Clinoptilolite in Drinking Water Treatment for Ammonia Removal

H. M. Abd El-Hady, A. Grünwald, K. Vlčková, J. Zeithammerová

In most countries today the removal of ammonium ions from drinking water has become almost a necessity. The natural zeolite clinoptilolite is mined commercially in many parts of the world. It is a selective exchanger for the ammonium cation, and this has prompted its use in water treatment, wastewater treatment, swimming pools and fish farming. The work described in this paper provides dynamic data on cation exchange processes in clinoptilolite involving the NH_4^+, Ca^{+2} and Mg^{+2} cations. We used material of natural origin – clinoptilolite from Nižný Hrabovec in Slovakia (particle-size 3–5 mm). The breakthrough capacity was determined by dynamic laboratory investigations, and we investigated the influence of thermal pretreatment of clinoptilolite and the concentration of regenerant solution (2, 5, and 10% NaCl). The concentrations of ammonium ion inputs in the tap water that we used were 10, 5, and 2 mg NH_4^+ l^{-1} and down to levels below 0.5 mg NH_4^+ l^{-1}. The experimental results show that repeated pretreatment sufficiently improves the zeolite's properties, and the structure of clinoptilolite remains unchanged during the loading and regeneration cycles. Ammonium removal capacities were increased by approximately 40 % and 20 % for heat-treated zeolite samples. There was no difference between the regenerates for 10% and 5% NaCl. We conclude that the use of zeolite is an attractive and promising method for ammonium removal.

Keywords: clinoptilolite, zeolite, ion exchange, ammonia removal, drinking water.

1 Introduction

Nitrogen is a nutrient essential to all forms of life as a basic building block of plant and animal protein. Nevertheless, too much of it can be toxic. The presence of nitrogen excess in the environment has caused serious distortions of the natural nutrient cycle between the living world and the soil, water, and atmosphere. Nitrogen in the form of nitrous oxide, nitric oxide, nitrate, nitrite or ammonia/ammonium is soluble in water and can end up in ground water and drinking water. One of the best-documented and best-understood consequences of human alterations of the nitrogen cycles is the eutrophication of estuaries and coastal seas (Oenema and Roest, 1998). According to the instruction of the European Community Council (CCE) of 15 July 1980, the maximum permissible level of ammonium in drinking water is 0.5 mg l^{-1}. The processes used for the removal of ammonium ions from drinking waters include air stripping, nitrification, breakpoint chlorination, and ion exchange. The properties of synthetic and natural zeolites as ion exchangers for removal of ammonium ions have been discussed in great detail (Jörgensen, 1976; Gaspard and Martin, 1983; Hlavay et al., 1983; Vokáčová, et al., 1986; Hódi et al., 1995; Booker et al., 1996; Beler Baykal and Akca Guven, 1997; Cooney et al., 1999). The behavior of the exchange and the quantities of ammonium removed are very much dependent on the origin of the material, the impurities contained, the counter ions, as well as the pretreatment performed on the zeolite.

The objective of our work is to treat drinking water spiked with NH_4^+ (10±0.5, 5±0.5, and 2±0.5) mg l^{-1} with the use of clinoptilolite and under pretreatments of the mineral.

2 Zeolites in drinking water treatment

Zeolites are natural minerals, which can be described chemically as aluminum silicates. They are used for various applications, e.g., ion exchange, molecular sieves, and air-drying. The simplified chemical composition and structure of zeolites can be seen in Fig. 1.

$$Me^{n+} {}_x Al_{nx} Si_y O_{2(nx+y)}$$
$$Y/X > 1$$

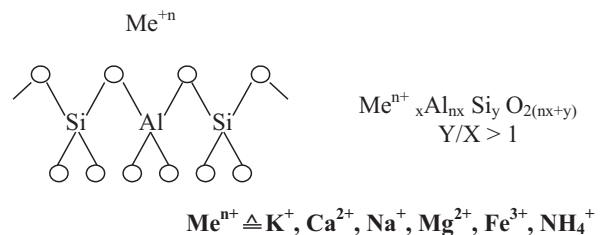$$Me^{n+} \triangleq K^+, Ca^{2+}, Na^+, Mg^{2+}, Fe^{3+}, NH_4^+$$

