

## Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia

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### Abstract

The paper presents the results of investigating the treatment of leakage waters from waste dumps using activated carbon and natural zeolite clinoptilolite, known as a very selective and efficient cation exchanger for ammonium ions. The results are presented of chemical and physical analyses of leakage waters characterized by a high content of ammonium ( $820 \text{ mg L}^{-1}$ ) and organic pollutants ( $1033 \text{ mg L}^{-1} \text{ C}$ ). Physical and chemical characteristics of zeolite and the exchange of ammonium ions in model and real solutions were determined in laboratory trials. Treatment of leakage water with 0.04–2.5% (w/w) activated carbon (Norit 0.8 Supra) led to a reduction of total organic carbon in leakage water from 1033 to  $510 \text{ mg L}^{-1}$ . Pretreatment of leakage water with activated carbon did not improve the exchange of ammonium ions on zeolite. Without pretreatment of leakage water, the exchange of ammonium ions amounted to  $4.2 \text{ mg NH}_4^+/\text{g zeolite}$ . Addition of activated carbon, regardless of its mass, increased the exchange of ammonium ions to only  $5.7 \text{ mg NH}_4^+/\text{g zeolite}$ . In the model solution of an equal concentration of ammonium as the real solution,  $17.70 \text{ mg NH}_4^+/\text{g zeolite}$  was exchanged. Organic pollutants that were not eliminated by activated carbon (most probably components of natural origin) adsorbed to zeolite and prevented the exchange of  $\text{NH}_4^+$  ions, which was also reduced due to the presence of  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions.

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### 1. Introduction

Vast quantities of wastewaters are a typical example of uncontrolled utilization of natural resources. In such waters, nitrogen commonly occurs as organic nitrogen, ammonia or in the form of ammonium, nitrate or nitrite compounds [1].

The traditional method of removing organic compounds and ammonium ions from wastewater is based on biological methods [2–4]. However, as the discharge limits of different pollutants are becoming more stringent, ion exchange is gaining on interest as a potential method for the treatment of waters polluted with ammonium ions.

In the last 20 years, characteristics of natural zeolites have been intensively studied for the needs of wastewater treatment [5–15]. Ion exchange in zeolites is due to

active hydrated cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in the channels making up the firm anion skeleton. In contrast to the aluminium and silicon structure atoms, which are mutually bound by chemical (covalent) bonds over common oxygen atoms, cations are bound with the aluminosilicate structure mainly by weaker electrostatic bonds, which causes their mobility and capability of being exchanged with solution cations. Organic resins are usually used because of their higher cation-exchange abilities, higher reaction rates and better chemical resistivity. Zeolites, in contrast, possess higher cation-exchange selectivity [5,16]. Mercer (1970) stated that the non-selective nature of convectional cation-exchange resins makes the costs of the process of ammonium ions removal from urban wastewaters too high and suggested the use of clinoptilolite (simplified formula  $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot 24\text{H}_2\text{O}$ ), the widespread natural zeolite, whose calcium and sodium forms are highly selective for ammonium ions [5]. This recommendation was based on the results of detailed laboratory and pilot investigations.

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This study was, therefore, focused on the possibility of purifying wastewater by using natural zeolite clinoptilolite.

Leakage water samples were taken from the waste dump at Jakuševac, Zagreb, enriched with ammonium ions, synthetic and natural organic compounds (proteins, amines, urea, etc.). The dumped waste is in direct contact with the thick gravely water-bearing deposits and there is a risk of pollution of the sources of drinking water for Zagreb. Leakage waters are collected by means of a drainage system in two specially equipped collection reservoirs with impermeable bottoms. Leakage water is periodically returned from the reservoirs to the waste dump. Water quantity is reduced by recirculation and evaporation of leakage water and the rest is foreseen for purification.

## 2. Materials and methods

### 2.1. Zeolite characterization

In the trial use was made of zeolite tuff with the predominant content of the zeolite mineral clinoptilolite from the Krapina region, Croatia. The investigations involved zeolite samples of particle sizes from 0.5 to 2.0 mm.

Identification of mineral components in the zeolite sample was performed using the X-ray diffraction analysis (XRD) on a dust sample (Fig. 1). X-ray analysis of zeolite was performed with a PHILIPS 1710 diffractograph using  $\text{Cu K}\alpha$  radiation.

Zeolite chemical composition was determined by the classical chemical analysis (Table 1).

Zeolite cation-exchange capacity was measured by successive zeolite saturation with a solution of ammonium ions (concentration  $2 \text{ mol L}^{-1}$ ). Adding up the molal concentrations ( $x \text{ mmol g}^{-1}$ ) of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $0.5 \text{ Ca}^{2+}$  and  $0.5 \text{ Mg}^{2+}$  ions exchanged with  $\text{NH}_4^+$  ions gave the cation-exchange capacity designated  $Q_1^0$ . The obtained sample in the  $\text{NH}_4^+$  form was further saturated with a solution of potassium ions

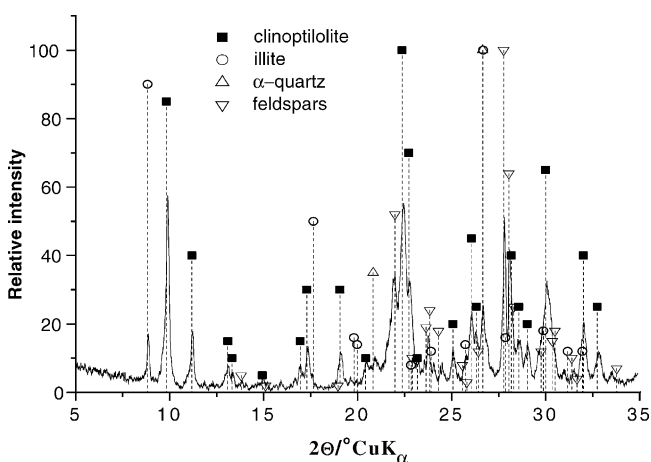


Fig. 1. X-ray of the natural zeolite sample.

