

## Evaluation of Croatian Clinoptilolite- and Montmorillonite-rich Tuffs for Ammonium Removal

Mirela Rožić,<sup>a</sup> Štefica Cerjan-Stefanović,<sup>b,\*</sup> Lidija Ćurković<sup>c</sup>

<sup>a</sup>Faculty of Graphic Arts, Getaldićeva 2, 10000 Zagreb, Croatia

<sup>b</sup>Departement of Analytical Chemistry, Faculty of Chemical Engineering and Technology, Marulićev trg 20, 10000 Zagreb, Croatia

<sup>c</sup>Faculty of Mechanical Engineering and Naval Architecture, Ivana Lučića 1, 10000 Zagreb, Croatia

Received December 13, 2000; revised May 2, 2001; accepted July 26, 2001

In this study, the ability of a Croatian clinoptilolite- and montmorillonite-rich tuffs to take up ammonium from aqueous solutions was investigated. Montmorillonite tuff was converted into the Na<sup>+</sup> and H<sup>+</sup> form by treatment with Na<sub>2</sub>CO<sub>3</sub> (*w* = 3–5%) and the solution of H<sub>2</sub>SO<sub>4</sub> (*w* = 15%). The properties of clay modified in this way were investigated as well. The results show that the clinoptilolite tuff efficiency for ammonium removal is far superior (by 45–50%) to the removal efficiency of montmorillonite tuff. Treatment of montmorillonite tuff with Na<sub>2</sub>CO<sub>3</sub> resulted in a slight improvement of its ammonium exchange efficiency. Acid modification of montmorillonite tuff causes a considerable decrease of ammonium exchange. Maximum loadings in ammonium exchange in clinoptilolite tuff, montmorillonite tuff, alkaline modified montmorillonite tuff, and acid modified montmorillonite tuff, as calculated by the Langmuir equation, are 1.20, 0.54, 0.64, and 0.21 mmol g<sup>-1</sup> NH<sub>4</sub><sup>+</sup>, respectively.

*Key words:* clinoptilolite-rich tuff, montmorillonite-rich tuff, alkaline modification, acid modification, ammonium removal.

### INTRODUCTION

In various types of agricultural, domestic and industrial wastewaters, nitrogen generally appears in the form of organic nitrogen, free ammonia,

---

\* Author to whom correspondence should be addressed. (E-mail: stefica.cerjan@zg.hinet.hr)

ammonium nitrate or nitrite. The presence of large quantities of nitrogen in such wastewaters may lead to eutrophication of surface waters. In order to preserve an adequate water quality, it is necessary to remove nitrogen from waters.<sup>1</sup>

Various methods of ammonium removal from waters have been developed, but the worldwide aim has been to discover new possibilities for removing ammonium from wastewaters. Natural zeolite exchangers have attracted significant interest in the scientific community over the last two decades. Their low price, abundant deposits and the fact that exchangeable cations from zeolites (sodium, calcium, magnesium, potassium) are not toxic, make natural zeolites attractive alternative materials for water purification.<sup>2–28</sup>

Many laboratory and pilot industrial investigations have been initiated to determine the ion exchange characteristics of these natural materials as well as the optimal conditions for achieving their maximum exchange potential. The ammonium exchange capacity of zeolites varies in dependence on the experimental conditions, such as the presence of interfering organic and inorganic cations, suspended solids and unexchangeable inorganic anions. The exchange also depends on the size and distribution of zeolite tuff particles, tuff zeolite concentration, and the composition and exchangeability of cations in the zeolite structure.<sup>5,20,29</sup>

Deposits of clinoptilolite-rich tuff in Croatia occur in porous sedimentary rocks of Donje Jesenje, Krapina, while montmorillonite-rich tuff is found in the Kutina area. Since they occur in large quantities, there is a need to evaluate and compare their potentials for removing various pollutants from wastewaters. We are particularly interested in waters polluted with metals bound to organic or inorganic ligands (*e.g.* from the printing industry) and waters with ammonium levels ranging from 5 to 50 mmol dm<sup>-3</sup> NH<sub>4</sub><sup>+</sup> (*e.g.* from mineral fertilizer production).<sup>30</sup>

Clinoptilolite is known as a cation ion exchanger and adsorbent highly selective for ammonium. There are, however, very few results on the ammonium exchange in clay minerals. Since antiquity, clays have been used as adsorbents for toxic and harmful substances and montmorillonite is the king of clays in this respect.<sup>31</sup> Hence, the primary objective of this paper was to compare clinoptilolite and montmorillonite tuffs from Croatia in terms of their capacity of removing ammonium from water.

## EXPERIMENTAL

### *Samples*

Tests were performed on the following samples:

- Sample 1: untreated clinoptilolite-rich tuff,
- Sample 2: untreated montmorillonite-rich tuff,

- Sample 3: sample 2 pre-treated with  $\text{Na}_2\text{CO}_3$ ,
- Sample 4: sample 2 pre-treated with  $\text{H}_2\text{SO}_4$  solution.

Samples 1 and 2 were crushed in an agate mortar. Grain size fractions of 0.1–0.2 mm of sample 1 and 0.03–0.06 mm of sample 2 were chosen for the experiments.

Sample 3 was delivered to the laboratory in powdery form of grain size below 0.06 mm. Treatment with  $\text{Na}_2\text{CO}_3$  involved grinding and squashing a mixture of sample 2 (*ca.* 30% moisture) and  $\text{Na}_2\text{CO}_3$ . The mass fraction of added sodium carbonate was 3–5%.

