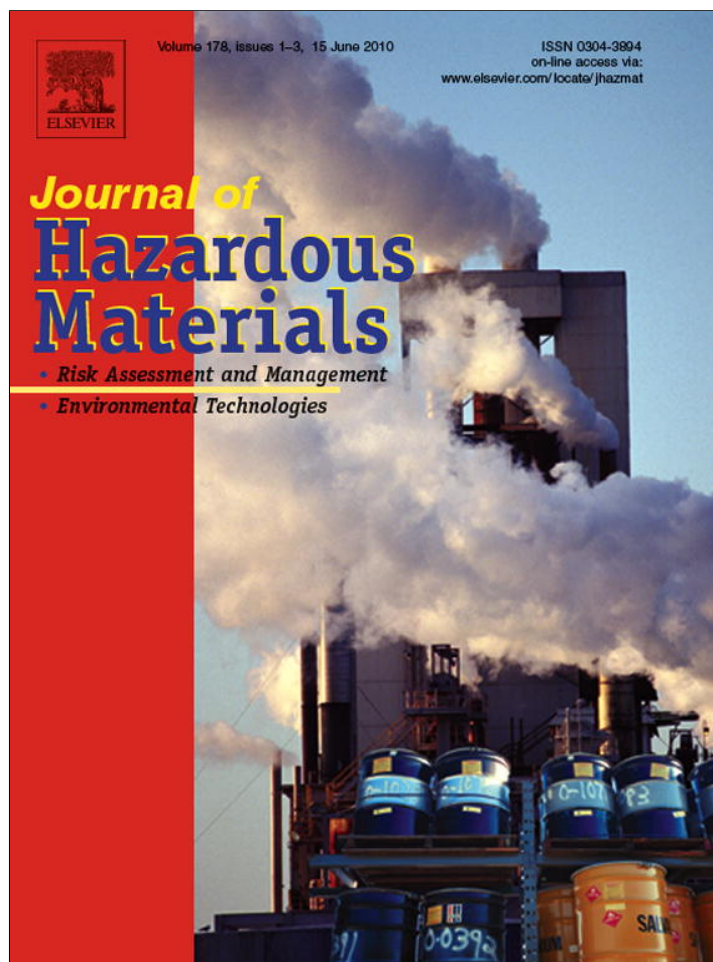


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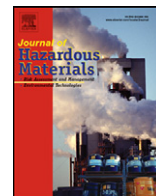
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The ground water ammonium sorption onto Croatian and Serbian clinoptilolite

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ABSTRACT

The removal of ammonium from the Valpovo region ground water (VGW) with the use of natural clinoptilolite samples from the Donje Jesenje deposit (Croatia) and the Zlatokop deposit in Vranjska Banja (Serbia) was studied. The natural Serbian (SZ) and Croatian zeolites (CZ) were transformed to the Na-form (Na-CZ and Na-SZ) in order to increase the exchange capacity of zeolite. The CZ and SZ theoretic ammonium sorption capacities were 24.24 mg NH₄⁺/g CZ and 32.55 mg NH₄⁺/g SZ, respectively. The application of natural and Na-form of clinoptilolite for efficient removal of ammonium ions from VGW was further investigated. For that purpose, the four “filter guard” vessels filled with zeolite samples were set in parallel in the ground water purification pilot plant. The complete ammonium removal, with the use of SZ and Na-SZ was achieved during 20 h. After having observed saturation of clinoptilolite, the samples were regenerated with the use of 2 mol/L NaCl, and reused for determination of ammonium sorption efficiency. The regenerated samples showed to be still very efficient for NH₄⁺ removal and, in addition, the SZ was shown as superior for ammonium removal in comparison to the CZ.

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1. Introduction

Ammonium is commonly used in the fertilizer and animal feed production and in the manufacture of fibres, plastics, explosives, paper, and rubber. It is used as a coolant, in metal processing, and as a starting product for many nitrogen-containing compounds [1]. Accordingly, the increased presence of ammonium in water is nowadays a serious environmental problem. Moreover, because of ammonium toxicity to fish and other aquatic life, as well as known eutrophication of lakes and other waters, the discharge limits for ammonium and other similar pollutants have become more stringent. The Council of the European Union has set a guide level of 0.05 mg/L and a maximum level of 0.5 mg/L of ammonium [2]. Even ground waters become more and more contaminated every day [3–5]. In accordance with that, in Northern Croatia, due to the geologic origin of the ground water, as well as the increased production and agricultural use of ammonium containing compounds, the ground water usually contains more than 1 mg/L of Fe, Mn and NH₄⁺-N [6,7]. The observed concentrations were higher than Croatian and European Union standards and therefore this ground water was unsuitable for use as drinking water without appropriate treatment [6–8]. Thus, available methods for the efficient treatment of waters polluted with ammonium ions are gaining increased inter-