Table 1

Chemical composition of the natural zeolite sample

Components	Values (%)
$\text{SiO}_2$	64.93
$\text{Al}_2\text{O}_3$	13.39
$\text{Fe}_2\text{O}_3$	2.07
$\text{Na}_2\text{O}$	2.40
$\text{K}_2\text{O}$	1.30
$\text{CaO}$	2.00
$\text{MgO}$	1.08
Loss on ignition at $1000^\circ\text{C}$	9.63

(concentration  $2 \text{ mol L}^{-1}$ ), and the exchanged  $\text{NH}_4^+$  ions were determined in the eluate. The cation-exchange capacity obtained by determining the molal concentration of exchanged ammonium ions was designated  $Q_2^0$ . Solution of  $\text{NH}_4^+$  ions was prepared by dissolving  $\text{NH}_4\text{Cl}$ , and the solution of  $\text{K}^+$  ions by dissolving  $\text{KCl}$  in distilled water. The results are given in Table 2. The method of atomic absorption spectrophotometry was used for quantitative determination of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Atomic absorption spectrophotometer PERKIN-ELMER 3110 was used for cation analysis. Ammonium ions were determined using the  $\text{NH}_3$  selective electrode METROHM, AG.

The cation-exchange capacity of zeolite was determined in more detail as follows:

- (1) Exactly 0.100 g of sample was weighed into a dry cuvette.
- (2) A 10.0 mL of  $\text{NH}_4^+$  ions solution was poured over the sample.
- (3) The sample was left to stand overnight.
- (4) The following day, the sample was centrifuged at a rate of  $3000^\circ \text{ min}^{-1}$ .
- (5) Upon centrifuging, the solution above the sediment was decanted into a volumetric flask of 100.0 mL.
- (6) A 10.0 mL of  $\text{NH}_4^+$  ions solution was again poured over the sample, which was then centrifuged. The solution above the sediment was decanted into the volumetric flask.
- (7) Procedure (6) was repeated three more times.
- (8) Upon the last decanting, the volumetric flask was made up to the mark with redistilled water and concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  ions were determined in the thus obtained solution. The sample in the cuvette was washed two to three times with distilled water.

Table 2

Cation-exchange capacities  $Q_1^0$  and  $Q_2^0$  of natural zeolite

Cations	$x \text{ (mmol g}^{-1}\text{)}$
$\text{Na}^+$	0.950
$\text{K}^+$	0.312
$0.5 \text{ Ca}^{2+}$	0.162
$0.5 \text{ Mg}^{2+}$	0.032
$Q_1^0$	1.456
$(Q_2^0)$	(1.45)

- (9) Upon washing, 10.0 mL of  $K^+$  ions solution was poured over the sample.
- (10) The sample was left to stand overnight.
- (11) The following day, the sample was centrifuged.
- (12) Upon centrifuging, the solution above the sediment was decanted into a volumetric flask of 100.0 mL.
- (13) A 10.0 mL of KCl solution was again poured over the sample, which was then centrifuged. The solution above the sediment was decanted into the volumetric flask.
- (14) Procedure (13) was repeated three more times.
- (15) Upon the last decanting, the volumetric flask was made up to the mark with redistilled water and the concentration of  $NH_4^+$  ions was determined in the thus obtained solution.

## 2.2. Leakage water analysis

Samples of leakage water were taken several times during a period of 6 months. Since phenols are subject to biological and chemical oxidation, the samples were adequately preserved. Each sample was acidified to pH 4 with  $H_3PO_4$ . One gram of  $CuSO_4$  per litre was added to inhibit biodegradation. The samples were then analyzed according to the “standard methods for the examination of wastewater” [17]. Table 3 gives the comparison of concentration ranges of the

tested parameters of leakage water samples. Table 4 presents the analysis of the leakage water sample that was used for further testing.

## 2.3. Exchange of $NH_4^+$ ions from leakage water on zeolite by the static procedure

Six Erlenmeyer flasks were filled with 2.00 g zeolite each and 100.0 mL leakage wastewater was added. Suspensions were shaken at a temperature of  $23 (\pm 1)^\circ C$  in an INNOVA 4080 shaker at a rate of 200 rpm, for 15, 30, 60, 120, 240 and 360 min. Upon shaking, the suspensions were centrifuged and the concentration of  $NH_4^+$  ions was determined in the solutions. From the differences between the starting concentration and the concentrations of ammonium ions in leakage water samples after shaking, masses of exchanged ammonium ions were calculated according to

$$q_t = \frac{(\gamma_0 - \gamma_t)v}{m_z} \quad (1)$$

where  $\gamma_0$  and  $\gamma_t$  ( $mg L^{-1}$ ) are the initial mass concentration of ammonium ions in solution and the mass concentration of ammonium ions in solution at time  $t$ , respectively,  $v$  the wastewater volume (L), and  $m_z$  is the zeolite mass in solution (g) (Fig. 2).

Table 3  
Comparison of concentration ranges of chemical and physical parameters of leakage waters