Fig. 1: Simplified chemical composition and structure of zeolites

In the regular structure of silicates a few places are occupied by aluminum ions, and so an additional charge is caused. This charge is compensated by other ions like sodium, potassium or ammonia, which are reversibly fixed by interactions and can easily be exchanged by other ions. The composition of this structure leads to various forms of zeolites. Of all these zeolite types, clinoptilolite has the best selectivity for ammonia. Preparing clinoptilolite so that all exchange places are filled with sodium ions results in a form with the best selectivity for ammonia (Jörgensen et al. 1979; Oldenburg M. and Sekoulov I., 1995).

3 Materials and methods

Physical description of the system

Fig. 2 consists of a column set with the following characteristics:

Internal diameter = 20 mm, total height of column = 60 cm, height of the bed of zeolite = 33 cm, 100 ml of material at a volumetric flow rate of 8.7 ml min^{-1}, which is equivalent to 5.25 bed volumes (BV) per hour, particle-size of material = 3–5 mm, mass of zeolite in column = 100 g. A nylon screen supported the zeolite in the column.
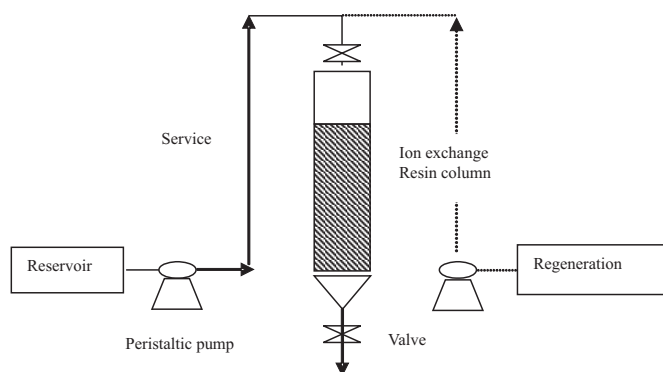
Fig. 2: Laboratory column

Analysis

All analyses were made according to standard methods (APHA, see Greenberg et al., 1992). Ammonia was determined by Nessler methods using a spectrophotometer (Model Hach DR/2000). Calcium and magnesium were determined by the EDTA titrimetric method.

Specification of the material

Two materials were used for the investigation:

a) Natural clinoptilolite (clino. 1). Origin: Nižný Hrabovec, Slovakia. The chemical composition is given as:

SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO
69.77 %	12.24 %	2.2 %	0.14 %	0.45 %	1.68 %	1 %
Na_2O	K_2O	MnO	P_2O_5	H_2O	Total	
2.7 %	2.11 %	0.034 %	0.08 %	7.3 %	99.704 %	

b) Activated clinoptilolite. The activation process was performed by heating for two samples: the samples were exposed to an elevated temperature of 400 °C for 6 h. Before being heated, the first sample (clino. 2) (previously used as natural clinoptilolite) was washed with distilled water, while the second sample (clino. 3) was heated in its natural form.

System operation parameters

The first experiment was carried out to see the exhaustion performance of (clino. 1) using distilled water spiked at 10 mg $NH_4^+ l^{-1}$ concentration. Then we applied tap water containing $Ca^{+2} = 60$ mg l^{-1} and $Mg^{+2} = 12$ mg l^{-1}. The concentrations of ammonium input were 10, 5 and 2 mg $NH_4^+ l^{-1}$ as (NH_4Cl) and down to levels below 0.5 mg l^{-1}. Clino. 2 and clino. 3 were applied only with tap water containing Ca^{+2}, Mg^{+2} and NH_4^+.