est [9–11]. The biological methods were frequently used for the wastewater treatment, but due to the presence of microorganisms, for the surface and drinking waters, as well as for the ground waters, ion exchange treatment was favourable [12–14]. Among many ion exchange materials, over the last 10 years zeolitic materials have become more attractive, constantly increasing in importance as the ion exchanger in water pollution control [15–17]. Zeolites are the microporous crystalline hydrated aluminosilicate minerals and can be structurally considered as inorganic polymers, built from an infinitely extending three-dimensional network of tetrahedral XO₄ units, where X is Si or Al. Every aluminum ion present in the zeolite structure yields a net negative charge, balanced by an extra framework cation (alkali and alkaline earth cations).

The zeolites contain channels, interconnected cavities or voids of a discrete size (3–20 Å). Moreover, the micropores ($r=1.5$ – 1.6 nm) present in a specific crystalline zeolite structure, the mesopores ($r=1.6$ – 200 nm) and macropores ($r>200$ nm) that exist between particles and accompanying materials in the natural zeolites can be, in diverse ways, occupied by different ions, complexes or water molecules, respectively [18]. Accordingly, the zeolitic materials are often used in scientific and industrial investigations, mostly due to their crystallinity, thermal stability, catalytic, sieve and ion exchange properties, as well as the well-defined cage structure of molecular size. Furthermore, their low cost, high occurrence and ease of availability in large quantities, worldwide present additional benefits in the zeolite application for the purpose of eliminating, or at least reducing, many long-standing

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pollution problems [19,20]. The clinoptilolite is the most abundant among many different types of the zeolitic compounds and, as a consequence, is frequently investigated in water treatment processes in order to achieve cheap and efficient ammonium removal [6,21]. The structure of natural clinoptilolite is formed by AlO_4 and SiO_4 tetrahedra that are connected by sharing an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge appears, and can be neutralised by the exchangeable cations. According to literature, in the last decade clinoptilolite, as a natural zeolite with the representative formula $(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72})\cdot 24\text{H}_2\text{O}$, channel dimensions $3.9 \text{ \AA} \times 5.4 \text{ \AA}$ and cation exchange capacity of 2.16 mequiv./g, seems to be very efficient for removal of contaminants from drinking and ground waters [22,23]. The similar typical unit cell formula is given either as $\text{Na}_6[(\text{Al}_2\text{O}_3)(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$, $(\text{Na,K,Ca})_6(\text{Si,Al})_{36}\text{O}_{72}\cdot 20\text{H}_2\text{O}$ or $(\text{Na,K})_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$ [24–26].

Generally, the clinoptilolite belongs to the heulandite group of minerals, and due to a high content of Si, it is known also as a high-silica heulandite. The clinoptilolite structure consists of four channels. Three channels are formed out of 8-membered rings of oxygen and one channel out of 10-membered rings of oxygen. The negative charge of the clinoptilolite framework that comes from tetrahedrally coordinated aluminum is counterbalanced mainly by monovalent cations (Na^+ , K^+) or by divalent cations (Ca^{2+} , Mg^{2+}). Those properties enable the ion exchange as well as the application of the clinoptilolite for numerous investigations. The large-scale cation exchange processes using natural zeolites were firstly developed in 1967, and the effectiveness of clinoptilolite for extracting ammonium from the municipal and agricultural waste stream was demonstrated [22]. Afterwards, various aspects of ammonium or other pollutants removal by clinoptilolite from aqueous solutions have been investigated by many researchers [27–31]. Although a lot of research has been conducted by use of zeolites for ammonium ion removal from different wastewaters, there are few data in literature concerning the removal of ammonium present in the real ground water.