Sample 4 was laboratory prepared by treating 20 g of sample 2 with 100 ml of 15% (*w*) solution of sulphuric acid for 30 minutes at 70 °C. After acid treatment, the clay was washed away with distilled water until the sample showed a negative reaction to sulphate. The sample was oven dried at 105 °C.

### *Sample Characterization*

Tuff samples used as filter materials did not contain pure mineral components but also a certain amount of mineral impurities. Mineral components were identified by X-ray diffraction analysis (XRD). Identification of mineral components was done by means of a Philips diffractometer PW 1065/40 equipped with a vertical goniometer and proportional counter, applying Cu-K $\alpha$  radiation, graphic monochromator, under the following recording conditions: X-ray tube voltage 40 kV, anode current 55 mA, recording region  $2\theta = 3\text{--}60^\circ$ , and counter rate  $0.5^\circ \text{ min}^{-1}$ .

Quantitative chemical composition of the tuff samples tested was determined by the standard analytical methods for silicate materials<sup>26</sup> (Table I).

### *Analytical Techniques*

Ammonium was determined colorimetrically using the Nessler reagent.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were quantitatively determined using atomic absorption spectrophotometry (atomic absorption spectrophotometer Perkin-Elmer model 3110).

TABLE I  
Chemical composition of tested samples (*w* × 100)

	Sample 1	Sample 2	Sample 3	Sample 4
SiO <sub>2</sub>	64.93	63.05	63.70	68.30
Al <sub>2</sub> O <sub>3</sub>	13.39	17.00	16.50	9.75
Fe <sub>2</sub> O <sub>3</sub>	2.07	5.76	5.97	2.36
Na <sub>2</sub> O	2.40	0.30	1.63	0.05
K <sub>2</sub> O	1.30	0.22	0.06	0.06
MgO	1.08	0.41	0.25	0.10
CaO	2.00	1.24	0.35	0.17
loss by glowing at 1000 °C	9.63	11.10	11.00	18.30

### Reagents

All chemicals used in these studies were analytical grade reagents. The ammonium stock solution of the concentration  $71.43 \text{ mmol dm}^{-3} \text{ NH}_4^+$ , was prepared by dissolving ammonium chloride salt in distilled water. Ammonium solutions of lower concentrations were prepared by diluting the stock solution with distilled water.

### Ammonium Removal Experiments

All experiments were carried out using the batch technique of its simplicity and reliability. The samples were equilibrated with 100 ml of ammonium chloride solutions of concentrations ranging from 1.43 to  $50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$ . Suspensions were shaken at  $23 (\pm 1) \text{ }^\circ\text{C}$  in an INNOVA 4080 shaker at a rotation speed of 200 rpm. Once equilibrium was established, the solid phase was separated by centrifugation, and ammonium concentration was determined in the liquid phase. The quantity of ammonium ions removal on the samples was calculated from the difference between the initial and the equilibrium ammonium concentration in the solution.

## RESULTS AND DISCUSSION

Mineralogical analysis revealed that zeolite tuff (sample 1) contained predominantly clinoptilolite, and feldspars, muscovite, illite and  $\alpha$ -quartz as mineral accompaniments (Figure 1). Clinoptilolite participated with 40–50% (*w*) in sample 1. Sample 2 contained 68–72% of montmorillonite, and  $\alpha$ -quartz, kaolinite and feldspars as mineral accompaniments (Figure 2). As seen from Figure 3, treatment of montmorillonite tuff with  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  caused no structure disruption.

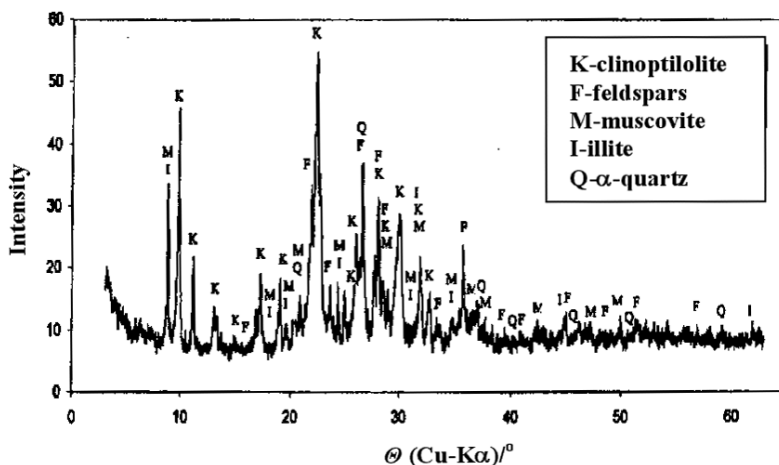


Figure 1. The XRD diffractogram of clinoptilolite-rich tuff (sample 1).

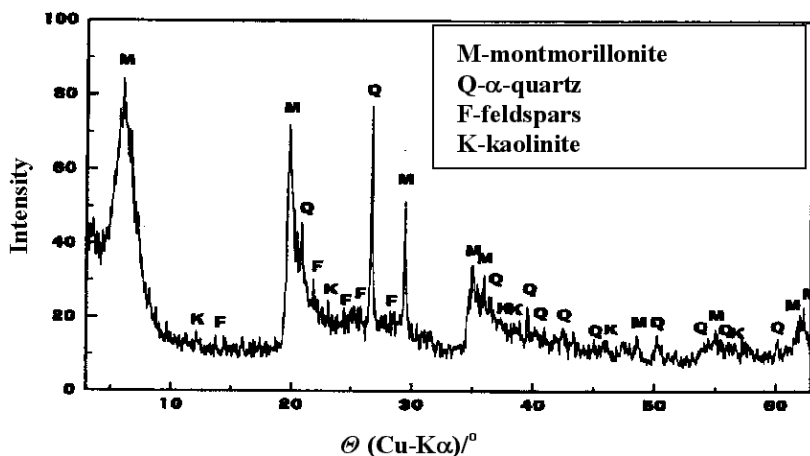


Figure 2. The XRD diffractogram of montmorillonite-rich tuff (sample 2).

