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Ammonium removal in drinking water using natural zeolite

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Preface

I would like to thank my two training supervisors Anneke Gijsbertsen and Joost Kappelhof for assisting me in this work and for their availability. I am also grateful to all Kiwa water treatment team for their help, their warm reception, and their kindness.

Summary

The traditional method for ammonium removal and also for removal of organic components in drinking water processes is based on biological treatment in sand filters. The efficiency of such a system is proven but it could also release few traces of microorganisms or components on which microorganisms can regrow in the drinking water. This may be due to the complex processes in the sand filters (biological activity to remove methane and ammonium, removal of iron flocs and oxidation of manganese) and is undesirable. Sometimes the ammonium concentration in the finished water comes close to the norm for drinking water of 0.2 mg/L. By removing the ammonium in a separate step, sand filtration can probably be better controlled. Furthermore, in the cold season, biological activity in sand filters decreases resulting in a lower ammonium removal efficiency. This efficiency drop is currently compensated for by the addition of phosphoric compounds in sand filters, which consequently complicates further treatment.

Therefore, in this project we study the removal of ammonium by zeolites for the low ammonium concentrations found in drinking water treatment.

According to some scientific publications, this common toxic pollutant, which is ammoniacal nitrogen NH_3 or NH_4^+, could be removed by ion exchange. Zeolites seem to be the most attractive material for ammonium removal due to its ammonium-ion selectivity and good performance in ammonium sorption at low temperatures.

Aim of this project is to check the ammonium removal capacity of clinoptilolite with raw waters presenting a low ammonium concentration and a certain hardness. Ammonium removal can be influenced by different parameters. The effects of the following parameters are quantified to reveal which ones are predominant.

- Ammonium concentration
- Grain size
- Water ionic composition
- Pre-treatment of clinoptilolite
- Process conditions

The batch experiments with the two raw waters (1 mg-N/L and 3 mg/L) show that more than 4 g/L of minerals would still required a contact time of 30 min to reduce the ammonium concentration by 75%. In the column experiments, for Amsterdam water (0.16 mg-N/L), 1000 BV of water can be treated before the outlet concentration is higher than 0.04 mg-N/L. At this point the ammonium removal capacity of the bed is 0.16 mg-N/g of clinoptilolite. With the water of Hydron (3 mg-N/L), 430 BV of water can be treated before the outlet concentration is higher than 1 mg-N/L, in that case the capacity of the bed is 1.3 mg-N/g.

The data generated in this study will be used to assess the design of an installation to remove ammonium with zeolites in practice. The results of this study show that ammonium can be removed reproducibly with zeolites, but that the removal is influenced by the presence of competitive cations (Na^+, K^+, Mg^{2+}; Ca^{2+}) in the water. This will be taken into account in the process design.

Contents

1 Introduction

1.1 Kiwa Water Research presentation

1.1.1 Overview

Kiwa Water Research is the Dutch research and knowledge institute for drinking water, wastewater and related ecological and environmental aspects. Key aspects of the work of about 120 employees are innovation and knowledge transfer. The focus is the entire process of extraction, treatment, distribution and quality assessment of drinking water, industrial water and domestic water.

Kiwa has been conducting the joint research program BTO of the Netherlands drinking water sector for more than thirty years on behalf of the Netherlands' water supply companies and their association VEWIN.

Like many other major technology institutes, Kiwa Water Research adopts a position between universities and consultancy organizations. Working with these parties enables the institute to provide a worldwide service to water companies, government and the business sectors.

Knowledge management and knowledge transfer is an essential tool for closing the gap between theory and practice. The fundamental approach is depicted in the Knowledge Cycle (Fig. 1).
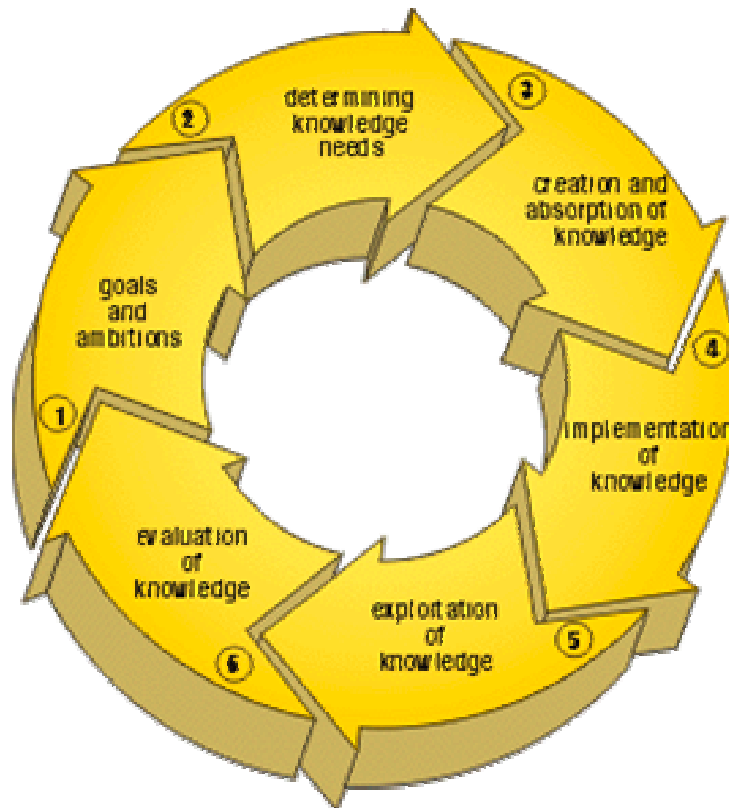