In the regeneration phase, 2.0% NaCl at pH range (11.5–12.5), at a volumetric flow rate of 8.7 ml min^{-1}, which is equivalent to 5.25 bed volumes (BV) per hour was investigated for clino. 1 in the first experiment and then at 5%, 10% NaCl for clino. 1. For clino. 2 and clino. 3, NaCl only was spiked at 5 %. After regeneration, the excess Cl^- was removed from the clinoptilolite, with the use of distilled water. This washing was repeated until visual tests with $AgNO_3$ revealed zero chloride.

4 Results and discussion

Breakthrough capacity and effects of activated clinoptilolite

Within the scope of this work, the results from the first experiment using distilled water for clino. 1 indicated that the breakthrough capacity defined as 0.5 mg l^{-1} in NH_4^+ was 0.47 mol l^{-1} for $NH_4^+ = 10$ mg l^{-1} as shown in Table 1. Figs. 3, 4 and 5 and Table 2 show that, for tap water containing calcium and magnesium ions, the breakthrough capacity were 0.038, 0.052, 0.058 mol l^{-1} for $NH_4^+ = 10$, 5, and 2 mg l^{-1}. For clino. 2 the values were 0.048, 0.063, 0.068 mol l^{-1} for
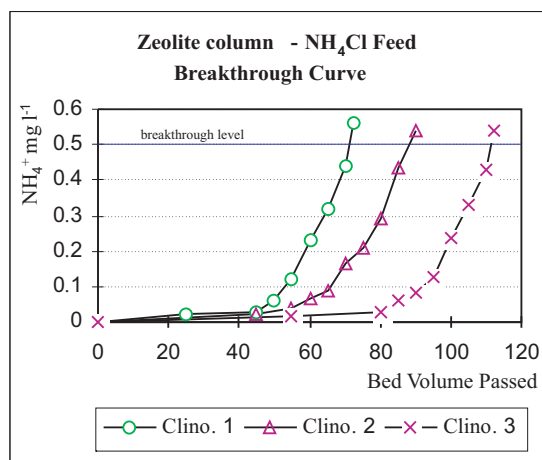
Fig. 3: Breakthrough curves of ion exchange resin for a tap water containing ($NH_4^+ = 10$ mg/l, $Ca^{2+} = 60$ mg/l, $Mg^{2+} = 12$ mg/l)
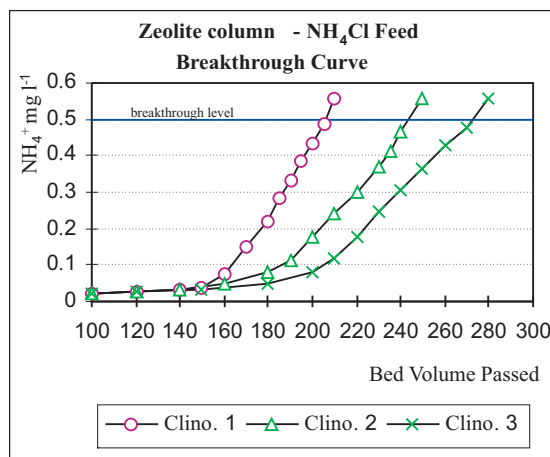
Fig. 4: Breakthrough curves of ion exchange resin for a tap water containing ($NH_4^+ = 5$ mg/l, $Ca^{2+} = 60$ mg/l, $Mg^{2+} = 12$ mg/l)

$NH_4^+ = 10$, 5, and 2 mg l^{-1}, and for clino. 3 the values were 0.06, 0.063, 0.076 mol l^{-1}, respectively. These values indicate that tap water provides a lower breakthrough capacity than distilled water, due to the presence of other ions, especially ions with a polyvalent charge in water, such as Ca^{+2} and Mg^{+2}.

http://ctn.cvut.cz/ap/

These results reveal that thermal activation increases clinoptilolite selectivity for ammonium ions. The results shown in Fig. 6 indicate that the breakthrough capacities of a thermally activated sample are on average roughly 20 %, 40 % for clino. 2 and clino. 3, respectively, higher than the value for untreated clinoptilolite. In addition, these results indicate that ammonium ions can be removed efficiency by the zeolite, and the exchange capacity of zeolites depends on the initial ammonia concentration at the column inlet.