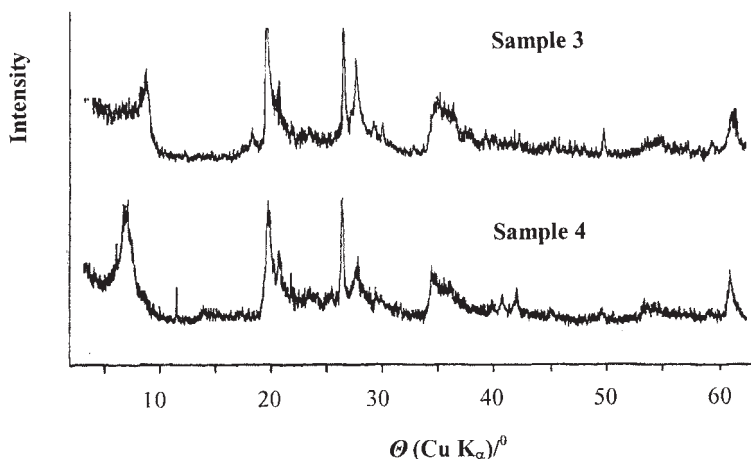


Figure 3. The XRD diffractogram of montmorillonite tuff pre-treated with  $\text{Na}_2\text{CO}_3$  (sample 3) and  $\text{H}_2\text{SO}_4$  solution (sample 4).

The results of chemical analyses are shown in Table I. Chemical analyses confirmed the assumption that sample 2 was converted to the sodium form by  $\text{Na}_2\text{CO}_3$  treatment. Acid treatment of sample 2 led to partial removal of the exchangeable cations, partial dealumination, and partial removal of iron oxides.

The cation content in the tested samples is given in Table II. The amount of cations exchanged with ammonium from a solution containing  $35.71 \text{ mmol dm}^{-3} \text{ NH}_4^+$  are given in Table III. Following cation amounts were ex-

TABLE II  
Total cation content ( $x/\text{mmol g}^{-1}$ ) of tested samples

Cations	$x / (\text{mmol g}^{-1})$			
	Sample 1	Sample 2	Sample 3	Sample 4
Na <sup>+</sup>	0.774	0.096	0.526	0.016
K <sup>+</sup>	0.276	0.047	0.013	0.013
Mg <sup>2+</sup>	0.268	0.103	0.062	0.050
Ca <sup>2+</sup>	0.357	0.221	0.062	0.030
$\Sigma$	1.675	0.467	0.663	0.109

TABLE III  
Cations of tested samples ( $x/\text{mmol g}^{-1}$ ) exchanged with NH<sub>4</sub>Cl solution containing 35.71 mmol dm<sup>-3</sup> NH<sub>4</sub><sup>+</sup>

Cations	$x / (\text{mmol g}^{-1})$			
	Sample 1	Sample 2	Sample 3	Sample 4
Na <sup>+</sup>	0.771	0.096	0.505	0.021
K <sup>+</sup>	0.099	0.024	0.008	0.017
Mg <sup>2+</sup>	0.012	0.020	0.003	0.000
Ca <sup>2+</sup>	0.082	0.180	0.020	0.010
$\Sigma$	0.964	0.320	0.536	0.048

changed from sample 1: Na, 99.6% ( $m_{\text{Na}}$ , the amount of Na in tuffs, calculated, 0.774 mmol g<sup>-1</sup>); K, 35.9% ( $m_{\text{K}}$ , 0.276 mmol g<sup>-1</sup>); Ca, 23.0% ( $m_{\text{Ca}}$ , 0.357 mmol g<sup>-1</sup>); Mg, 4.5% ( $m_{\text{Mg}}$ , 0.268 mmol g<sup>-1</sup>). The amounts of cations exchanged with ammonium from sample 2 were: Na 100%, K 51.1%, Ca 81.4%, Mg 19.4%, and from sample 3: Na 96%, K 6.1%, Ca 32.2%, Mg 5.6%. These results point to big differences in cation exchangeability. Clinoptilolite-rich tuff (sample 1) contains sodium as the major exchangeable cation. Potassium, calcium and magnesium are more strongly bound in clinoptilolite than sodium. The major exchangeable cation in montmorillonite-rich tuff (sample 2) is calcium, but it is more strongly bound in montmorillonite than sodium. It is apparent that Na<sup>+</sup> ions are the weakest bound ions in clinoptilolite and montmorillonite. For this reason, Na<sup>+</sup> can be most easily exchanged with cations from the solution. The results point to the conclusion that the ion exchange characteristics of the tested samples depend on the type of ex-

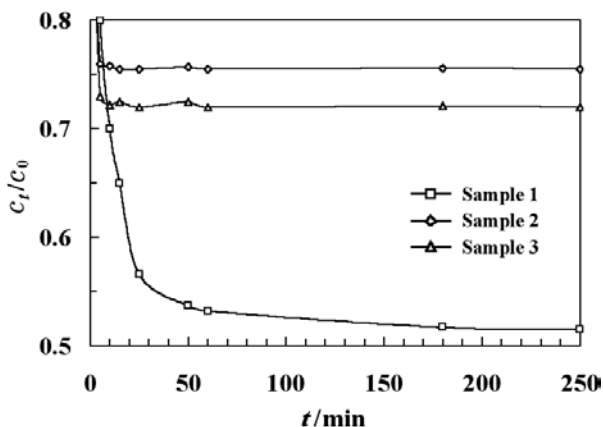


Figure 4. Rates of ammonium exchange by samples 1, 2, 3;  $c_0(\text{NH}_4^+) = 14.29 \text{ mmol dm}^{-3}$ ;  $m(\text{sample}) = 1.00 \text{ g}$ ;  $v(\text{solution}) = 100 \text{ ml}$ .

