LULEÅ
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Department of Environmental Engineering
Division of Sanitary Engineering

SBV099 Senior Design Project in Sanitary Engineering

# Removal of Ammonium from Wastewater by Clinoptilolite

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## Preface

This report is a part of course SBV099 Senior Design Project in Sanitary Engineering which was conducted at Luleå University of Technology under the supervision of Annelie Hedström. This project was a minor part of a VA-Forsk project. The zeolite material used in the experiment was supplied from Zeosand, which is acknowledged.

## Abstract

Swedish environmental legislation promotes reduction of nutrient supply to water bodies and reuse of nutrients found in wastewater. Therefore, in a small wastewater treatment unit, ammonium entrapment may be done in the winter by zeolite unit which is known to adsorb ammonium and could be used as a fertilizer in agriculture. The aim of the this report was to obtain information of ammonium exchange capacity and functionality of clinoptilolite (zeolite) using wastewater in temperatures of about +4 °C. Moreover, desorption of adsorbed ammonium onto zeolite and possible nitrification was studied. Clinoptilolite in this study adsorbed 2.2 mg $NH_4$-N/g (grain size 7-15 mm) average hydraulic retention time being 19 minutes. Finer grain size (4-8 mm) adsorbed somewhat more ammonium than the coarser one; 2.6 mg/g. The results are within the range of several other studies, but low. Ammonium retention capacity of clinoptilolite decreased rapidly and at the end of testing period it was about 10%. The decrease in ammonium retention may be due to used adsorption sites and microbiological growth on zeolite. Desorption of ammonium and nitrification occurred in the used filter material. The maximum desorption was 23% of adsorbed ammonium while leaching with tap water.

# 1. Introduction

There are 15 environmental goals in Sweden with the guiding principle of preserving natural resources. One of them comprises of diminishing eutrophication of water coarse. To achieve this goal, single wastewater treatment units need to be updated in order to diminish phosphorus and organic matter reaching lakes and watercourses, and nitrogen to coastal waters. Phosphorus can effectively be taken up by different kinds of filter materials (*e.g.* sand, leca), and theoretically, reused in agriculture. However, nitrogen uptake is done by microorganisms, and thereafter the nutrient is released into the atmosphere as nitrogen gas. Therefore, nitrogen found in wastewater can not been reused in agriculture. Moreover, activity of microorganisms decreases drastically during winter.

In the municipality of Luleå, two pilot units for wastewater treatment (each receiving sewage water from five house-holds) are being planned to be constructed which will among other things reduce nitrogen of wastewater. Nitrogen reduction may be done in the winter by an ammonium adsorption unit composed of clinoptilolite (zeolite) since zeolites are known to be selective for ammonium adsorption (Dyer & White, 1999) and temperature has a minor effect on ammonium exchange process (Atkins and Scherger, 1997). Furthermore, ammonium saturated clinoptilolite can be used as a fertilizer in agriculture.

In this laboratory experiment, the aim was to evaluate ammonium exchange capacity (AEC) using wastewater and functionality of zeolite in low temperatures (about +4 °C). Furthermore, desorption of ammonium from zeolite and possible nitrification was studied.

# 2 Material and Methods

## *2.1 Ammonium adsorption capacity of zeolite*

Three separate laboratory experiments of ammonium adsorption from wastewater by zeolite were carried out in the temperature of about +4 °C. Wastewater used in the experiments was collected from Uddebo Wastewater Treatment Plant in Luleå, and it was primary treated in step screen. Furthermore, in the second and third experiment wastewater was filtrated (Munktell 3) in order to avoid clogging of column. The zeolite used in the experiments was clinoptilolite of two different grain sizes. Clinoptilolite is a naturally occurring aluminium silicate with high cation exchange capacity. The unit cell formula of a natural zeolite can be given as:

$$(\mathrm{Li, Na, K})_a\ (\mathrm{Mg, Ca, Sr, Ba})_d\ [\mathrm{Al}_{(a+2d)}\ \mathrm{Si}_{n-(a+2d)}\ \mathrm{O}_{2n}]m\mathrm{H_2O}$$

where the unit cell of clinoptilolite is usually characterized on the basis of 72 oxygen atoms ($n$=36) and, 24 water molecules ($m$=24) (Abusafa & Yücel, 2002). Chemical and physical properties of the clinoptilolite used in the experiments are presented in Table 1. Information of the experiment variables and parameters are given in Table 2 and the experiment layout is presented in Figure 1.