The main aim of this study was to obtain efficient ammonium removal from the VGW, and, therefore, the uptake of ammonium onto Croatian and Serbian natural clinoptilolite was measured and compared. The natural clinoptilolite samples (CZ and SZ) were transformed to Na-form, and the efficiency of ammonium sorption was investigated and compared to the efficiency of natural clinoptilolite samples. The regeneration of saturated clinoptilolites (CZ, Na–CZ, SZ and Na–SZ) was further investigated. The reuse of regenerated samples for additional continuous ammonium removal from the VGW was studied. Besides, in this work the applications of clinoptilolite as a cheap and effective adsorbent that are frequently used for ammonium removal within the last decade were reviewed and compared to the obtained results.

2. Experimental

2.1. Zeolite tuffs and their modification with NaCl

Natural zeolite samples (CZ and SZ), used in this study, were obtained from the Donje Jesenje deposit, Croatia (CZ) and Zlatokop deposit in Vranjska Banja, Serbia (SZ). The samples were crushed in an agate mortar and washed with distilled water in order to remove the surface dust. Grain size fractions smaller than 0.063 mm were chosen for this investigation due to the highest uptake of ammonium observed during the previous study [32]. Natural Croatian and Serbian clinoptilolite samples (2.5 kg) were pre-treated with 30 L of 2 mol/L NaCl solutions (Chromeco, Zagreb) to obtain Na-form zeolites (Na–CZ and Na–SZ). The mixtures were stirred at 36 °C and 120 rpm by an industrial magnetic stirrer (Vodotehnika, Zagreb)

for 72 h. The initial and final pH values were 6.20 ± 0.05 . After the treatment, the clinoptilolite samples were carefully washed with distilled water until reaching the negative reaction to chloride ions, filtered (blue band filter) and dried at 100 °C until constant weight was achieved. Dried clinoptilolite samples were analysed for their properties and placed in a desiccator until use. The bulk chemical compositions of all samples were determined by the classical chemical analysis [33] in combination with the AAS technique on the Atomic Absorption Spectrometer Perkin Elmer model 3110, as previously described in detail [34].

2.2. Theoretical sorption capacity

The theoretical sorption capacity of CZ and SZ zeolites for NH_4^+ ions by natural clinoptilolite was calculated as a function of initial chemical composition of clinoptilolite and its fraction in the zeolite tuff sample according to:

$$K_T = \frac{\text{Al} \times 1000}{M_r(\text{clinoptilolite})} \text{ (mequiv./gZ)} \quad (1)$$

where Al (equiv./mol) is the number of Al atoms in the clinoptilolite unit cell (6.61 equiv./mol), 1000 is the correction factor (mequiv./equiv.), and M_r is the molar weight of clinoptilolite– $\text{Na}_{3.78}\text{K}_{1.31}\text{Ca}_{0.61}\text{Mg}_{0.23}[\text{Fe}_{0.15}\text{Al}_{6.61}\text{Si}_{29.19}\text{O}_{72}]\cdot 20\text{H}_2\text{O}$ that is 2681.13 g/mol [34].

2.3. The ground water from the Valpovo region

The ground water from the Valpovo region (VGW), used in this study, was previously treated by aeration and sand filtration for the removal of iron, manganese, ammonium and other present pollutants, as schematically shown in Fig. 1. The physical and chemical parameters of the ground water and ammonium concentration were determined in the VGW after the pre-treatment.

2.4. The application of natural and modified clinoptilolite samples (CZ, SZ, Na–CZ and Na–SZ) for the removal of ammonium from the VGW

The pilot plant for the pre-treatment of water, containing the aeration unit and sand filter, was used for the first treatment step. The pilot plant is schematically presented in Fig. 1. The aeration system of the existing drinking water production plant supplied the ground water with oxygen at the concentration of $10 \pm 1 \text{ mg O}_2/\text{L}$; afterwards, the water flowed through a filter. The filter media was MnO_2 . The first treatment step enabled a partial removal of Mn and Fe. The outlet ground water was used for the ammonium removal study.

For the investigation of the application of natural (CZ and SZ) and modified clinoptilolite samples (Na–CZ and Na–SZ) for the removal of ammonium ions from the VGW, the four filter vessels (“filter guard”; 65 mm \times 285 mm) were set up in the parallel, as shown in Fig. 1. The vessels were previously filled with 2500 g of dry clinoptilolite samples (CZ, SZ, Na–CZ and Na–SZ). The VGW was pumped through “filter guard” vessels at 420 L/h. The influent and effluent ammonium concentrations were monitored at predetermined time intervals during 14 h or until the saturation of clinoptilolite samples was observed. The tests were conducted in triplicate and the data presented are the average values.