changeable cations in their structure, which is in agreement with the results obtained by other authors. Literature data indicate that an increase in the quantity of  $\text{Na}^+$  in zeolite and clay structure increases its affinity toward ions in solution.<sup>5,17,24</sup>

The rate of the ammonium removal process is a very important factor for exchanger application, since low exchange rates often pose serious limitations to the applicability of the process. The rate of reaching the ion exchange equilibrium depends on a number of process parameters such as the temperature, size and distribution of aluminosilicate particles, hydrodynamics of the reaction system, concentration and the hydrated radii of exchangeable ions. In our experiments, the rate of ammonium exchange was investigated from a solution containing  $14.29 \text{ mmol dm}^{-3} \text{ NH}_4^+$ . Results on the time change of the  $\text{NH}_4^+$  concentration in solution during the ion exchange are given in Figure 4. Ammonium removal by clinoptilolite tuff (sample 1) is a rapid process (1–2 hours). Ammonium removal by montmorillonite tuff (sample 2) and alkali treated montmorillonite tuff (sample 3) is considerably shorter, just 5 min.

To investigate the pH effect on ammonium removal, a number of equilibrium batch processes were conducted. Solutions of initial concentration of  $14.29 \text{ mmol dm}^{-3} \text{ NH}_4^+$  were used. Initial pH values of solutions were adjusted by addition of conc. HCl and 15% (*w*) NaOH solution. The results are shown in Figure 5. The obtained results indicate that ammonium exchange increases with increasing the pH up to pH = 8. At pH > 8, ammonium exchange shows a rapid decrease. It is assumed that in alkaline media ammonium is expelled from solution as  $\text{NH}_3$ . In very acid media (pH = 1–3), the

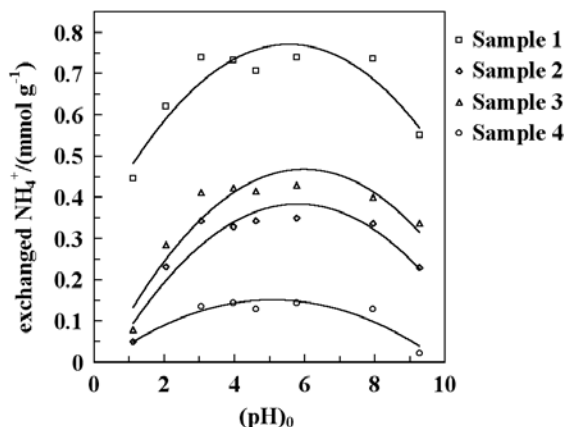
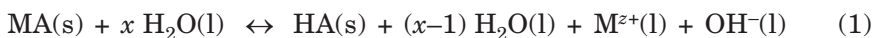


Figure 5. Effect of the initial pH of  $\text{NH}_4\text{Cl}$  solution on ammonium exchange;  $c_0(\text{NH}_4^+) = 14.29 \text{ mmol dm}^{-3}$ ;  $m(\text{sample}) = 1.00 \text{ g}$ ;  $v(\text{solution}) = 100 \text{ ml}$ .

exchange of ammonium ions is considerably reduced compared to their exchange in slightly acid, neutral and slightly alkaline media ( $\text{pH} = 3\text{--}8$ ). Ammonium exchange was not much influenced by the change of  $\text{H}^+$  concentration in the wide range of pH values ( $\text{pH} = 3\text{--}8$ ). According to reaction (1):



where  $\text{M}^{z+}$  is the exchangeable cation and  $z$  is the charge number of cations in the aluminosilicate structure A, with the decrease of the solution pH, the equilibrium is shifted to the right, *i.e.* the concentration of exchangeable ions in solution increases. Thus, the conditions of ion exchange are more favourable in a more acid medium, however a stronger attraction of  $\text{H}^+$  ions to exchangeable sites may occur. For this reason, the experiments were performed in a stable pH range, optimal to study the binding of ammonium ions.

Exchange isotherms are of the utmost importance for exchange capacity determinations. Values of ammonium exchanged after shaking 1.00 g of sample with 100 ml of solution containing  $1.43\text{--}50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$  were fitted into the Langmuir equation:

$$q = \frac{x}{m} = \frac{Q_0 b c_e}{1 + b c_e} \quad (2)$$

where  $x/m$  is the molal concentration of ammonium in zeolite/clay phase ( $\text{mmol g}^{-1}$ );  $Q_0$  is the maximum value for  $x/m$  or the maximum loadings in ammonium exchange;  $b$  is the Langmuir energy constant (affinity index) or binding strength ( $\text{cm}^3 \text{ g}^{-1}$ ); and  $c_e$  is the equilibrium molar concentration