Fig. 1. Knowledge Cycle

All activities at Kiwa Water Research are related, from spatial planning, hydrology, ecology, process technology, distribution technology and asset management to knowledge of materials, toxicology, chemistry, biology, microbiology and knowledge management. Facilities include well equipped laboratories and testing plants. Knowledge and resources are deployed on an integrated basis form the five specialization areas of Kiwa Water Research:

- Water systems management
- Water treatment
- Water infrastructure
- Microbiological water quality and health
- Chemical water quality and health

1.1.2 International knowledge network

Kiwa Water Research co-ordinates research agendas and maintains close links with various respected knowledge partners in the Netherlands and other countries. These contacts, often based on formal memoranda of understanding allow Kiwa Water Research's customers access to a worldwide knowledge database. Customers can therefore make an efficient and conscious choice between purchasing existing knowledge and arranging for new knowledge to be generated.

On an international level, Kiwa Water Research operates in the platform EWRI (European Water Research Institutes, regrouping centers such as Veolia Environnement (France), ONDEO (France), Studie- en samenwerkingverband Vlaams Water (Belgium), WRc plc (UK), Technologiezentrum Wasser (Germany) and Laboratorio Nacional de Engenharia (Portugal). EWRI acts as co-coordinator between various research programs and is responsible for submitting joint research proposals to the European union. Kiwa Water Research also runs EWRI's secretariat.

1.1.3 Professional management systems

Kiwa Water Research has an ISO 9001 certification quality management system, which is also based on the management model of the Netherlands Quality Institute (INK). Health & Safety management and environmental management have been set up on the basis of OHSAS 18001 and ISO 14001 respectively.

1.2 Background

In The Netherlands, drinking water suppliers have made the choice to develop processes of post treatment without residual chlorine in the distributed water. To prevent the microorganism growing in pipes, instead of using an oxidant as chlorine, they remove the nutrients for microorganisms, such as ammonium.

The traditional method for ammonium removal and also for removal of organic components in drinking water processes is based on biological treatment in sand filters. The efficiency of such a system is proven but it could also release few traces of microorganisms or components on which microorganisms can regrow in the drinking water. This may be due to the complex processes in the sand filters (biological activity to remove methane and ammonium, removal of iron flocs and oxidation of manganese) and is undesirable. Sometimes the ammonium concentration in the finished water comes close to the norm for drinking water of 0.2 mg/L. By removing the ammonium in a separate step, sand filtration can probably be better controlled.

Furthermore, in the cold season, biological activity in sand filters decreases resulting in a lower ammonium removal efficiency. This efficiency drop is currently

compensated for by the addition of phosphoric compounds in sand filters, which consequently complicates further treatment.

Therefore, in this project we study the removal of ammonium by zeolites for the low ammonium concentrations found in drinking water treatment.

According to some scientific publications, this common toxic pollutant, which is ammoniacal nitrogen NH_3 or NH_4^+, could be removed by ion exchange. Zeolites seem to be the most attractive material for ammonium removal due to its ammonium-ion selectivity and good performance in ammonium sorption at low temperatures. Zeolites are aluminosilicate minerals containing exchangeable alkaline metal and alkaline earth metal cations in addition to water in their structural framework, manifesting ion-exchange behaviour.

1.3   Aim of this project and layout of the report

Aim of this project is to check the ammonium removal capacity of clinoptilolite with waters with a low ammonium concentration. Two different processes can be applied to remove ammonium: the first one is to add zeolite grains in the water during a certain contact time. Batch experiments represent of such a process. The second one is to use a bed of zeolite as an ion exchanger. Removal ammonium in this option is studied with the column experiments.

Values of ammonium removal found in literature will be compared in § 4.1 to those found in first experiments to check the clinoptilolite samples and regeneration method applied for this study.

Ammonium removal can be influenced by different parameters. The effects of the following parameters will be quantified to reveal which ones are predominant.

- Ammonium concentration   § 4.1
- Grain sizes   § 4.1; § 4.3.3
- Water ionic composition   § 4.1.3; § 4.2; § 4.3
- Treatment of clinoptilolite   § 4.3.3
- Process condition   § 4.3.3

Furthermore the wo possibilities of treatment process will be checked for water from our sponsors (WLB Amsterdam and Hydron Zuid Holland) in § 4.2 and 4.3.2

Some regeneration experiments were realized and are presented in § 4.4 to give directions for the future experiments which will be more concerned with that point.