Table 1: Important parameters measured during the experiment using distilled water spiked with NH_4^+ inf. = 10 mg l^{-1} for clino. 1

Solution volume – L	50	61	72	82	88.5
NH_4^+ eff. – mg l^{-1}	0.06	0.088	0.094	0.29	0.503
BV	500	610	720	820	885

Table 2: Important parameters measured during the experiment using tap water spiked with ammonia

Materials	Clino. 1			Clino. 2			Clino. 3		
NH_4^+ inf [mg l^{-1}]	10	5	2	10	5	2	10	5	2
Volume L	7.25	21	70	9	25	81	11.25	28	91
BV	72.5	210	700	90	250	810	112.5	280	910
Capacity [mol l^{-1}]	0.038	0.052	0.058	0.048	0.063	0.068	0.06	0.063	0.076

Fig. 6: Exchange capacity

Fig. 7: Comparison of calcium breakthrough of ion exchange resin for a tap water containing (NH_4^+, Ca^{2+} = 60 mg/l, Mg^{2+} = 12 mg/l)
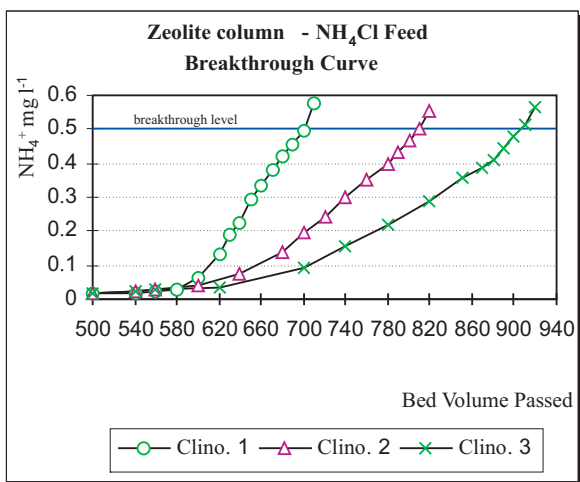

Fig. 5: Breakthrough curves of ion exchange resin for a tap water containing (NH_4^+ = 2 mg/l, Ca^{2+} = 60 mg/l, Mg^{2+} = 12 mg/l)

Fig. 8: Comparison of magnesium breakthrough of ion exchange resin for a tap water containing (NH_4^+, Ca^{2+} = 60 mg/l, Mg^{2+} = 12 mg/l)

Comparing the results summarized in Figs. 7, 8, it can be seen that the removal of calcium and magnesium at breakthrough level of ammonia for clino. 2 and clino. 3 was lower than for clino. 1 at all concentrations of ammonia, which agrees with the selectivity rules for ionic exchange in untreated clinoptilolite zeolite. These results reveal that the removal efficiency of calcium and magnesium for clino. 1 was higher than for clino. 2 and clino. 3.
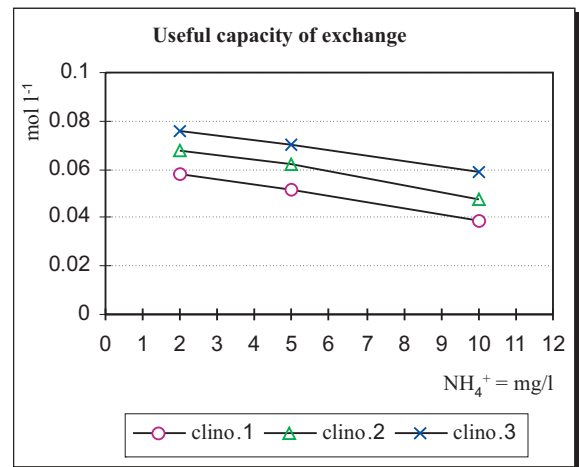
Regeneration effects