Parameter	Value			Prescribed values	
	Minimum	Maximum	Average	Natural recipients <sup>a</sup>	Public drainage system <sup>b</sup>
BOD <sub>5</sub> (mg O <sub>2</sub> L <sup>-1</sup> )	200	2800	1050	25	250
COD (mg O <sub>2</sub> L <sup>-1</sup> )	1093	5910	1500	125	700
TOC (mg C L <sup>-1</sup> )	873	3660	3500	30	–
Nitrates (mg NL <sup>-1</sup> )	0.4	2.68	2	10.0	–
$NH_4^+$ (mg L <sup>-1</sup> )	130	850	400	15.0	–
<i>o</i> -Phosphates (mg PL <sup>-1</sup> )	0.02	1	1	1.0	–
Total hardness, CaCO <sub>3</sub> (mg L <sup>-1</sup> )	517	3225	3200	–	–
Total dissolved matter (mg L <sup>-1</sup> )	1000	5950	5000	35	80
pH	7.08	7.85	7.3	6.5–8.0	5.0–9.5
Calcium (mg L <sup>-1</sup> )	14	1080	1000	–	–
Magnesium (mg L <sup>-1</sup> )	79	200	100	–	–
Sodium (mg L <sup>-1</sup> )	252	1098	700	–	–
Chloride (mg L <sup>-1</sup> )	555	1520	980	–	1000
Sulphates (mg L <sup>-1</sup> )	279	430	380	–	400
Chromium total (mg L <sup>-1</sup> )	0.275	0.3	0.3	1.0	2.0
Cadmium (mg L <sup>-1</sup> )	b.d.l.	b.d.l.	–	–	–
Copper (mg L <sup>-1</sup> )	<0.02	0.67	0.5	0.1	0.5
Lead (mg L <sup>-1</sup> )	0.315	9.43	0.5	0.2	2.0
Nickel (mg L <sup>-1</sup> )	b.d.l.	b.d.l.	–	1.0	2.0
Iron (mg L <sup>-1</sup> )	5.53	19.45	7	2.0	10.0
Zinc (mg L <sup>-1</sup> )	0.02	5.28	2	1.0	2.0
Total phenols (mg L <sup>-1</sup> )	0.15	2.0	1.0	0.1	10.0

b.d.l.: Below detection limit.

<sup>a</sup> Marginal values of concentrations of hazardous and other substances in wastewaters that may be discharged into natural recipients of category II according to the Croatian By-law on margin values for indicators of hazardous and other substances in wastewaters.

<sup>b</sup> Marginal values of concentrations of hazardous and other substances in wastewaters that may be discharged into the public drainage system according to the Croatian By-law on margin values for indicators of hazardous and other substances in wastewaters.

Table 4  
Overall analysis of the studied leakage water sample

Parameter	Values
pH	7.77
Conductivity ( $\mu\text{S cm}^{-1}$ )	11700
COD ( $\text{mg L}^{-1}$ )	1940
BOD <sub>5</sub> ( $\text{mg L}^{-1}$ )	200
TOC ( $\text{mg L}^{-1}$ )	1033
Total phenols ( $\text{mg L}^{-1}$ )	0.157
NH <sub>4</sub> <sup>+</sup> ( $\text{mg L}^{-1}$ )	820
Nitrites ( $\text{mg N L}^{-1}$ )	0.03
Nitrates ( $\text{mg N L}^{-1}$ )	0.47
Total hardness ( $\text{CaCO}_3$ ) ( $\text{mg L}^{-1}$ )	1150
Magnesium ( $\text{mg L}^{-1}$ )	196
Calcium ( $\text{mg L}^{-1}$ )	128
Total oils and fats ( $\text{mg L}^{-1}$ )	7.9
Mineral oils and fats (carbohydrates) ( $\text{mg L}^{-1}$ )	1.01
Total P ( $\text{mg L}^{-1}$ )	1.18
Chloride ( $\text{mg L}^{-1}$ )	1350
Sodium ( $\text{mg L}^{-1}$ )	1085
Potassium ( $\text{mg L}^{-1}$ )	801
Zinc ( $\text{mg L}^{-1}$ )	2
Iron ( $\text{mg L}^{-1}$ )	7.04
Lead ( $\text{mg L}^{-1}$ )	0.48
Copper ( $\text{mg L}^{-1}$ )	<0.02
Cadmium ( $\text{mg L}^{-1}$ )	b.d.l.
Nickel ( $\text{mg L}^{-1}$ )	b.d.l.
Chromium ( $\text{mg L}^{-1}$ )	0.33
Manganese ( $\text{mg L}^{-1}$ )	0.90
Evaporable residue filtrate ( $\text{mg L}^{-1}$ )	5715
Evaporable residue total ( $\text{mg L}^{-1}$ )	5845

b.d.l.: below detection limit.

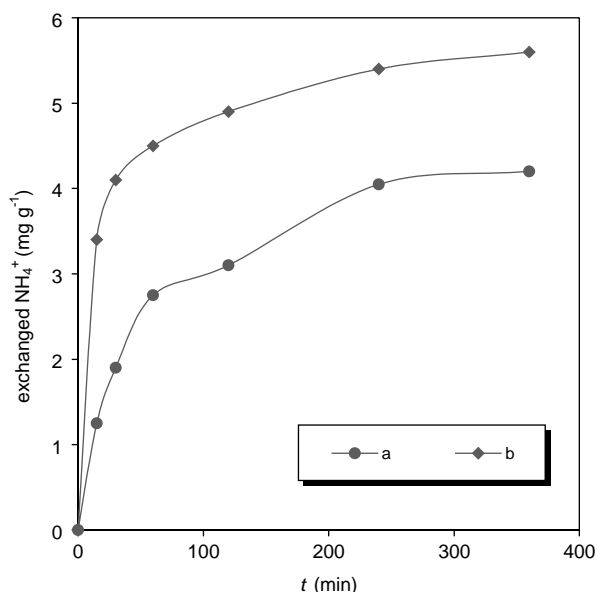


Fig. 2. Exchange of NH<sub>4</sub><sup>+</sup> ions on 2.00 g zeolite from 100.0 mL leakage water in dependence on the stirring time: (a) without leakage water pretreatment, and (b) with leakage water pretreatment by 0.04% (w/w) activated carbon.

#### 2.4. Removal of organic carbon from leakage water samples with activated carbon

Today, activated carbon is being increasingly used for removal of organic micropollutants (e.g. phenols) from water [18–23]. In this study, the applicability of activated carbon Norit 0.8 Supra to leakage water treatment was investigated. The activated carbon tested satisfies the requirements of the U.S. Food Chemical Codex. Pursuant to the specification of the said activated carbon, phenol absorption amounts to 6% (w/w).