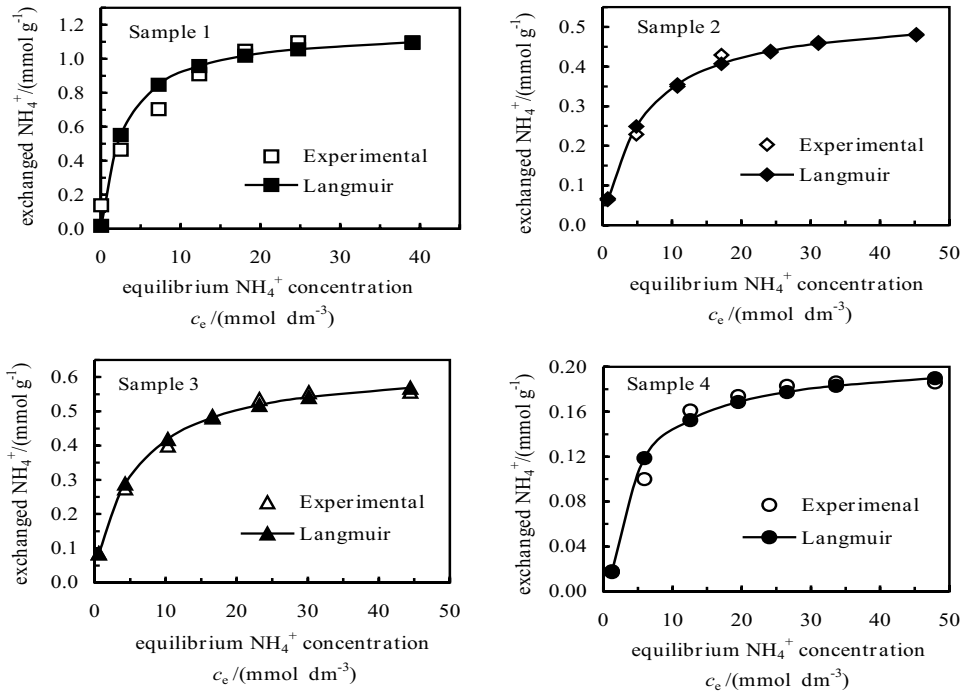


Figure 6. Langmuir exchange isotherms;  $m(\text{sample}) = 1.00 \text{ g}$ ;  $v(\text{solution}) = 100 \text{ ml}$ .

of ammonium in solution ( $\text{mmol dm}^{-3}$ ). A comparison of the experimental equilibrium data and the Langmuir isotherms is given in Figure 6. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient ( $R^2$ ). Langmuir model described the ammonium exchange processes adequately, with correlation coefficient values ranging from 0.9840 to 0.9982 (Table IV). Maximum loadings in am-

TABLE IV

Langmuir parameters for ammonium exchange from  $\text{NH}_4\text{Cl}$  solutions containing  $1.43\text{--}50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$

	$Q_0 / (\text{mmol g}^{-1})$	$b / (\text{cm}^3 \text{ g}^{-1})$	$R^2$
Sample 1	1.20	0.0228	0.9840
Sample 2	0.54	0.0125	0.9982
Sample 3	0.64	0.0133	0.9965
Sample 4	0.21	0.0154	0.9929

<sup>a</sup>  $m(\text{sample}) = 1.00 \text{ g}$ ;  $v(\text{solution}) = 100 \text{ ml}$ .

monium exchange in samples 1, 2, 3, and 4 calculated by the Langmuir equation were 1.20, 0.54, 0.64, and 0.21  $\text{mmol g}^{-1} \text{NH}_4^+$ , respectively. The  $Q_0$  of montmorillonite tuff (sample 2) was by 45% lower than the  $Q_0$  of clinoptilolite tuff (sample 1). The  $Q_0$  of the sample 3 was by 15.0% higher, and the  $Q_0$  of sample 4 was by 61.5% lower than that of sample 2. The higher  $b$  value estimated for clinoptilolite tuff (sample 1), as compared with the  $b$  values calculated for clay samples, indicates a higher affinity of clinoptilolite for ammonium.

To find out how much clinoptilolite or montmorillonite tuff was needed to reduce the ammonium concentration in 100 ml of solution below 0.0714  $\text{mmol NH}_4^+$  (1.3  $\text{mg NH}_4^+$ ), the effect of sample mass on the ammonium exchange was investigated. Clinoptilolite tuff masses were 1.00, 3.00, 5.00, 7.00, 10.00, 12.00, 14.00, 18.00, and 20.00 g. Solution volume was 100 ml. Dependence of ammonium concentration in 100 ml of solution on the mass of added clinoptilolite tuff is represented in Figure 7. After equilibrating 1.00 g clinoptilolite tuff with a solution containing 1.43  $\text{mmol dm}^{-3} \text{NH}_4^+$ , 0.00429  $\text{mmol NH}_4^+$  was determined in 100 ml solution. In solutions with 7.14 and 14.29  $\text{mmol dm}^{-3} \text{NH}_4^+$ , an increase in clinoptilolite tuff from 1.00 to 3.00 g led to an appreciable increase of ammonium removed. In solutions containing 21.43, 28.57 and 35.71  $\text{mmol dm}^{-3} \text{NH}_4^+$ , the rapidly obtained increase in ammonium removal ranged from 1.00 to 5.00 g. Ammonium removal was only very

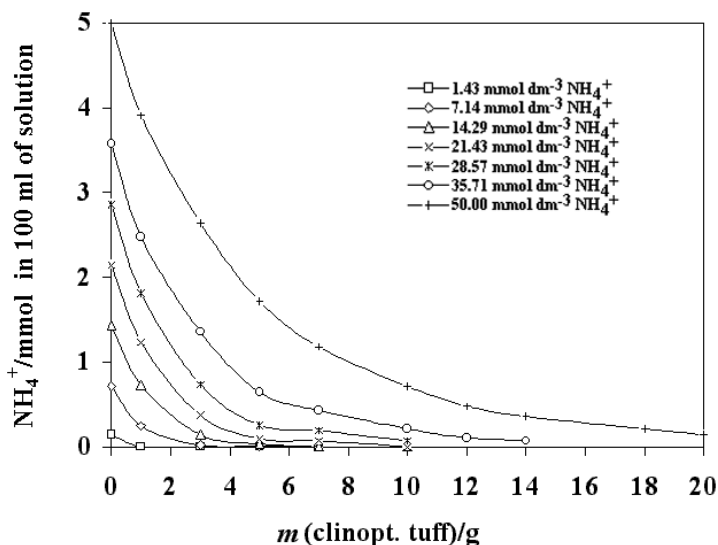


Figure 7. The amount of  $\text{NH}_4^+$  ( $n(\text{NH}_4^+) / \text{mmol}$ ) in 100 ml of solution after equilibration with different masses of clinoptilolite tuff (sample 1);  $m(\text{sample}) = 1.00\text{--}20.00$  g;  $v(\text{solution}) = 100$  ml.