**Table 1.** The chemical content and physical properties of zeolite used in experiments

| Element | Wt.-% |
|---|---|
| $SiO_2$ | 65.72 |
| $Al_2O_3$ | 10.88 |
| $TiO_2$ | 0.07 |
| $Fe_2O_3$ | 1.19 |
| $Na_2O$ | 0.65 |
| $K_2O$ | 2.98 |
| CaO | 2.55 |

| | |
|---|---|
| MgO | 0.98 |
| $P_2O_5$ | 0.035 |
| $SO_3$ | 0.06 |
| Bulk density | 1.422 g/cm$^3$ |
| Packed density | 2.145 g/cm$^3$ |
| Pour density | 0.420 g/cm$^3$ |
| Specific surface | 13.900 cm$^2$/g |

Samples were taken before and after the column, and of the samples were analysed with respect to the concentrations of $NH_4$-, $NO_3$-, $NO_2$- and total-N. The samples after the column were taken from a container where percolated wastewater was collected. Furthermore, pH and temperature of the samples and the volume of wastewater percolated the column were measured. When performing the third experiment, compiled potassium samples before and after the column were taken. A percentage of percolated water on each occasion was gathered into a container and analysed afterwards. All of the samples were stored frozen before analysis. While sampling, the temperature of the surroundings was measured.

**Table 2.** The information of experiment variables and parameters

| Exp | Flowrate [BV/h] | Flowrate [l/h] | Waste water | Mass of Zeolite [g] | Grain size [mm] | Duration [h] | pH of Inf. | Temp [°C] | | Avr. HRT [min] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Sur. | Inf. | |
| A | 1.6-7.4 | 0.25-1.16 | Unf | 129.384 | 7-15 | 52 | 7.2-7.4 | 3.5-5 | 7.8-10.5 | 8-29 |
| B | 2.6-3.2 | 0.40-0.50 | Filt | 124.700 | 7-15 | 145 | 7.0-.7.4 | 3.5-5.5 | 7.1-9.1 | 19 |
| C | 2.7-3.2 | 0.42-0.50 | Filt | 142.922 | 4-8 | 147 | 7.2-.7.5 | 4-5 | 7.3-10.7 | 19 |

Exp = experiment
Unf = unfiltrated
Filt. = filtrated
Inf. = influent
Sur. = surroundings
Avr. = average
HRT = hydraulic residence time
BV/h = Bed volume/hour