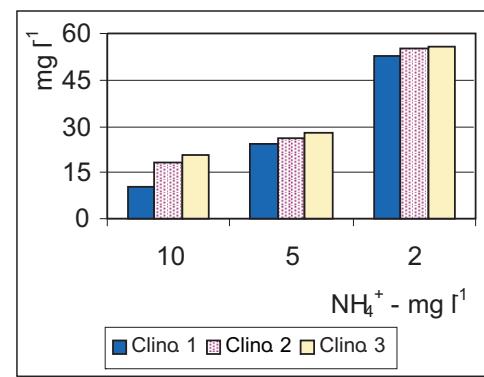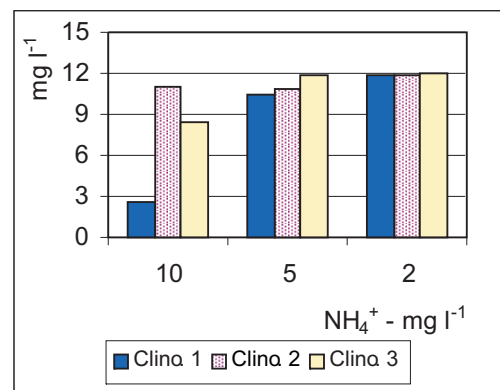The result from the first regeneration using 2% NaCl indicate that 140 BV of a NaCl solution is sufficient for ammonium elution from clino. 1. The elution curves (Figs. 9, 10 and Table 3) indicate that no difference between regeneration by 10% and 5% NaCl solution for clino. 1. 65 BV of a NaCl solution is sufficient for ammonium elution. On the other hand, complete elution of ammonia from clino. 2 and clino. 3

Table 3: Elution of ammonia from the resins using NaCl

Clino. 1								
NaCl 2%			NaCl 5%			NaCl 10%		
Volume (ml)	NH_4^+ (mg l^{-1})	BV	Volume (ml)	NH_4^+ (mg l^{-1})	BV	Volume (ml)	NH_4^+ (mg l^{-1})	BV
1000	24.1	10	1000	27.6	10	1000	659	10
5000	2.65	50	5000	1.08	50	6000	25	60
6000	0.098	60	6000	0.098	60	1000	0.98	100
6500	0.036	65	6500	0.04	65	14000	0.028	140

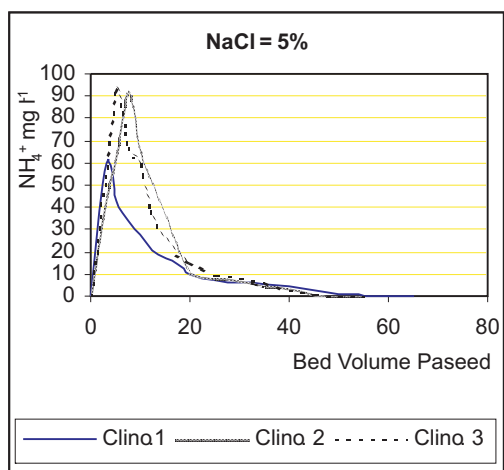| NaCl 5%					
Clino. 2			Clino. 3		
Volume (ml)	NH_4^+ (mg l^{-1})	BV	Volume (ml)	NH_4^+ (mg l^{-1})	BV
1000	40.39	10	1000	23.77	10
6000	3.01	60	6000	2.66	60
10000	0.255	100	10000	0.266	100
11000	0.05	110	11000	0.04	110

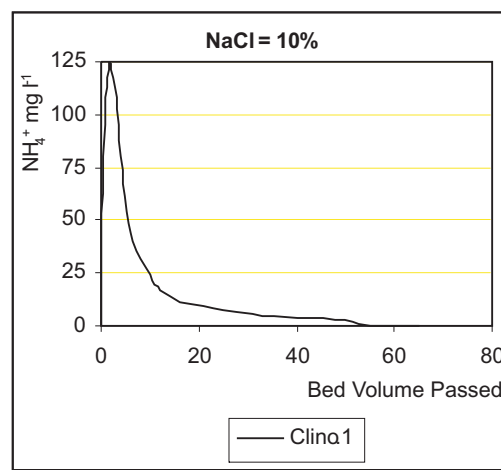Fig. 9: Typical regeneration curves for elution of ammonia from reins using NaCl = 5%

Fig. 10: Typical regeneration curves for elution of ammonia from reins using NaCl = 10%

require 110 BV of using 5% NaCl solution. These results reveal that clino. 1 is slightly more economical than clino. 2, and clino. 3 and 5% NaCl should be used.