slightly changed by further increase of the clinoptilolite tuff mass. 0.0214 and 0.143 mmol  $\text{NH}_4^+$  were determined after 3.00 g clinoptilolite tuff was equilibrated with solutions containing 7.14 and 14.29 mmol  $\text{dm}^{-3}$   $\text{NH}_4^+$ , respectively. 5.00 g clinoptilolite tuff was needed to reduce the ammonium content from 14.29 mmol  $\text{dm}^{-3}$  to 0.0357 mmol/100 ml. 0.0929 and 0.257 mmol  $\text{NH}_4^+$  were determined after 5.00 g clinoptilolite tuff was equilibrated with solutions containing 21.43 and 28.57 mmol  $\text{dm}^{-3}$   $\text{NH}_4^+$ , respectively. 7.00 and 10.00 g clinoptilolite tuff was needed to reduce the ammonium concentration from 21.43 and 28.57 mmol  $\text{dm}^{-3}$  to 0.0714 mmol/100 ml. After 10.00 g of sample 1 was equilibrated with a solution containing 35.71 mmol  $\text{dm}^{-3}$   $\text{NH}_4^+$ , 0.214 mmol  $\text{NH}_4^+$  was recorded in 100 ml solution. 14.00 g clinoptilolite tuff was needed to bring the ammonium content from 35.71 mmol  $\text{dm}^{-3}$  below 0.0714 mmol  $\text{NH}_4^+$ . 20.00 g clinoptilolite tuff failed to reduce the ammonium concentration to below 0.07 mmol in a solution with 50.0 mmol  $\text{dm}^{-3}$   $\text{NH}_4^+$ . In these conditions, 0.143 mmol  $\text{NH}_4^+$  was determined in solution after equilibration.

Data on montmorillonite-rich tuff (sample 2) are given in Figure 8. Sample masses amounted to 1.00, 3.00, 5.00, 7.00, 10.00, 20.00, and 40.00 g. Increase of montmorillonite tuff mass resulted in a much slower increase of the ammonium removed, as compared to sample 1. After 1.00, 3.00, and 7.00 g of montmorillonite tuff were equilibrated with 100 ml of solution con-

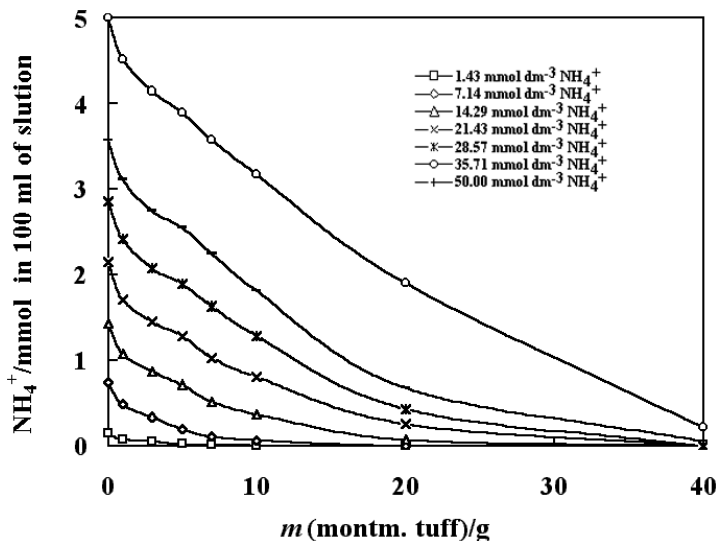


Figure 8. The amount of  $\text{NH}_4^+$  ( $n(\text{NH}_4^+) / \text{mmol}$ ) in 100 ml of solution after equilibration with different masses of montmorillonite tuff (sample 2);  $m(\text{sample}) = 1.00\text{--}40.00$  g;  $v(\text{solution}) = 100$  ml.

taining  $1.43 \text{ mmol dm}^{-3} \text{ NH}_4^+$ ,  $0.0757$ ,  $0.0521$ , and  $0.0150 \text{ mmol NH}_4^+$ , respectively, were found in solution.  $0.0664 \text{ mmol NH}_4^+$  was determined after  $10.00 \text{ g}$  of montmorillonite tuff was equilibrated with a solution containing  $7.14 \text{ mmol dm}^{-3} \text{ NH}_4^+$ . The mass of ammonium removed from solutions with  $14.29$ ,  $21.43$ ,  $28.57$ , and  $35.71 \text{ mmol dm}^{-3} \text{ NH}_4^+$  increased fairly rapidly with a rise in montmorillonite tuff mass from  $1.00$  to  $20.00 \text{ g}$ . Further increase of sample mass, however, led to a very slight increase in ammonium removal.  $0.0714$ ,  $0.257$ ,  $0.429$ , and  $0.679 \text{ mmol NH}_4^+$  were determined after these solutions were equilibrated with  $20.00 \text{ g}$  of montmorillonite tuff.  $0$ ,  $0$ ,  $0$ , and  $0.0571 \text{ mmol NH}_4^+$  were determined after these solutions were equilibrated with  $40.00 \text{ g}$  of montmorillonite tuff.  $40.00 \text{ g}$  of montmorillonite tuff failed to reduce the concentration from the initial  $50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$  to  $0.0714 \text{ mmol/100 ml}$ . From the solution of this concentration,  $4.79 \text{ mmol NH}_4^+ / 100 \text{ ml}$  was removed.