To test the removal of organic pollution from leakage water with activated carbon, total organic carbon was determined in wastewaters treated with different masses of activated carbon (0.04, 0.10, 0.20, 0.50, 1.00, 2.50, 3.50 and 5.00% (w/w)). Suspensions were shaken for 360 min, centrifuged and total organic carbon was determined in the obtained filtrates (Fig. 3). Total organic carbon was determined using the Carbon analyzer IONICS 1555, “Ionics”.

#### 2.5. Exchange of NH<sub>4</sub><sup>+</sup> ions from samples of leakage water pretreated with activated carbon

A 100.0 mL of the leakage water samples treated with 0.04% (w/w) activated carbon were transferred into each of the six Erlenmeyer flasks into which 2.00 g zeolite had been previously added. Suspensions were shaken for 15, 30, 60, 120, 240 and 360 min. Upon shaking, the suspensions were centrifuged. Concentrations of NH<sub>4</sub><sup>+</sup> ions were determined in the solutions and masses of exchanged ammonium ions were calculated (Fig. 2).

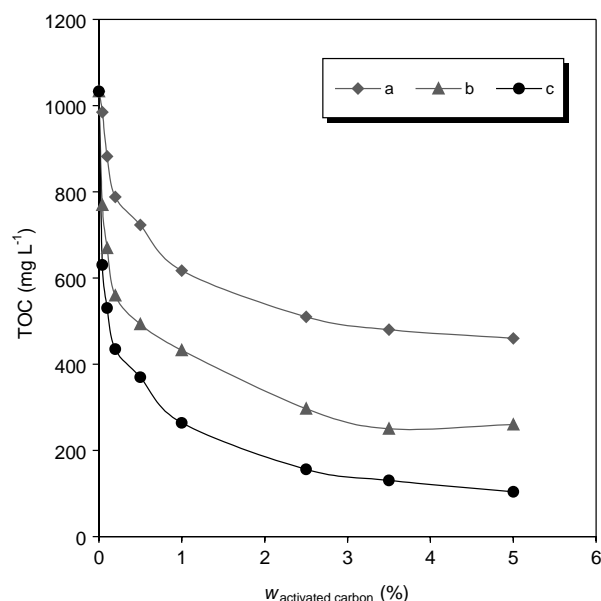


Fig. 3. Concentrations of total organic carbon in samples of leakage water: (a) upon treatment with activated carbon (0.04, 0.10, 0.20, 0.50, 1.00, 2.50, 3.50 and 5.00% (w/w)), (b) upon subsequent treatment with 2.00% (w/w) zeolite, and (c) 5.00% (w/w) zeolite.

Table 5

Exchange of  $\text{NH}_4^+$  ions on zeolite from the leakage water pretreated with 0.10–5.00% (w/w) activated carbon:  $v(\text{solution}) = 100.0 \text{ mL}$ ,  $m(\text{zeolite}) = 2.00 \text{ g}$

Activated carbon (% (w/w))	$\text{NH}_4^+$ ( $\text{mg g}^{-1}$ )
0.10	5.75
0.20	5.62
0.50	5.64
1.00	5.60
2.50	5.72
3.50	5.60
5.00	5.70

A 100.0 mL of leakage water samples treated with 0.10, 0.20, 0.50, 1.00, 2.50, 3.50 and 5.00% (w/w) of activated carbon were transferred into each of the seven Erlenmeyer flasks into which 2.00 g zeolite was previously added. Suspensions were shaken for 360 min and then centrifuged. Concentrations of  $\text{NH}_4^+$  ions were determined in the solutions and masses of exchanged ammonium ions were calculated (Table 5).

### 2.6. Removal of organic carbon from leakage water samples with zeolite

Leakage water samples treated with different masses of activated carbon (0.04, 0.10, 0.20, 0.50, 1.00, 2.50, 3.50 and 5.00% (w/w)) were subsequently treated with 2.00 and 5.00% (w/w) zeolite. Suspensions were shaken for 360 min, centrifuged and total organic carbon was determined in the obtained filtrates (Fig. 3).

### 2.7. Testing the $\text{K}^+$ and $\text{Ca}^{2+}$ effect on the exchange of $\text{NH}_4^+$ ions from model solutions using the static procedure

Effect of  $\text{Ca}^{2+}$  ions with starting concentrations of 100, 200 and 400  $\text{mg L}^{-1}$  and the effect of  $\text{K}^+$  ions with starting concentrations of 250, 500 and 800  $\text{mg L}^{-1}$  on the exchange of ammonium ions were tested. Solutions of  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions were prepared by dissolving  $\text{KCl}$  and  $\text{CaCl}_2$  in distilled water. The concentration of ammonium ions in solutions was 800  $\text{mg L}^{-1}$ .

Zeolite samples (2.00 g) were equilibrated by shaking for 15, 30, 60, 120, 240 and 360 min with 100.0 mL of model solutions each. Upon equilibration, concentrations of  $\text{NH}_4^+$  ions in solutions were determined and used to calculate the masses of exchanged ammonium ions (Figs. 4 and 5).

### 2.8. Exchange of $\text{NH}_4^+$ ions from leakage and model waters on zeolite using the column procedure

Two fibreglass columns, connected with plastic tubes, with a 7.0 cm diameter and 60.0 cm long, were used (Fig. 6). The first column was filled with 1300 g of silica sand and 46.5 g of activated carbon, while the second column was filled with 1440 g of zeolite. A glass bottle with the tested in-