2.5. The regeneration of saturated clinoptilolite samples

The desorption of ammonium ions from the saturated clinoptilolite samples was performed by treating used natural (CZ and SZ) and modified samples (Na–CZ and Na–SZ) with 30 L of NaCl (2 mol/L). The mixtures were stirred at 120 rpm on the industrial

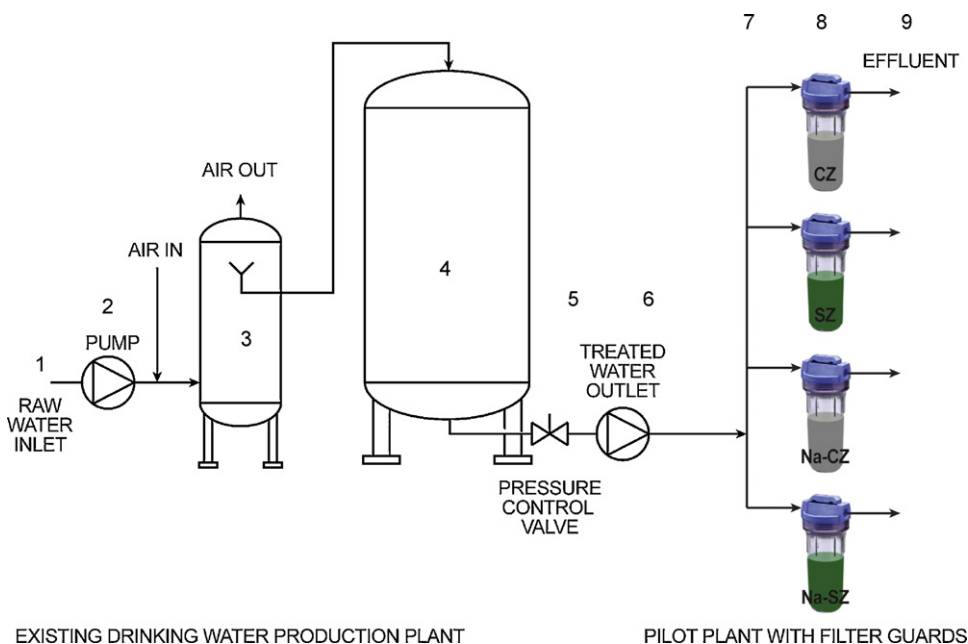


Fig. 1. Scheme of drinking water production plant (1–5) and pilot plant “filter guards” (6–9): 1 – raw groundwater influent; 2 – pump; 3 – aeration tank; 4 – filtration tank; 5 – effluent VGW; 6 – pump; 7 – VGW influent; 8 – “filter guards” vessels filled with zeolite samples and 9 – effluent water.

magnetic stirrer at 25 °C during 2 days. This lower temperature and increased time period for regeneration was applied due to economical reasons and according to the industrial use of zeolites, although the optimal temperature for regeneration should have been approximately 90 °C. The initial and the final pH values were 6.00 ± 0.05 . After stirring, the clinoptilolite samples were carefully separated by decantation and were thoroughly washed by distilled water and dried at 90 °C. The waste solutions, obtained after the regeneration and from the backwashing of filters (obtained in the first treatment step), were mixed and further processed in the wastewater treatment plant.

2.6. The application of regenerated clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) for the removal of ammonium from the VGW

The use of regenerated clinoptilolite samples was further investigated in order to determine the efficiency of regenerated clinoptilolite for ammonium removal from the Valpovo region ground water. The tests were conducted in the same way as the ammonium removal previously described.

2.7. Analytical methods

The general chemical parameters of the water, such as alkalinity, total hardness, $KMnO_4$, and the concentrations of iron were determined using standard analytical methods [35]. The manganese concentration was measured spectrophotometrically with 1-(2-pyridylazo)-2-naphthol (PAN). The PAN adsorbs Mn (II) and forms an Mn (II)-PAN complex [36]. The ammonium concentration was determined by the method according to Wagner [37]. The reagent that contained sodium salicylate, trisodium citrate dihydrate and sodium nitroprusside was added to the filtered samples, immediately after sampling and thoroughly mixed, and then the sodium dichloroisocyanurate solution was added. After mixing the flasks were placed in a water bath at 25 ± 1 °C for 60 min. The absorbance was measured at 655 nm. A field spectrophotometer (HACH, Model DR2000) was used for the spectrophotometric measurement. The initial and the final pH values of the VGW were monitored with pH Meter MA 5730 (Iskra, Kranj, Slovenia).