A comparison of Figures 7 and 8 clearly indicates that the amounts of ammonium removed by clinoptilolite tuff from solutions containing  $1.43$  to  $50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$  are substantially higher than those removed by montmorillonite tuff. The biggest differences were obtained with the use of  $1.00 \text{ g}$  of samples. Differences decreased with increasing sample masses, particularly in waters with low ammonium concentrations. From solutions containing  $1.43$ ,  $7.14$ ,  $14.29$ ,  $21.43$ , and  $50.0 \text{ mmol dm}^{-3} \text{ NH}_4^+$ ,  $1.00 \text{ g}$  of clinoptilolite tuff removed  $51.5$ ,  $50.3$ ,  $52.8$ , and  $56.2\%$  (*w*) more ammonium, respectively, than montmorillonite tuff. From the same solutions,  $3.00 \text{ g}$  of clinoptilolite tuff removed  $36.5$ ,  $45.4$ ,  $60.9$ , and  $63.6\%$  more ammonium respectively.  $7.00 \text{ g}$  of clinoptilolite tuff removed  $10.5$ ,  $15.1$ ,  $46.2$ , and  $62.6\%$  while  $10.00 \text{ g}$  removed  $4.0$ ,  $9.3$ ,  $37.7$ , and  $57.3\%$  more ammonium, respectively.

To achieve certain characteristics of clay suspension, the type of exchangeable clay cation has to be selected very carefully. Univalent cations ( $\text{Na}^+$ ) stabilize the suspension, whereas polyvalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) have the opposite effect because they coagulate clay particles. Since sample 3 has the property of swelling in water, the possibility of suspension filtration after equilibration with ammonium solutions is more complex with this clay sample. An increase in the electrolyte concentration in water reduces swelling and stability of clay suspension. If  $\geq 10 \text{ g}$  of sample 3 are added into the studied solutions, the clay suspension loses fluidity and turns into a gelatinous mass. For this reason, it is not recommended to add sample 3 into  $100 \text{ ml}$  of solution with a mass surpassing  $10 \text{ g}$ .

As seen from the results, batch experiments can be used to compare the performance of zeolite and clay materials in removing ammonium from wastewaters. Both clinoptilolite and montmorillonite tuffs are minerals important for environmental protection. Montmorillonite tuff, however, is not as effec-

tive as clinoptilolite tuff. In all experiments, clinoptilolite tuff removed more ammonium than montmorillonite tuff. By pre-treating montmorillonite tuff with  $\text{Na}_2\text{CO}_3$ , ammonium exchange improved a little. Acid modification of montmorillonite tuff caused a considerable decrease in ammonium exchange.

The studied exchangers are natural materials, which also contain mineral impurities, characteristic of the Croatian deposits. They can serve as filtration materials for treatment of polluted waters from fertilizer production, which are saturated with ammonium salts. When a natural exchanger is ammonium saturated, it can be used as a fertilizer, which will release ammonium into soil. This ammonium is strongly bound in the aluminosilicate structure, which considerably reduces its loss by leaching.<sup>33</sup>

Wastewaters from chemical processes have a strong impact on the environment since they contaminate ground and surface waters, as well as plants and animals. In some segments of the chemical industry, application of selective ion exchangers can definitely solve the problem of ammonium in water, which has been the aim of this paper.

## REFERENCES

1. S. E. Jorgensen, O. Libor, K. L. Graber, and K. Barkacs, *Water Res.* **10** (1976) 213–224.
2. C. Colella, *Mineral. Deposita* **31** (1996) 554–562.
3. M. Pansini, *Mineral. Deposita* **31** (1996) 563–575.
4. S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, *Water Res.* **33** (1999) 2469–2479.
5. Š. Cerjan-Stefanović, L. Čurković, and T. Filipan, *Croat. Chem. Acta* **69** (1996) 281–290.
6. L. Čurković, Š. Cerjan-Stefanović, and T. Filipan, *Water Res.* **31** (1997) 1379–1382.
7. Š. Cerjan-Stefanović and L. Čurković, *Selectivity of natural zeolites for toxic ions*, in: G. Kirov, L. Filizova, and O. Petrov (Eds.), *Natural Zeolites-Sofia '95*, Pensoft, 1997, pp. 121–126.
8. S. H. Gharaibeh and I. M. Dwairi, *Chem. Tech.* **48** (1996) 215–218.
9. M. P. Elizalde-Gonzalez, J. Mattusch, W. D. Einicke, and R. Wennrich, *Chem. Eng. J.* **81** (2001) 187–195.
10. I. R. Phillips, *J. Soil Contam.* **7** (1998) 191–212.
11. M. Rivera-Garza, M. T. Olguin, J. Garcia-Sosa, D. Alcantara, and G. Rodriguez-Fuentes, *Microporous and Mesoporous Materials* **39** (2000) 431–444.
12. S. A. Adeleye, R. Rautiu, D. A. White, and P. G. Clay, *J. Mat. Sci.* **30** (1995) 583–586.
13. R. Hernandez-Huesca, L. Diaz, and G. Aguilar-Armenta, *Sep. Purif. Technol.* **15** (1999) 163–173.
14. T. Filipan, N. Ružinski, Štefica-Cerjan-Stefanović, and A. Farkaš, *Sigurnost* **42** (2000) 1–11.
15. C. Galindo, D. W. Ming, M. J. Carr, A. Morgan, and K. D. Pickering, *Use of Ca-exchanged clinoptilolite for ammonium removal from Nasa's advanced life-support*