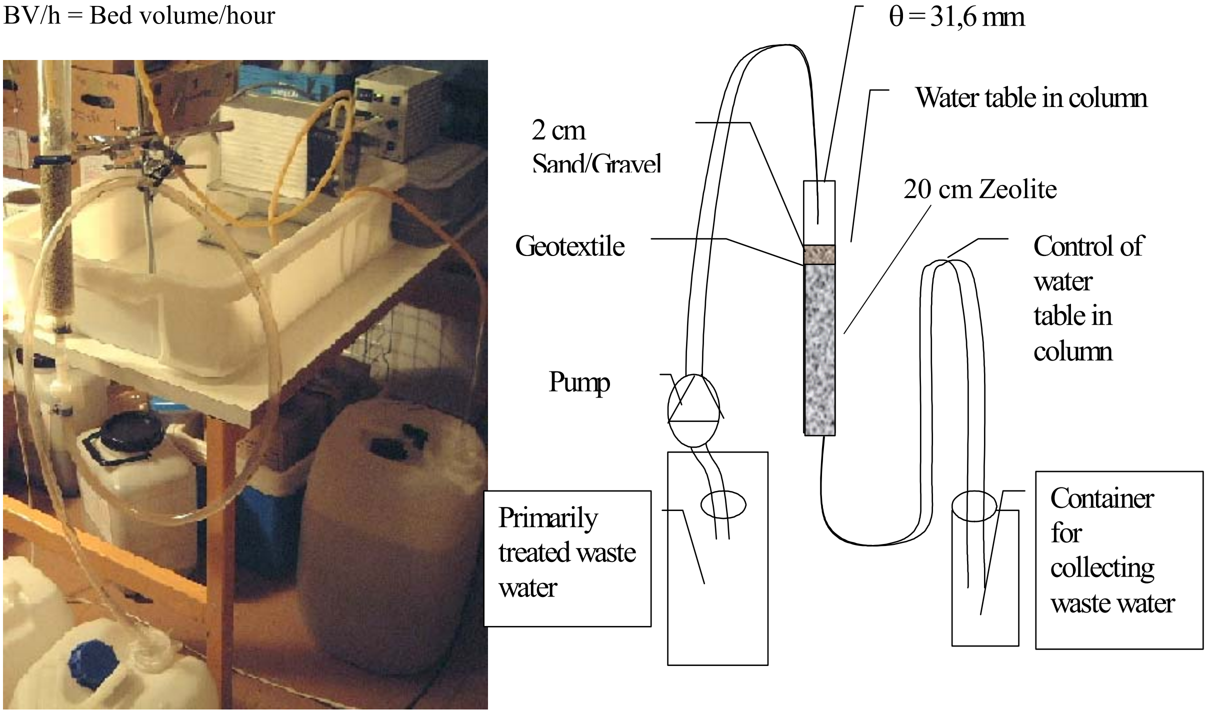

**Figure 1.** The experiment layout.

### *2.2. Desorption of ammonium and possible nitrification*

In two laboratory experiments the release of ammonium adsorbed during the experiments B (Exp. 1) and C (Exp. 2) was examined. Moreover, possible nitrification of ammonium was studied. Both of the experiments were carried out in room temperature of about 22°C. The column after the adsorption examinations was allowed to dry in room temperature for a week before experiment 1, and for two days before experiment 2. Experiment 1 was conducted with the same layout as experiments A, B and C with the difference of tap water was used instead of wastewater. Furthermore, the column was alternately saturated with tap water and non-saturated. Samples were taken after the column from a container, where percolated water was collected. The samples were analysed with respect to the concentrations of $NH_4$-, $NO_3$-, $NO_2$- and total-N, and pH, volume of percolated water and temperature were measured. In experiment 2, the column was filled with tap water, and the water was changed every 24 h within the three first days, and thereafter about every 35 h. After emptied the column from water, it was non-saturated for 5 to 10 min. The water held in the column was analysed with respect to the amount of $NH_4$-, $NO_3$-, $NO_2$- and total-N, and pH. Volume of water and temperature were measured. More information of the two experiments is given in Table 3.

**Table 3.** Variables and parameters of Experiment 1 and 2

| Exp. | Mtrl from exp | Duration [h] | Flowrate [l/h] | Vol. Of Percolated Water [l] | Vol. of Leachate [ml] | Temp [°C] | |
|---|---|---|---|---|---|---|---|
| | | | | | | Wat. | Sur. |
| 1 | B | 48 | 0.48-0.50 | 23.6 | - | 20.0-21.2 | 21-22 |
| 2 | C | 143 | - | 0.76 | 136-162 | 22.4-24.0 | 21-23 |

Tot. = total

## 3 Results and discussion

### *3.1 Ammonium exchange capacity and functionality of zeolite*

The highest $NH_4$ exchange capacity for clinoptilolite was 2.6 mg $NH_4$-N/ g zeolite as can be seen in Table 4. It was achieved with the smallest grain size used in the experiments (4-8 mm) and with an average HRT of 19 minutes. However, the difference in adsorption capacity (with the same HRT) to next coarser media (2.2 mg $NH_4$-N/g zeolite) was small. The lowest adsorption capacity of zeolite was 1.4 mg $NH_4$-N/g zeolite, and it was achieved at the first experiment with unstable conditions (*e.g* fluctuating wastewater flow).

**Table 4.** Adsorption capacity

| Experiment | Grain size [mm] | Avr. HRT [min] | Ads. capacity [mg $NH_4$-N/g zeolite] | Concentration of K [mg/l] | |
|---|---|---|---|---|---|
| | | | | In | Out |
| A | 7-15 | 8-29 | 1.4 | - | - |
| B | 7-15 | 19 | 2.2 | - | - |
| C | 4-8 | 19 | 2.6 | 14.2 | 22.7 |