2.8. The calculation of sorption parameters

Ammonium loading and volumetric ammonium sorption rate during the ammonium removal test in the continuous-flow filter guard vessel were calculated as follows:

$$\text{Ammonium-nitrogen load} = (C)_{In} \times R(\text{mg NH}_4^+ \text{-N/h}) \quad (2)$$

$$\text{Volumetric ammonium sorption rate} = ((C)_{In} - (C)_{Out}) \times R(\text{mg NH}_4^+ \text{-N/h}) \quad (3)$$

where C_{In} and C_{Out} represented the influent and effluent ammonium-nitrogen concentrations (mg $\text{NH}_4^+ \text{-N/L}$) and R , the influent ground water flow rate (L/h).

The amount of ammonium sorbed from the aqueous solution in a certain filtration time period was determined by the formula [22]:

$$q_t = \frac{(C_{In} - C_t) \times Q_t}{m} (\text{mg NH}_4^+ \text{-N/g Zh}) \quad (4)$$

where q_t is the amount of ammonium ions sorbed in time expressed in mg $\text{NH}_4^+ \text{-N/g Zh}$, m is the clinoptilolite mass (g), C_{In} is the initial concentration of NH_4^+ ions expressed in mg $\text{NH}_4^+ \text{-N/L}$, C_t is the concentration of NH_4^+ ions in the solution after filtration through the filter guard vessel for a period of time t (mg $\text{NH}_4^+ \text{-N/L}$), Q_t is the real flow rate of the ammonium solution (L/h), and t is the time of process duration (h).

The sorption efficiency was evaluated according to:

$$E = \frac{((C)_{In} - (C)_{Out})}{(C)_{In}} \times 100(\%) \quad (5)$$

where E is the ammonium sorption efficiency expressed in %.

3. Results and discussion

3.1. Zeolite and ground water analysis

The application of natural (CZ and SZ) and modified clinoptilolite samples (Na-CZ and Na-SZ) for the removal of ammonium ion from the Valpovo region ground water was investigated with the use of

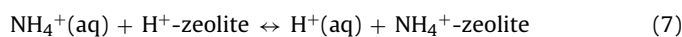
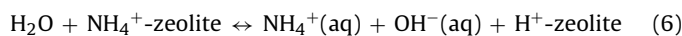
Table 1
Chemical composition of the natural and modified clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ).

Components (%)	Clinoptilolite sample			
	CZ	Na-CZ	SZ	Na-SZ
SiO ₂	63.86	64.04	66.24	65.97
Al ₂ O ₃	14.64	14.52	14.06	13.54
Fe ₂ O ₃	2.28	2.02	2.08	2.04
Na ₂ O	2.27	4.98	1.16	4.43
K ₂ O	1.08	0.88	0.94	0.74
CaO	2.84	1.48	3.12	1.82
MgO	0.88	0.80	1.02	0.84
As (III)	–	–	–	–
As (V)	–	–	–	–
Loss of ignition	11.22	10.56	10.28	9.48

natural zeolite samples. The properties of CZ and SZ are shown in Table 1. The BET surface areas of CZ, Na-CZ, SZ, and Na-SZ samples were 18, 18, 24, and 25 m²/g, respectively. The refined phase composition of CZ sample was: clinoptilolite (54.5%), feldspar plagioclase (35.2%), quartz (7.4%) and mica (2.9%) whereas the refined phase composition of natural SZ was: clinoptilolite (73.2%), feldspar plagioclase (21.5%), and quartz (7.4%). The analyses of the mineralogical composition were described in detail in our previous structural investigation of clinoptilolite [34]. The clinoptilolite zeolite Na_{3.78}K_{1.31}Ca_{0.61}Mg_{0.23}[Fe_{0.15}Al_{6.61}Si_{29.19}O₇₂]-20H₂O as naturally existing zeolite can exchange ammonium ions with sodium or potassium. The theoretical sorption capacity of clinoptilolite calculated according to Eq. (1) is 2.4653 mequiv./g. Since 1 mequiv. NH₄⁺ corresponds to 18.0386 mg NH₄⁺ (M_r/charge), the theoretical sorption capacity for an ammonium ion, K_T(NH₄⁺), for the pure clinoptilolite is 44.471 mg NH₄⁺/gZ (2.4653 × 18.0386). Accordingly, for the SZ sample with 73.2% of clinoptilolite the K_T(NH₄⁺) is 32.55 mg NH₄⁺/gSZ and for the CZ sample with 54.5% of clinoptilolite the K_T(NH₄⁺) is 24.24 mg NH₄⁺/gCZ. The observed values are in agreement with the previously published data [38]. Although, the ion exchange capacity of clinoptilolite is lower than some other zeolites, in general, it exhibits a high selectivity for NH₄⁺ ion and therefore is broadly investigated for the ammonium removal [39,40]. The selectivity of ion exchange on natural clinoptilolite was reported in the order of K⁺ > NH₄⁺ > Na⁺ > Ca²⁺ > Mg²⁺ [23,41,42].