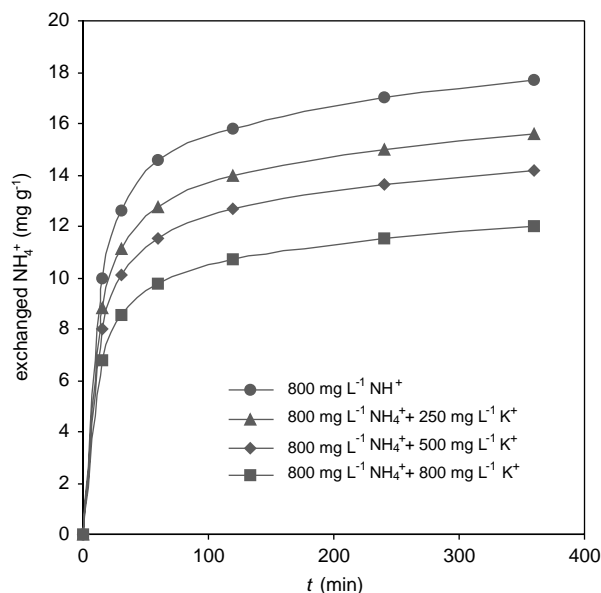


Fig. 4. Exchange of  $\text{NH}_4^+$  ions on natural zeolite from model solutions of ammonium and potassium ions:  $v(\text{solution}) = 100.0 \text{ mL}$ ,  $m(\text{zeolite}) = 2.00 \text{ g}$ .

fluent was placed above the columns. Water flow ( $1.5 \text{ L h}^{-1}$ ) was controlled during the column operation. Curves of the breakthrough of ammonium ions from leakage water as well as from model water (ammonium ions concentration 820  $\text{mg L}^{-1}$ ) were determined. Effluents in which ammonium ions concentrations were determined had a volume of 1 L.

pH values, conductivity,  $\text{BOD}_5$ , TOC, total phenols and total hardness of effluent were monitored in the collected

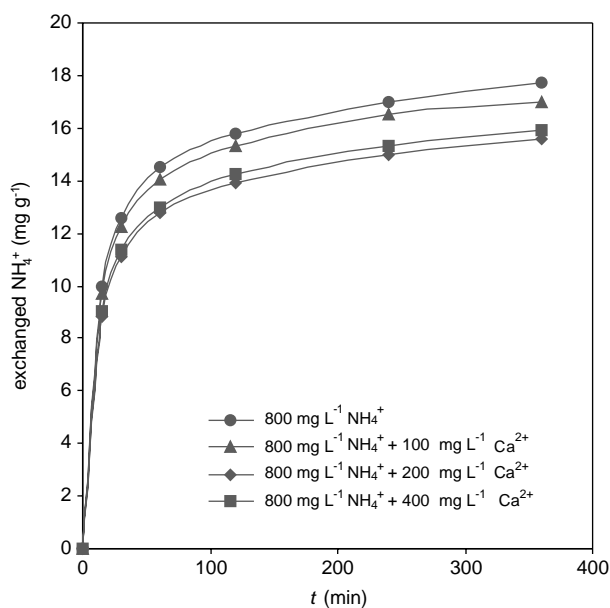


Fig. 5. Exchange of  $\text{NH}_4^+$  ions on natural zeolite from model solutions of ammonium and calcium ions:  $v(\text{solution}) = 100.0 \text{ mL}$ ,  $m(\text{zeolite}) = 2.00 \text{ g}$ .

Table 6  
Results of physical and chemical parameters of leakage water passed through the columns

Parameter	Untreated leakage water	First litre of leakage water passed	Fifth litre of leakage water passed	Tenth litre of leakage water passed
pH	7.77	7.60	7.41	7.30
Conductivity ( $\mu\text{S cm}^{-1}$ )	11700	11500	10830	10220
BOD <sub>5</sub> ( $\text{mg L}^{-1}$ )	200	50	57	154
TOC ( $\text{mg L}^{-1}$ )	1033	200	418	800
Total phenols ( $\text{mg L}^{-1}$ )	0.157	0.002	0.015	0.047
NH <sub>4</sub> <sup>+</sup> ( $\text{mg L}^{-1}$ )	820	0	0	35
Total hardness, CaCO <sub>3</sub> ( $\text{mg L}^{-1}$ )	1150	1000	848	1340
Mg <sup>2+</sup> ( $\text{mg L}^{-1}$ )	196	100	117	122
Ca <sup>2+</sup> ( $\text{mg L}^{-1}$ )	128	140	158	334

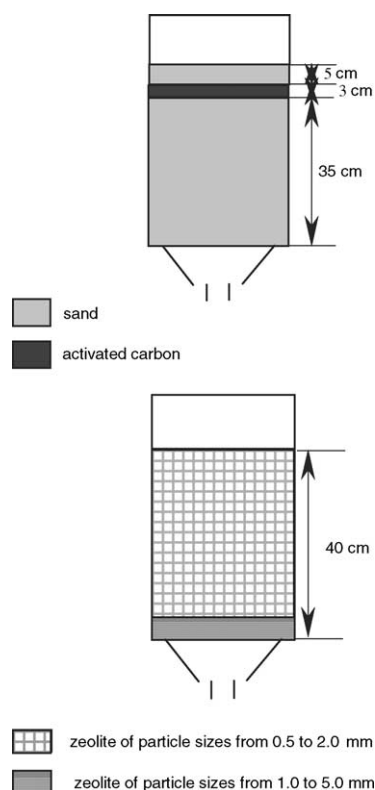


Fig. 6. Schematic presentation of columns.

first, fifth and tenth litre of leakage water (Table 6). A total amount of 13 L leakage water and 25 L model water were passed through the columns.

The columns were packed with fresh materials for each solution—both model and real solutions.

### 3. Results and discussion

#### 3.1. Zeolite characterization

X-ray diffraction analysis was used to determine the qualitative mineralogical composition of clinoptilolite tuff. Fig. 1 shows the XRD of the zeolite tuff sample. Its analysis re-

vealed the presence of clinoptilolite as the main mineral component, then feldspar (plagioclase, labradorite, bytownite, oligoclase), illite and  $\alpha$ -quartz. According to earlier studies, natural zeolite tuff contains 50–60% of clinoptilolite [14].

Quantitative chemical composition of the studied zeolite sample was determined by the classical chemical analysis. Results of the chemical analysis are given in Table 1. The chemical analysis has shown that natural zeolite contains 2.4% Na<sub>2</sub>O, 2.0% CaO, 1.3% K<sub>2</sub>O and 1.08% MgO.