The operating ammonium exchange capacity results from other researchers in their column and batch experiments have been all within the range of 1-7 mg $NH_4$-N/g (Hedström, 2001). Results achieved here compared to others are within the range, but low. This might be due to that in other studies smaller grain sizes than 4 mm were used. According to Ames (1960) using grain sizes of smaller than 1.0 mm drastically decreases the ammonium exchange capacity. Furthermore, the filter media used in present experiment was not totally fed with ammonium as can be seen in Figure 2; the concentrations of ammonium in effluent are lower than the ones in influent at the end of the experiments. Therefore, bigger amounts of ammonium could possibly have been absorbed by zeolite, and higher AECs could have been achieved. Hlavay *et.al.* (1982) found that higher ammonium concentrations in influent resulted slightly higher amounts of exchanged ammonium. The range of influent ammonium-nitrogen concentrations in his studies was 17-45 mg/l, and the concentrations of ammonium in these experiments were somewhat over 20 mg/l. Moreover, there were competing ions in present experiments which can decrease adsorption capacity. However, HRT in the experiments was about optimal since several studies do not recommend HRTs below 10 min. (Beler-Baykal *et. al.*, 1996; Beler-Baykal and Guven, 1997 and Booker *et. al.*, 1996). Moreover, pH values in the experiment were also about optimal as in two studies, the pH values of 6 (Koon and Kaufmann, 1975) and 7 (Kithome *et. al.*, 1998) were found to be favourable for ammonium adsorption. The low temperature in experiments here ought not to be influenced ammonium exchange capacity since Koon and Kaufmann (1975) did not found any impact of temperatures between 10° and 20° C on the ammonium adsorption process.