The physical and chemical parameters of the raw VGW are presented in Table 2. The ammonium concentration in the VGW after pre-treatment was 1.13 ± 0.03 mg NH₄⁺-N/L.

During the removal of NH₃ in pure water, under dynamic conditions (flow system at pH 6 and low concentration of ammonium) the most probable reactions are:



where “(aq)” represents species existing in the water phase.

Table 2
Physical and chemical parameters of the raw Valpovo ground water.

Parameters	Ground water	Maximum contamination level
pH	7.02	6.5–9.5
Temperature (°C)	13.2	25
Free CO ₂ (mg CO ₂ /L)	30.8	–
Alkalinity, CaCO ₃ (mg/L)	631	>30
Total hardness, CaCO ₃ (mg/L)	292	>60
KMnO ₄ (mg O ₂ /L)	5.1	5.0
Iron, Fe (mg/L)	2.4	0.2
Manganese, Mn (mg/L)	0.12	0.05
Ammonium (mg NH ₄ ⁺ -N/L)	1.15	0.5

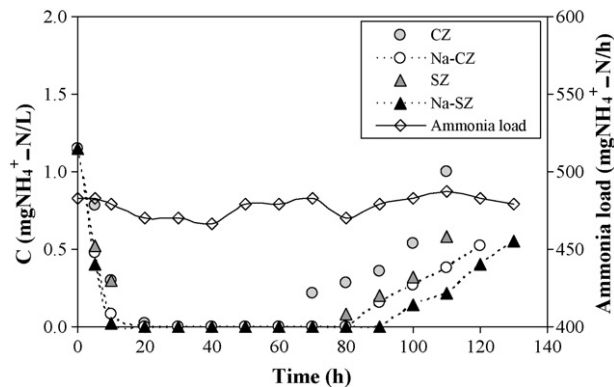


Fig. 2. The ammonia load and dynamics of ammonia concentration at the filter guard vessels exit.

Generally speaking, the stability of NH₄⁺ on the ion exchange site of a zeolite possessing strong acid sites is greater than that of a zeolite possessing weak acid sites. Thus, the NH₄⁺ on ion exchange sites of the zeolite possessing strong acid sites is less subject to hydrolysis (forward reaction in Eq. (6)) and ion exchange with H⁺ ions existing in the water phase (back reaction in Eq. (7)), than the NH₄⁺ on zeolites possessing weak acid sites. Therefore, Na-form of zeolite, in the comparison to the natural zeolite, was superior in ion exchange.

3.2. The application of natural and modified clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) for the removal of ammonium from the VGW

The results of ammonium sorption onto natural clinoptilolite (CZ and SZ) and modified clinoptilolite samples (Na-CZ and Na-SZ) are shown in Figs. 2 and 3. The complete ammonium removal, at the ammonium load of 470 ± 20 mg NH₄⁺-N/h, was achieved after 10 h of the process duration. The ammonium concentrations in the effluent were brought to zero after 10 h (Fig. 2). They gradually rose to 1 mg NH₄⁺-N/L after 60 h of the treatment depending on the type of zeolite (CZ, SZ, Na-CZ and Na-SZ). Thus, the partial saturation of CZ, Na-CZ, SZ, and Na-SZ was noticed after 60, 80, 80, and 90 h, respectively. Furthermore, almost complete saturation of CZ was observed after 110 h. The ammonium sorption efficiency of 100% yielded from 10 to 90 h with the use of Na-SZ (Fig. 3), but it was sharply decreased after 70 h with use of CZ or Na-CZ. As can be seen in Fig. 3, the Na-SZ was superior for ammonium removal from