Characteristic traits of cation exchangers depend on the type and number of exchangeable cations and on their structure. Cation-exchange capacities determined by consecutive saturation of the zeolite sample with high-concentration solutions of ammonium and potassium ions are presented in Table 2. Cation-exchange capacity  $Q_1^0$  is 1.46 mmol g<sup>-1</sup>, and  $Q_2^0$  is 1.45 mmol g<sup>-1</sup>. Agreement of the  $Q_1^0$  and  $Q_2^0$  values indicates that ammonium ions bind to the sample through ion exchange. The obtained results have shown that predominantly Na<sup>+</sup> ions are exchanged from zeolite, and to a smaller extent K<sup>+</sup> ions.

#### 3.2. Analysis of leakage water

The results of experimental testing of leakage water from collection reservoirs during 6 months point to varying concentrations of ammonium ions and other compounds that, according to the Croatian By-law on the marginal values of indicators of hazardous and other substances in wastewaters, surpass the maximal allowable concentrations in wastewaters. Concentrations of organic and inorganic pollutants in wastewater varied in dependence on water inflow and on meteorological conditions. Table 3 presents the results of some physical and chemical characteristics of wastewaters. pH values ranged from 7.0 to 7.85, which is within the allowable limits. The average chemical consumption of oxygen of 1500 mg L<sup>-1</sup> is higher than the margin value for wastewaters that may be let out into natural recipients (125 mg L<sup>-1</sup> O<sub>2</sub>). The average biochemical consumption of oxygen of 1050 mg L<sup>-1</sup> indicates water enrichment with biodegradable substances. The average content of dissolved solids was 5000 mg L<sup>-1</sup>. Average concentrations of ammonium ions

were  $400 \text{ mg L}^{-1}$ , and the typical concentration range was  $130\text{--}850 \text{ mg L}^{-1}$ . Pollution by phenol compounds was also observed. The average of total phenol concentrations in leakage water samples amounted to  $1.0 \text{ mg L}^{-1}$ .

Table 4 gives the analysis of the leakage water sample used in further investigations. Concentration of  $\text{NH}_4^+$  ions in the leakage water sample was  $820 \text{ mg L}^{-1}$ ,  $\text{K}^+$  ions  $801 \text{ mg L}^{-1}$ ,  $\text{Ca}^{2+}$  ions  $128 \text{ mg L}^{-1}$ , total organic carbon  $1033 \text{ mg L}^{-1}$  while the  $\text{BOD}_5$  value was  $200 \text{ mg L}^{-1}$ .

### 3.3. Exchange of $\text{NH}_4^+$ ions from leakage water on zeolite

Fig. 2 shows the exchange of  $\text{NH}_4^+$  ions from the studied sample of leakage water on zeolite after 15, 30, 60, 120, 240 and 360 min of equilibration. After 360 min of equilibration, only  $4.2 \text{ mg NH}_4^+/\text{g}$  zeolite was exchanged on zeolite, while  $17.70 \text{ mg NH}_4^+/\text{g}$  zeolite was exchanged from the model solution of ammonium ions of a concentration of  $800 \text{ mg L}^{-1}$  (Figs. 4 and 5). Thus, about 75% less ammonium ions was exchanged in the leakage water sample.

### 3.4. Exchange of $\text{NH}_4^+$ ions on zeolite from leakage water samples pretreated with activated carbon

Upon leakage water treatment with 0.04% (w/w) activated carbon,  $5.60 \text{ mg NH}_4^+/\text{g}$  zeolite was exchanged on zeolite after 360 min of equilibration (Fig. 2). Activated carbon enhanced the exchange of ammonium ions only by about  $1.5 \text{ mg/g}$  zeolite. Further addition of activated carbon had no effect on the mass of exchanged ammonium ions (Table 5).

### 3.5. Removal of organic carbon from leakage water samples using activated carbon and zeolite

It can be seen from Fig. 3 that the increase in the mass of activated carbon reduced the content of total organic carbon in leakage water up to about 2.50% (w/w) of activated carbon added. Further increase of the mass of activated carbon caused no considerable reduction of the water content of organic carbon. After wastewater treatment with 0.04% (w/w) activated carbon, total organic carbon in water dropped from  $1033$  to  $985 \text{ mg L}^{-1}$ , after treatment with 0.50% (w/w) activated carbon to  $723 \text{ mg L}^{-1}$ , after treatment with 2.50% (w/w) activated carbon to  $510 \text{ mg L}^{-1}$ , and after treatment with 5.00% (w/w) activated carbon to  $460 \text{ mg L}^{-1}$ .

After being treated with activated carbon, water samples were equilibrated with 2.00 and 5.00% (w/w) zeolite. Upon wastewater treatment with 0.04% (w/w) activated carbon and subsequent treatment with 2.00% (w/w) zeolite, total organic carbon in water dropped to  $769 \text{ mg L}^{-1}$ , upon treatment with 0.50% (w/w) activated carbon and subsequent treatment with 2.00% (w/w) zeolite to  $493 \text{ mg L}^{-1}$ , upon treatment with 2.50% (w/w) activated carbon and subsequent treatment with 2.00% (w/w) zeolite to  $297 \text{ mg L}^{-1}$  and upon treatment with 5.00% (w/w) activated carbon and subsequent treatment with 2.00% (w/w) zeolite to  $260 \text{ mg L}^{-1}$ .