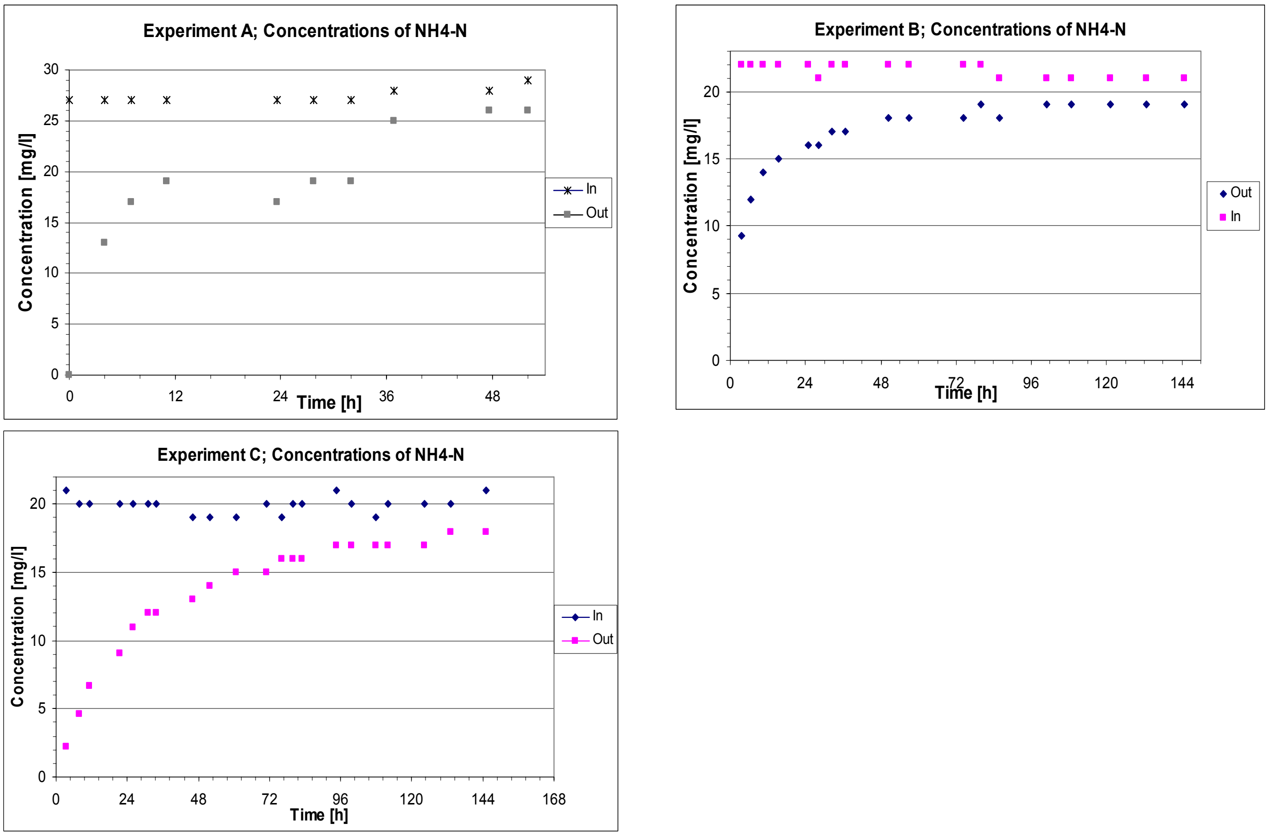

**Figure 2.** The influent and effluent ammonium concentrations in the experiments A, B and C.

The highest reduction rates of ammonium were 80 % (see Figure 3) during the first 8h in experiment C, and after the first day, the reduction rate was less than 50 %. When the ammonium retention was high (about 80 %), the effluent ammonium concentrations were below 5 mg/l, and after the first day somewhat over 10 mg/l. Generally, ammonium reduction rates decreased rapidly in the experiments as can be seen in Figure 3. After three days, the reduction rates were about the same (below 20 %) for the zeolite of the two different grain sizes, and effluent ammonium concentrations were between 15-19 mg/l. Potassium has higher affinity than ammonium ion for clinoptilolite (Hedström, 2001). Therefore, compiled potassium samples were taken from Experiment C since ammonium exchange capacity decreased rapidly at Experiment B after the first two days. The concentration of potassium after the column was higher than before indicating release of potassium. Therefore, the rapid decrease in ammonium exchange capacity can not (solely) be due to competition between potassium ion but due to used adsorption sites and microbiological growth. The growth on the surfaces of zeolite grains decreases the contact between ammonium ions and zeolite. On the surface of zeolite, a layer of microbiological growth could be seen at the second experiment day for coarser material and at the third day for finer one. In Figure 4, pictures of the column used in experiment C can be seen with the biological growth at the fifth day. Furthermore, the microbiological film caused increased loss of hydraulic head during the experiments. The increase in ammonium reduction rates in experiment A at 24-32h is due to decreased or even stopped flow of wastewater. Moreover, the low reduction rates after 36h are due to drastically increased wastewater flow. Particles in the wastewater gave rise to clogging of the column especially at the first experiment which may have decreased the ammonium adsorption.

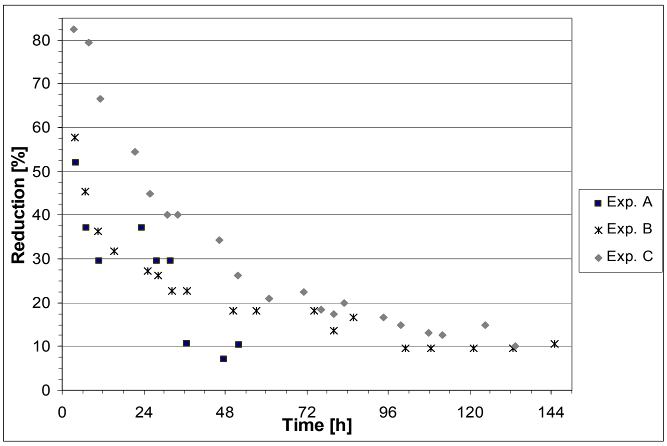

**Figure 3.** The reduction rates of ammonium in the experiments A, B and C.

**Figure 4.** Pictures of the column at fifth day from experiment C. At the left side is the uppermost part, the middle part and on the right side is the lowest part of the column. The green material between grains is a microbiological film.

### *3.2 Desorption of ammonium and possible nitrification*

The release of ammonium during the experiments decreases as can be seen in Figure 5. In experiment 1, desorption is higher when the column was saturated with water than water just percolating through the column. This is probably due to better contact between liquid-solid surfaces. Even though, leached concentrations of ammonium are higher in experiment 2, the total amount of desorbed ammonium was higher at experiment 1 than in experiment 2. This was due to bigger volume of leaching water used in experiment 1. The desorbed ammonium in experiment 1 was 60.6 mg which is 23 % of adsorbed ammonium, and at experiment 2, respectively, 5.5 mg and 1.5 %. However, a part of ammonium adsorbed into zeolite can have been nitrified and further denitrified before the leaching experiments since the columns stayed dry for some days (Exp. 2) to a week (Exp. 1) in room temperature. Therefore, the amount of desorbed ammonium in the experiments may be bigger.