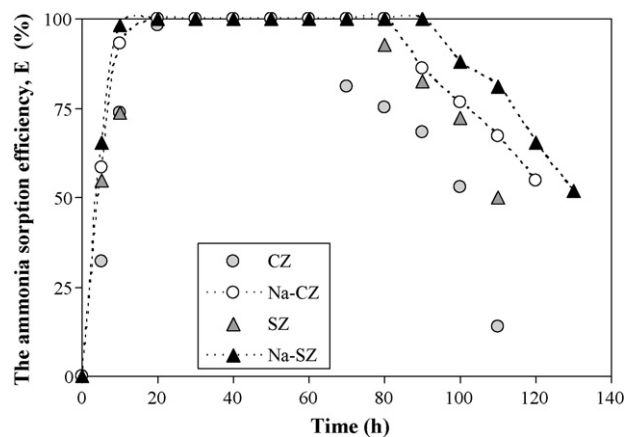


Fig. 3. The ammonia sorption efficiency, E during the investigations of ammonia removal with natural and modified clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) from the Valpovo region ground water.

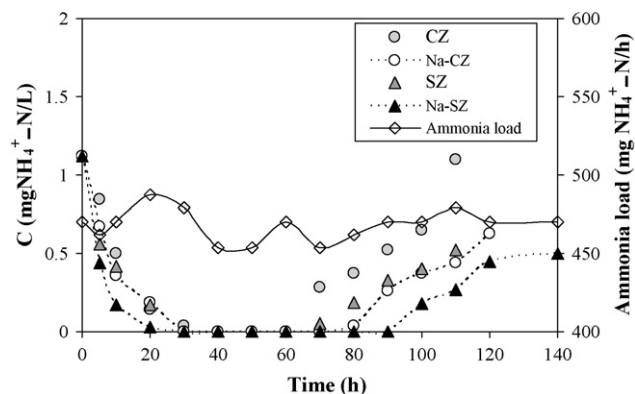


Fig. 4. The ammonia load and dynamics of ammonia concentration at the filter guard vessels exit during the investigations of ammonia removal with regenerated natural and modified clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) from the Valpovo region ground water.

the Valpovo region ground water in comparison to other tested zeolites. According to the chemical, mineralogical composition, and the BET surface area, the Serbian zeolite (SZ and Na-SZ) contains increased amounts of clinoptilolite. The BET surface area of this was 33.3% higher in comparison with the surface area of the Croatian zeolite. Therefore, beside the clinoptilolite content, the increased BET surface area of SZ was one of the reasons for superior ammonia removal.

After the observation of increased ammonium concentrations in the effluent, the test was stopped and the zeolite was regenerated. According to literature, for regeneration of zeolites NaCl solutions were frequently used [29,43,44]. Subsequently, Koon and Kaufman [44] pointed out that zeolites can be almost completely regenerated with a NaCl solution at pH > 12. Some researchers use biological methods to regenerate zeolite [45–47], since those methods are environmentally friendly and less energy consuming. Yet, the biological regeneration needs a continuous monitoring of process parameters, such as pH and temperature, and also requires the addition of a carbon source and the removal of by-products such as nitrite. Moreover, in some cases, the zeolite could be filled up with sludge which could result in the reduction of the adsorption capacity. Accordingly, the use of NaCl was efficient and cost-effective for the regeneration of the investigated clinoptilolite samples. During the regeneration, the starting pH and final pH values were 6.2 ± 0.05 . The obtained pH values can be explained by the presence of other nonzeolitic phases in the clinoptilolite sample. The regenerated zeolite was filled into the “filter guard” vessel and the next test set was conducted.

3.3. The application of regenerated clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) for the removal of ammonium from the VGW

The results observed during this investigation were presented in Figs. 4 and 5. The regenerated samples (CZ, SZ, Na-CZ, and Na-SZ) were still able to adsorb ammonium from the ground water. During the first 30 h the ammonium removal increased, reaching almost 100% ammonium removal. The complete ammonium removal was achieved during 70 h with the use of SZ, Na-CZ and Na-SZ, but from that point on, the gradual saturation of zeolite was observed. The ammonium sorption efficiency with use of natural Croatian clinoptilolite was 100% after 30 h, but after 60 h, $0.28 \text{ mg NH}_4^+ \text{-N/L}$ was observed in the effluent. The saturation of CZ started at 70 h with a sharp decrease of the adsorbed ammonium amount (Fig. 4). Once again, the complete saturation of CZ was achieved during 110 h. Repeatedly, the Serbian clinoptilolite showed superiority in ammonium removal, as demonstrated in Figs. 3 and 4. During the