Differences in the values of total organic carbon in water after treatment with activated carbon and subsequent treatment with 2.00% (w/w) zeolite were roughly constant from  $200$  to  $230 \text{ mg L}^{-1}$ . After wastewater treatment with 0.04% (w/w) activated carbon and subsequent treatment with 5.00% (w/w) zeolite, total organic carbon dropped to  $630 \text{ mg L}^{-1}$ , upon treatment with 0.50% (w/w) activated carbon and subsequent treatment with 5.00% (w/w) zeolite to  $370 \text{ mg L}^{-1}$ , upon treatment with 2.50% (w/w) activated carbon and subsequent treatment with 5.00% (w/w) zeolite to  $156 \text{ mg L}^{-1}$ , and upon treatment with 5.00% (w/w) activated carbon and subsequent treatment with 5.00% (w/w) zeolite to  $104 \text{ mg L}^{-1}$ . Differences in the values of total organic carbon in water after treatment with activated carbon and subsequent treatment with 5.00% (w/w) zeolite were also roughly constant—about  $350 \text{ mg L}^{-1}$ . The results indicate that some of the organic components that were not adsorbed onto activated carbon were adsorbed onto zeolite.

### 3.6. Influence of $\text{K}^+$ and $\text{Ca}^{2+}$ ions upon exchange of $\text{NH}_4^+$ ions

Wastewaters contain large amounts of  $\text{K}^+$  ions, which due to high clinoptilolite selectivity for  $\text{K}^+$  ions (clinoptilolite selectivity to alkaline and earth-alkaline cations decreases in the sequence:  $\text{K}^+ > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$ ) can reduce the efficiency of the exchange of ammonium ions on zeolite. Therefore, the influence of  $\text{K}^+$  ions on the exchange of ammonium ions was investigated as well. Besides  $\text{K}^+$  ions, the influence of  $\text{Ca}^{2+}$  ions on the exchange of ammonium ions was also investigated. Results on the exchange of ammonium ions in the presence of calcium and potassium ions from simulated solutions on natural zeolite are presented in Figs. 4 and 5. Due to zeolite selectivity, exchange of ammonium ions was more strongly affected by  $\text{K}^+$  ions than by  $\text{Ca}^{2+}$  ion. From the model solution (concentration  $800 \text{ mg L}^{-1} \text{ NH}_4^+$ ) containing  $250 \text{ mg L}^{-1} \text{ K}^+$  ions,  $15.62 \text{ mg NH}_4^+/\text{g}$  zeolite was exchanged, and from the solution containing  $800 \text{ mg L}^{-1} \text{ K}^+$  ions  $12.02 \text{ mg NH}_4^+/\text{g}$  zeolite. From the solution containing  $100 \text{ mg L}^{-1} \text{ Ca}^{2+}$  ions  $17.20 \text{ mg NH}_4^+/\text{g}$  zeolite was exchanged, and from the solution containing  $400 \text{ mg L}^{-1} \text{ Ca}^{2+}$  ions  $15.93 \text{ mg NH}_4^+/\text{g}$  zeolite. Thus, from the solution containing  $800 \text{ mg L}^{-1} \text{ NH}_4^+$ , potassium ions of a  $800 \text{ mg L}^{-1}$  concentration reduced the exchange of ammonium ions by ca. 32%, and calcium ions of a  $100 \text{ mg L}^{-1}$  concentration by ca. 2.8%.

### 3.7. Exchange of $\text{NH}_4^+$ ions from leakage water on zeolite using the column procedure

Passing wastewater through a column packed with zeolite resulted very soon in deposition of colloid particles and formation of sticky deposits on zeolite particles, which influenced a considerable reduction of water flow through the column. To avoid an adverse effect, a silica sand filter was used to remove suspended colloid substances. Schematic

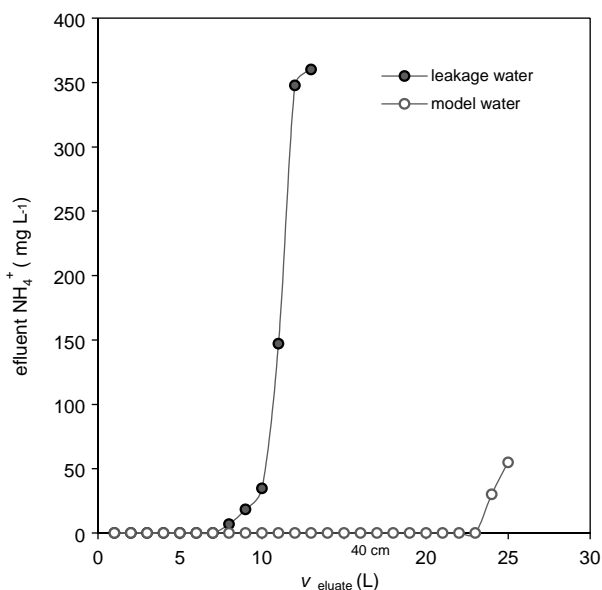


Fig. 7. Breakthrough curves of  $\text{NH}_4^+$  ions from leakage water and model water of ammonium ions:  $m(\text{zeolite}) = 1440 \text{ g}$ , flow =  $1.5 \text{ L h}^{-1}$ ,  $v(\text{fractions}) = 1 \text{ L}$ .

presentation of the columns is given in Fig. 6. Fig. 7 displays the curve of the breakthrough of  $\text{NH}_4^+$  ions from leakage water in passing through the pre-column and column. Breakthrough of ammonium ions occurred after 7 L of water were passed through the column. Total capacity of ammonium ions exchange for 10 L of wastewater passed amounted to  $6.90 \text{ mg NH}_4^+/\text{g zeolite}$ , and the breakthrough capacity was  $3.98 \text{ mg NH}_4^+/\text{g zeolite}$ . Fig. 6 also shows the curve of  $\text{NH}_4^+$  ions breakthrough from model water of ammonium ions. Breakthrough of ammonium ions occurred after 23 L of water had been passed. The total exchange capacity of ammonium ions for 24 L wastewater passed was  $13.65 \text{ mg NH}_4^+/\text{g zeolite}$ , while the breakthrough capacity was  $13.1 \text{ mg NH}_4^+/\text{g zeolite}$ . During the passage of leakage water through the columns, parameters such as water pH, conductivity,  $\text{BOD}_5$ , TOC, phenols, total hardness,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were monitored as well. Results of the analysis are given in Table 6. It can be seen from these results that the concentration of ammonium ions and phenols, considered to be very toxic substances, were appreciably reduced. Application of activated carbon and zeolite reduced the proportion of organic pollution. However, the level of organic pollution approached the starting pollution already upon passing 10 L of water, most probably because the quantity of activated carbon in the pre-column was too small.