- wastewater system, in: C. Colella and F. A. Mumpton (Eds.), *Natural zeolites for the third millennium*, De Frede Editore, Napoli, 2000, pp. 363–371.
16. R. M. Carland, and F. F. Aplan, *Miner. Metall. Process.* **12** (1995) 210–218.
  17. G. Blanchard, M. Maunaye, and G. Martin, *Water Res.* **18** (1984) 1501–1507.
  18. H. T. Dryden, and L. R. Weatherley, *Aquacult. Eng.* **8** (1989) 109–126.
  19. M. Pansini, C. Colella, and M. de' Gennaro, *Desalination* **83** (1991) 145–157.
  20. B. J. Watten and M. J. English, *Aquaculture* **46** (1985) 221–235.
  21. E. Czaran, J. Papp, A. Meszaros-Kis, and E. Domokos, *Acta Chim. Hung.* **126** (5) (1989) 673–683.
  22. P. Ciambelli, P. Corbo, L. Liberti, and A. Lopez, *Ammonium recovery from urban sewage by natural zeolites*, in: D. Kallo and H. S. Sherry (Eds.), *Occurrence, properties and utilization of natural zeolites*, Akademiai Kiado, Budapest, 1988, pp. 501–509.
  23. M. J. Semmens and W. P. Martin, *Water Res.* **22** (1988) 537–542.
  24. S. Kesraoui-Ouki, C. R. Cheeseman, and R. Perry, *J. Chem. Tech. Biotechnol.* **59** (1994) 121–126.
  25. A. Langella, M. Pansini, P. Cappelletti, B. de' Gennaro, M. de' Gennaro, and C. Colella, *Microporous and Mesoporous Materials* **37** (2000) 337–343.
  26. D. W. Breck, *Zeolite Molecular Sieves*, Krieger Publ. Comp., Malabar, Florida, 1984, pp. 588–590.
  27. N. A. Booker, E. L. Cooney, and A. J. Priestley, *Water Sci. Technol.* **34** (1996) 17–24.
  28. C. Colella, *Natural zeolites in environmentally friendly processes and applications*, in: I. Kiricsi, G. Pal-Borbely, J. B. Nagy and H. G. Karge (Eds.), *Porous Materials in Environmentally Friendly Processes*, Studies in Surface Science and Catalysis, Vol. 125, Elsevier Science B.V., 1999, pp. 641–653.
  29. M. L. Nguyen and C. C. Tanner, *New Zealand J. Agricult. Res.* **41** (1998) 427–446.
  30. G. V. Tsitsishvili, N. S. Skhirtladze, T. G. Andronikashvili, V. G. Tsitsishvili, and A. V. Dolidze, *Natural zeolites of Georgia: occurrences, properties, and application*, in: I. Kiricsi, G. Pal-Borbely, J. B. Nagy, and H. G. Karge (Eds.), *Porous Materials in Environmentally Friendly Processes*, Studies in Surface Science and Catalysis, Vol. 125, Elsevier Science B.V., 1999, pp. 715–722.
  31. *Encyclopedia of glass, ceramics, clay and cement*, John Wiley and Sons Inc., New York, 1985, p. 320.
  32. R. Harjula and J. Lehto, *Harmonisation of ion exchange formulations and nomenclature: what can be done?*, in: A. Dyer, M. J. Hudson, and P. A. Williams (Eds.), *Progress in Ion Exchange, Advances and Applications*, Hartnolls Ltd., 1995, pp. 439–447.
  33. D. W. Ming and E. R. Allen, *Recent advances in the United States in the use of natural zeolites in plant growth*, in: C. Colella and F. A. Mumpton (Eds.), *Natural zeolites for the third millennium*, De Frede Editore, Napoli, 2000, pp. 417–426.

**SAŽETAK****Primjenljivost hrvatskih klinoptilolitom i montmorillonitom obogaćenih tufova za uklanjanje amonijevih iona***Mirela Rožić, Štefica Cerjan-Stefanović i Lidija Ćurković*

Istražena je mogućnost uklanjanja amonijevih iona klinoptilolitnim i montmorillonitnim tufovima karakterističnim za hrvatska tla. Montmorillonitni tuf je obradom sa  $\text{Na}_2\text{CO}_3$  ( $w = 3-5\%$ ) te otopinom  $\text{H}_2\text{SO}_4$  ( $w = 15\%$ ) preveden u  $\text{Na}^+$  i  $\text{H}^+$  oblike, pa su ispitana i svojstva tako modificirane gline. Rezultati pokazuju da je djelotvornost uklanjanja amonijevih iona klinoptilolitnim tufovima znatno bolja (45–50%) od djelotvornosti montmorillonitnog tufa. Obradom montmorillonitnog tufa sa  $\text{Na}_2\text{CO}_3$  neznatno se poboljšala njegova djelotvornost. Kisela modifikacija montmorillonitnog tufa znatno smanjuje zamjenu amonijevih iona. Maksimalna zamjena amonijevih iona na klinoptilolitnom tufu, montmorillonitnom tufu, alkalijama obrađenom montmorillonitnom tufu te kiselinom obrađenom montmorillonitnom tufu, izračunana prema Langmuirovu modelu bila je 1,20; 0,54; 0,64 i 0,21  $\text{mmol g}^{-1} \text{NH}_4^+$ .