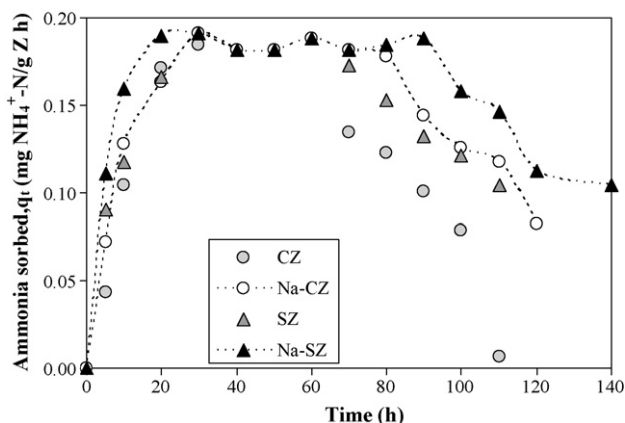


Fig. 5. The amount of ammonium ions sorbed on zeolite in time, q_t during the investigations of ammonia removal with natural and modified clinoptilolite samples (CZ, SZ, Na-CZ and Na-SZ) from the Valpovo region ground water.

application of natural and modified clinoptilolite samples (CZ, SZ, Na-CZ, and Na-SZ) for the removal of ammonium from the VGW, the amount of ammonium ions sorbed (q_t), calculated according to Eq. (4), was in the range of $0.062\text{--}0.188 \text{ mg NH}_4^+ \text{-N/g Z h}$, while at this investigation the amount of ammonium ions sorbed (q_t) was $0.044\text{--}0.188 \text{ mg NH}_4^+ \text{-N/g Z h}$.

Generally, the theoretical sorption capacity for ammonium ion for CZ and SZ was $24.24 \text{ mg NH}_4^+ \text{/g CZ}$ and $32.55 \text{ mg NH}_4^+ \text{/g SZ}$, or $18.82 \text{ mg NH}_4^+ \text{-N/g CZ}$ and $25.27 \text{ mg NH}_4^+ \text{-N/g SZ}$, respectively. According to that, the theoretical volume of ground water that should flow over CZ and SZ in the presence of 2500 g of clinoptilolite samples, should be $60,600 \text{ mg NH}_4^+ \text{/g CZ}$ and $81,375 \text{ mg NH}_4^+ \text{/g SZ}$, or $47,050 \text{ mg NH}_4^+ \text{-N/g CZ}$ and $63,187.5 \text{ mg NH}_4^+ \text{-N/g SZ}$, respectively. At real flow rate of 420 L/h and in the presence of the average initial ammonium concentration of $1.13 \text{ mg NH}_4^+ \text{-N/L}$ in the VGW, the saturation of CZ and SZ may occur after 112 and 150 h, respectively. In the real conditions, as mentioned before the almost complete saturation of CZ was achieved after 110 h. Accordingly, theoretic values were confirmed by a real test. Furthermore, with the use of Serbian clinoptilolite the ammonium removal was achieved faster and more efficiently.

4. Conclusions

The application of natural and Na pre-treated zeolite samples from the Donje Jesenje deposit (Croatia) and the Zlatokop deposit in Vranjska Banja (Serbia) were investigated for the removal of ammonium from the Valpovo region ground water. At the ammonium load of $470 \pm 20 \text{ mg NH}_4^+ \text{-N/h}$, complete ammonium removal was achieved after 10 h of treatment, but it rose up to $1 \text{ mg NH}_4^+ \text{-N/L}$ after 60 h, depending on the type of zeolite (CZ, SZ, Na-CZ, and Na-SZ). After regeneration of the saturated clinoptilolite, the ammonium removal increased and reached nearly 100% during the first 30 h.

The comparison of the results obtained with Croatian and Serbian zeolites indicates that their composition and the BET surface areas have a significant impact on the effective ammonium removal. Accordingly, Serbian zeolites having a higher clinoptilolite content and a greater BET surface area have proven to be more effective sorbent for ammonium and can be successfully applied for efficient ammonia removal from ground waters.

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