#### 4. Conclusions

- The results indicate that the characteristics of wastewater have a strong influence on the efficiency of zeolite as a cation exchanger. Besides by inorganic cations, exchange

capacity is also influenced by organic molecules occupying adsorption sites.

- We assumed that organic substances of natural origin, due to their adsorption onto zeolite, greatly reduce the efficiency of the exchange of ammonium ions on zeolite. Macromolecular natural organic compounds may also exert an adverse effect on adsorption of synthetic organic micropollutants onto activated carbon through the mechanisms of site competition and pore blockage [19].
- Exchange of  $\text{NH}_4^+$  ions in the leakage water sample was lower by some 75% compared to the model solution of ammonium ions.  $\text{K}^+$  ions, due to the high selectivity of clinoptilolite, reduced the exchange of ammonium ions in model water by ca. 32%.
- As there are very few papers on the influence of organic compounds on the properties of zeolites as cation exchangers, further research is necessary in this area.

#### References

- [1] M.C.M. Van Loosdrecht, M.S.M. Jetten, Microbiological conversion in nitrogen removal, *Water Sci. Technol.* 38 (1998) 1–7.
- [2] C. Hellinga, A.A.J.C. Schellen, J.W. Mulder, M.C.M. Van Loosdrecht, J.J. Heijnen, The Sharon process: an innovative method for nitrogen removal from ammonium-rich waste water, *Water Sci. Technol.* 37 (1998) 135–142.
- [3] C. Fux, M. Boehler, P. Huber, I. Brunner, H. Siegrist, Biological treatment of ammonium-rich wastewater by partial nitrification and subsequent anaerobic ammonium oxidation (anammox) in a pilot plant, *J. Biotechnol.* 99 (2002) 295–306.
- [4] J. Carrera, J.A. Baeza, T. Vicent, J. Lafuente, Biological nitrogen removal of high-strength ammonium industrial wastewater with two-sludge system, *Water Res.* 37 (2003) 4211–4221.
- [5] B.W. Mercer, L.L. Ames, C.J. Touhill, W.J. Van Slike, R.B. Dean, Ammonia removal from secondary effluents by selective ion exchange, *J. WPCF* 42 (1970) R95.
- [6] J.H. Koon, W.J. Kaufman, Ammonia removal from municipal wastewaters by ion exchange, *J. WPCF* 47 (1975) 449–465.
- [7] E. Czarán, A. Meszaros-Kis, E. Domokos, J. Papp, Separation of ammonia from wastewater using clinoptilolite as ion exchanger, *Nucl. Chem. Waste Manage.* 8 (1988) 107–113.
- [8] H.T. Dryden, L.R. Weatherley, Aquaculture water treatment by ion exchange: continuous ammonium ion removal with clinoptilolite, *Aquacult. Eng.* 8 (1989) 109–126.
- [9] B. Beler-Baykal, M. Oldenburg, I. Sekoulov, The use of ion exchange in ammonia removal under constant and variable loads, *Environ. Technol.* 28 (1996) 717–726.
- [10] N.A. Booker, E.L. Priestley, A.J. Priestley, Ammonia removal from sewage using natural Australian zeolite, *Water Sci. Technol.* 34 (1996) 17–24.
- [11] M.L. Nguyen, C.C. Tanner, Ammonium removal from wastewaters using natural New Zealand zeolites, *N. Z. J. Agr. Res.* 41 (1998) 427–446.
- [12] M. Pansini, C. Colella, M. de’Gennaro, Chromium removal from water by ion exchange using zeolite, *Desalination* 83 (1991) 145–157.
- [13] E. Maliou, M. Loizidou, N. Spyrellis, Uptake of lead and cadmium by clinoptilolite, *Sci. Tot. Environ.* 149 (1994) 139–144.
- [14] M.V. Mier, R.L. Callejas, R. Gehr, B.E.J. Cisneros, P.J.J. Alvarez, Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange, *Water Res.* 35 (2001) 373–378.



- [15] L. Čurković, Š. Cerjan-Stefanović, T. Filipan, Metal ion exchange by natural and modified zeolites, *Water Res.* 31 (1997) 1379–1382.
- [16] C. Colella, Ion exchange equilibria in zeolite minerals, *Miner. Deposita* 31 (1996) 554–562.
- [17] APHA, Standard Methods for the Examination of Water and Wastewater, 16th ed., American Public Health Association, Washington, DC, 1985.
- [18] C. Brasquet, P. Le Cloirec, Adsorption onto activated carbon fibers: application to water and air treatments, *Carbon* 35 (1997) 1307–1313.
- [19] C. Pelekani, V.L. Snoeyink, Competitive adsorption in natural water: role of activated carbon pore size, *Water Res.* 33 (1999) 1209–1219.
- [20] R. Hopman, W.G. Siegers, J.C. Kruithof, Organic micropollutant removal by activated carbon fiber filtration, *Water Supply* 13 (1995) 257–261.
- [21] G. Newcombe, M. Drikas, R. Hayes, Influence of characterized natural organic material on activated carbon adsorption. II. Effect on pore volume distribution and adsorption of 2-methylisoborneol, *Water Res.* 31 (1997) 1065–1073.
- [22] P.H. Chen, Removing aquatic organic substances by anion-exchange resin and activated carbon, *Environ. Int.* 25 (1999) 655–662.
- [23] F. Li, A. Yuasa, K. Ebie, Y. Azuma, T. Hagishita, Y. Matsui, Factors affecting the adsorption capacity of dissolved organic matter onto activated carbon: modified isotherm analysis, *Water Res.* 36 (2002) 4592–4604.