5 Conclusions

The experimental results indicate that ammonium ions can be removed efficiency by zeolites. Pretreatment of the zeolite considerably improves its ion exchange capacity, and clino. 3 can be used for ammonia removal as a more economical exchanger than clino. 1 and clino. 2. Ammonium removal capacities were increased by approximately 40 % and 20 % for heat-treated zeolite samples. There was no difference between the regenerates for 10% and 5% NaCl. The removal efficiency of calcium and magnesium for clino. 1 was higher than for clino. 2 and clino. 3. We conclude that the use of zeolite is an attractive and promising method for ammonium removal.

References

[1] APHA: *Standard methods for examination of water and waste water*. 18th Edition, 1992, Published by American Public Health Association, Washington, USA

[2] Beler Baykal, B. and Akca Guven, D.: *Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater*. Wat. Sci. Technol., 1997, Vol. 35, No. 7, pp. 47–54

[3] Booker, N., Cooney, E. and Priestly, A.: *Ammonia Removal from Sewage Using Natural Australian Zeolite*. Wat. Sci. Technol., 1996, Vol. 34, No. 9, pp. 17–24

[4] Cooney, E., Booker, N., Shallcross, D. and Stevens, G.: *Ammonia Removal from Wastewater Using Natural Australian Zeolite. I. Characterization of the Zeolite*. Sep. Sci. Technol., 1999, Vol. 34, No. 12, pp. 2307–2327

[5] Gaspard, M. and Martin, A.: *Clinoptilolite in Drinking Water treatment for NH_4^+ Removal*. Wat. Res., 1983, Vol. 17, No. 3, pp. 279–288

[6] Hlavay, J., Vigh, Gy., Olaszi, V. and Inczédy, J.: *Ammonia and iron removal from drinking water with clinoptilolite tuff*. Zeolite 3, 1983, pp. 188–190

[7] Hódi, M., Polyák, K. and Hlavay, J.: *Removal of pollutants from drinking water by combined ion exchange and adsorption methods*. Envir. International, 1995, Vol. 21, No. 3, pp. 325–331

[8] Jörgensen, S. E., Libor, O., Barkacs, K. and Kuna, L.: *Equilibrium and capacity data of clinoptilolite*. Wat. Res., 1979, Vol. 13, pp. 159–165

[9] Jörgensen, S. E.: *Ammonia removal by use of clinoptilolite*. Wat. Res., 1976, Vol. 10, pp. 213–224

[10] Oenema, O. and Roest, C. W. J.: *Nitrogen and phosphorus losses from agriculture into surface waters: the effects of policies and measures in the Netherlands*. Wat. Sci. Technol., 1998, Vol. 37, No. 2, pp. 19–26

[11] Vokáčová, M., Matejka, Z. and Ellášek, J.: *Sorption of Ammonium-Ion by Clinoptilolite and by Strongly Acidic Cation Exchangers*. Acta Hydrochim, 1986, Vol. 14, No. 6, pp. 605–611

Hossam Monier Abd El-Hady
phone: +420 2 2435 4605
e-mail: hoss@fsv.cvut.cz

Prof. Ing. Alexander Grünwald, CSc.
phone: +420 2 2435 4638
e-mail: grunwald@fsv.cvut.cz

Ing. Karla Vlčková
Ing. Jitka Zeithammerová
Department of Sanitary Engineering
Czech Technical University in Prague
Faculty of Civil Engineering
Thákurova 7, 166 29 Praha 6, Czech Republic