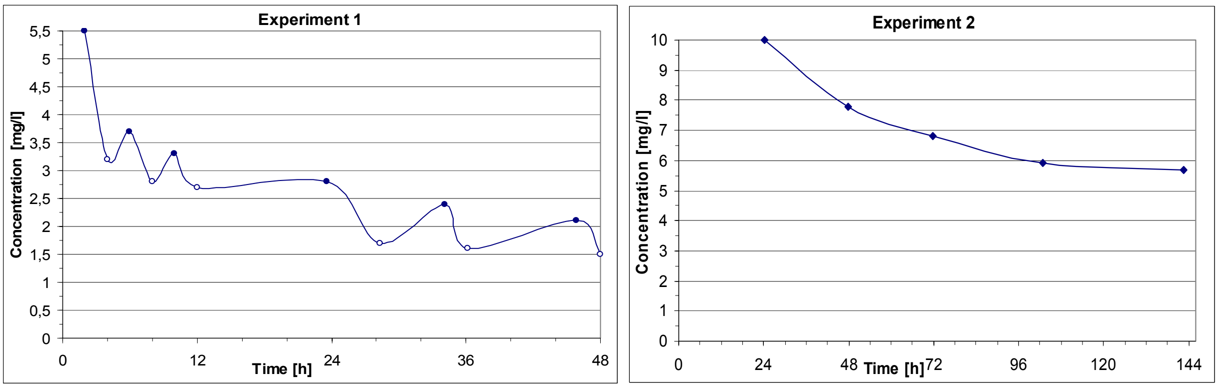

**Figure 5.** The concentrations of desorbed ammonium during experiments 1 and 2. In experiment 1, data of saturated conditions are marked with filled circles and the unsaturated conditions with unfilled circles.

As can be seen in Figure 6, in Experiments 1 and 2 minor nitrification occurred. The amount of $NO_3$-N (nitrified from $NH_4^+$) in the Experiment 1 was 1.5 mg which is 0.6% of adsorbed ammonium, and in Experiment 2, respectively, 0.05 mg and 0.01%. However, nitrification was ceasing in both of the experiments. At Experiment 1, decreasing nitrification could be due to decreasing ammonium concentrations and lack of oxygen, and at Experiment 2 due to lack of oxygen.

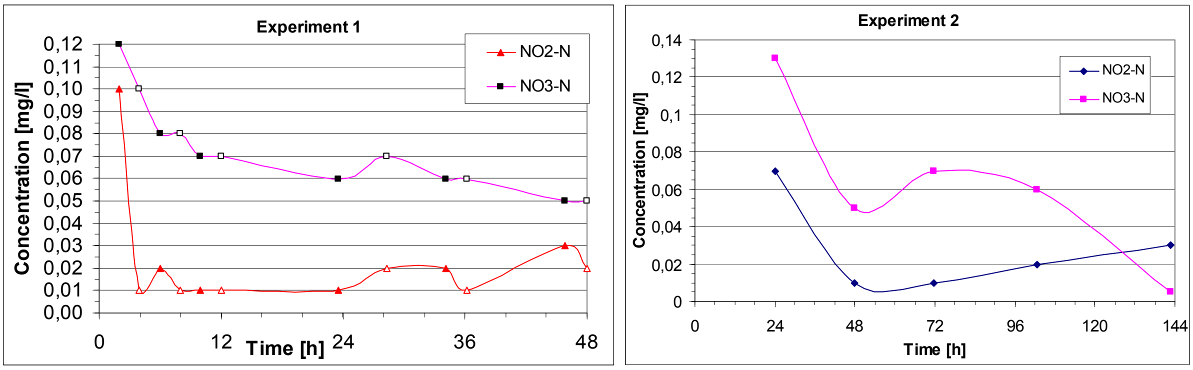

**Figure 6.** The concentrations of nitrate and nitrite nitrogen during the experiments 1 and 2. In experiment 1, data of saturated conditions are marked with filled marks and the unsaturated conditions with unfilled marks.

## 4 Conclusions

Studied zeolite clinoptilolite adsorbed ammonium in wastewater at low temperatures. The ammonium exchange capacity of clinoptilolite was bigger with finer filter material, but the difference with coarser one was minor. The obtained AEC was 2.6 mg/g zeolite for grain size 4-8 mm, and 2.2 mg/g zeolite for grain size 7-15 mm. The received results are within the range of other studies, but low. Ammonium exchange capacity decreased rapidly, and at the end of the testing period, ammonium reduction stabilised to about 10%. The decrease might be due to occupied adsorption sites and microbiological growth on the zeolite.

In the experiments adsorbed ammonium on to zeolite could be desorbed and nitrified. However, nitrification ceased possibly due to lack of oxygen. The maximum desorption achieved was 23% of adsorbed ammonium. By water saturation and high leachate volumes, bigger desorption rates can be achieved.

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