 6B).

290 The amount of NH_4^+ adsorbed by the different zeolitic mixtures after 48 h of incubation was in the

291   order ZSS > ZNS, and ZSC > ZNC (Figs. 6A and 6B). NH_4^+ adsorption rate by zeolitic mixtures

292   was fast at the beginning of the incubation and then it slowed down (Figs. 6A and 6B). After 2

293   hours, zeolitic mixtures adsorbed about 80% of NH_4^+ from the solution. The aforementioned results

294   fall within the range observed by Alshameri et al. [33] and Kotoulas et al. [34]. Those authors

295   analysed clinoptilolite with a grain size similar to that used in the present study (i.e., 0.71-1.0 mm),

296   and found that around 80% of NH_4^+ was removed from mono-component solution between one and

297   six hours of incubation.

298   NaCl treatment had no effect on NH_4^+ adsorption rate by ZSC, whereas it improved that of the ZSS

299   (Figs. 6A and 6B). Indeed, ZSS adsorbed more NH_4^+ and saturated faster than ZNS. Such a

300   behaviour remains unsolved. It might be ascribed to the different mineralogy of the tested zeolitic

301   mixtures. In fact, ZNS contains less mordenite and more clinoptilolite and stellerite as compared to

302   ZNC (Table 1). Indeed, it could either be related to a different binding strength of the -OH hydroxyl

303   groups, which is closely linked to the different framework, or to the different exposure in the

304   framework of the -OH groups on the surface, which may or may not facilitate NH_4^+ binding.

305   The kinetics of NH_4^+ adsorption by the zeolitic mixtures was mathematically analysed by the

306   application of non-linear model reported in the eqs. 1 and 2.

307   The bimodal first-order kinetic model returned the highest R^2 and the lowest χ^2 values than the

308   monomodal first-order kinetic model, thus suggesting a better fitting of the experimental data than

309   the former model (Table 3). Indeed, although the monomodal first order kinetic model returned also

310   significant high R^2 values, the fitting curve was not able to include some of the experimental points

311   (see sharp-bend in Fig. 6A). Conversely, the bimodal model well fitted all the experimental points

312   (Fig. 6B). Based on such results, the sorption process can be described as two simultaneous pseudo

313   first-order reactions where the two sorption constants (k_1 and k_2), calculated according to eqs. 1 and

314   2, suggest two different NH_4^+ sorption mechanisms [35] both based on the number of active sites

315   present in the solid systems. Based on such findings, we can argument that k_1 is related to the

316   adsorption process of NH_4^+ on the zeolitic mixtures surface, whereas k_2 to the ion exchange process

317   between NH_4^+ in solution and cations placed on the zeolitic mixture surface [36]. In fact, both

318   untreated zeolitic mixtures revealed the similar k_1 and k_2 values, being in all cases $k_1 > k_2$. After the

319   NaCl treatment the kinetic constant remained similar among the treated zeolitic mixtures, but $k_2 >$

320   k_1. Such speculation derives from the following deductions: before the NaCl treatment, both

321   monovalent and divalent cations are adsorbed on the zeolitic mixtures, with divalent cations

322   stronger adsorbed than the monovalent ones due to the high charge per unit of surface. In such a

323   case, the adsorption process of NH_4^+ is favoured over the ion exchange process. After the NaCl

324   treatment, both monovalent and divalent cations adsorbed on the zeolitic mixtures are substituted by

325   Na^+. In the latter case, NH_4^+ easily may substitute Na^+ by ion exchange process. Indeed, it is

326   conceivable that a faster replacement mechanism of Na^+ with NH_4^+ occurs ($k_2>k_1$), compared to a

327   slower one ($k_1>k_2$) when NH_4^+ exchanges with all the other cations among which the divalent ones

328   (Ca^{2+} and Mg^{2+}; Fig. 7). Considering that k_1 is greater than k_2 for zeolitic mixtures not treated with

329   NaCl and that the opposite occurs following the treatment with NaCl, we may hypothesize that k_1 is

330   an expression of the adsorption process whereas k_2 of the ion exchange one. Thus, such results also

331   suggested that the treatment with NaCl improved the rate of NH_4^+ sorption and that such

332   improvement does not depend on zeolitic mixtures mineralogy.

333   **3.5   The isotherms evaluation**

334   Isotherms models that describe the physical-chemical sorption process are important for the

335   interpretation and prediction of sorption data [15,22]. Thus, for the effective use of a natural zeolite

336   as an ion exchanger, different isotherm models have been used to accurately describe the NH_4^+

337   sorption equilibrium. In addition, isotherms models are needed to describe the equilibrium

338   relationship between the amounts of ions adsorbed by zeolite and their equilibrium concentration in

339   the solution. The fitting goodness of the different isotherm models tested in this study (eqs. 3, 4, and

340   6) was evaluated on the basis of R^2 and χ^2 values. Based on such values, sorption of NH_4^+ by

341   zeolitic mixtures was significantly consistent with all models, with a preference for the model

342 described by eq. 6 that showed the highest R^2 and the lowest χ^2 values, respectively (Table 4; Fig.

343 8A, 8B).

344 The parameters calculated through the non-linear method by applying eq. 6 to NH_4^+ adsorbed on

345 ZNS and ZSS suggested that the treatment with NaCl increased the number of active sites (lower

346 value of the "n" parameter) leading to higher NH_4^+ adsorption (higher value of q_{max}). Such results

347 agree with data obtained from static experiment where NH_4^+ adsorbed by ZSS was higher than that

348 adsorbed by ZNS (Fig. 4).

349 Also, the equilibrium constant, K_L, calculated by eq. 6, suggested higher affinity of ZSS for NH_4^+.

350 Indeed, ZSS showed higher K_L value compared to ZNS suggesting the shift of the equilibrium Z +

351 $NH_4^+ \rightleftharpoons (Z\text{-}NH_4)$ towards the associated phase ($Z\text{-}NH_4$).

352 The higher affinity of ZSS for NH_4^+ can be attributed to the greater ability of ZSS to form H-bonds

353 or ionic linkages with NH_4^+. The formation of H-bonds between zeolite and NH_4^+ can be accepted

354 by assuming that the isomorphic substitution of Al^{3+} with Si^{4+} results in insufficient positive

355 charges in the crystal lattice [37]. On the one hand, the existence of excessive net negative charges

356 means that some O atoms in the structure exist in unbound form. Therefore, the bound and unbound

357 O atoms are considered as independent sites on which the -H in NH_4^+ can bind [37,38]. On the other

358 hand, ionic bonding is conceivable since the zeolite and the adsorbate have different charge

359 densities.

360 With regard to the ZNC and ZSC, the parameters calculated by applying the eq. 6 to NH_4^+ adsorbed

361 data confirmed the absence of NaCl treatment effect on adsorption capacity of zeolitic mixtures.

362 Indeed, the n and K_L parameters did not show significant differences among ZNC and ZSC; only

363 q_{max} was of 3.6 mg of NH_4^+ per g of zeolite higher in ZSC compared to ZNC (Fig. 8B).

364

365 **4. CONCLUSION**

366 The specific surface area as well as the mineralogical composition of zeolitic mixtures affected their

367 ability in adsorbing NH_4^+ from a mono-component solution: high presence of mordenite enhanced

such an ability. The treatment with NaCl increased the amount of 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 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 NH_4^+ on zeolitic mixtures. Furthermore, it suggested two

different mechanisms of 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 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.

ACKNOWLEDGEMENTS

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