This report follows the usual order and presentation of a scientific publication.

2 Literature study

2.1 Zeolite selection

Over the last decades, three zeolites have been studied for industrial applications: clinoptilolite, phillipsite, and mordenite. All zeolites are aluminosilicate minerals. Their structure is porous, containing interconnected cavities where cations and water molecules are contained. Cavities are made of rings composed by oxygen atoms and metal atoms (Al or Si). The framework of clinoptilolite, mordenite and phillipsite are shown in Fig. 2, Fig. 3 and Fig. 4. Their crystallographic information, extracted from the IZA structural commission database [1], is resumed in table 1, table 2 and table 3.
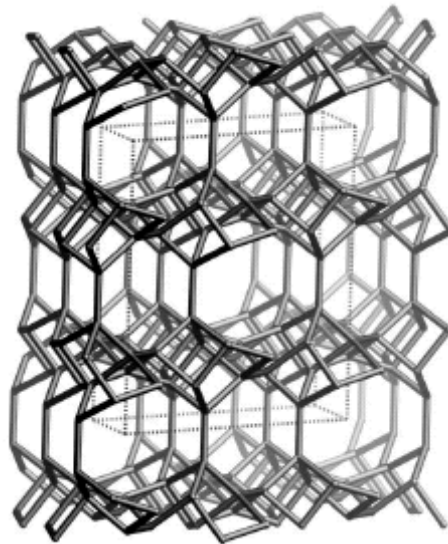
Fig. 2: Clinoptilolite framework viewed along the [001] axis
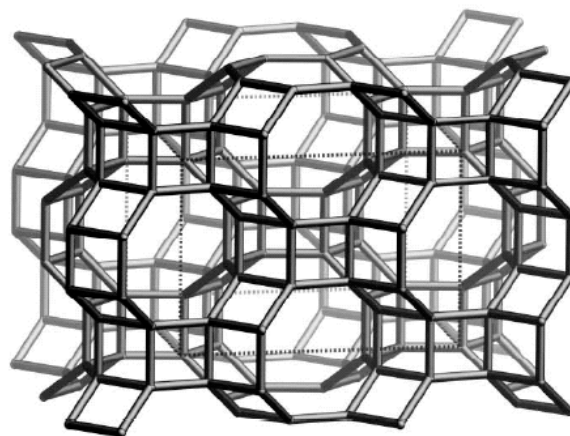
Fig. 3: Phillipsite framework viewed along the [001] axis
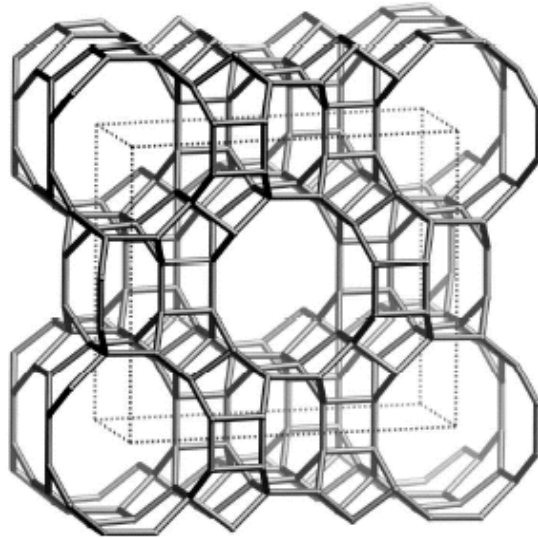
Fig. 4: Mordenite framework viewed along the [001] axis

Table 1. Crystallographic information of Clinoptilolite
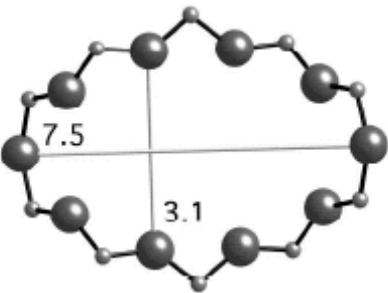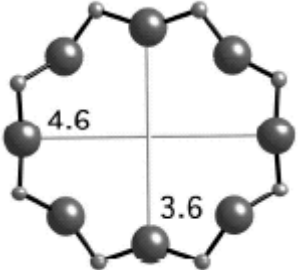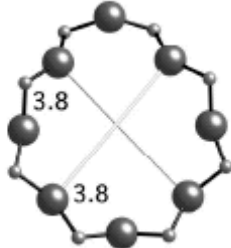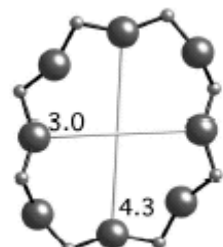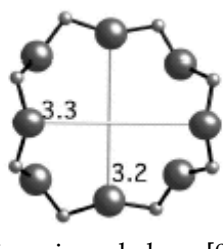
Idealized cell constant	monoclinic, C2/m, a = 17.5Å, b = 17.6Å, c = 7.4Å, β = 116.1° $|Ca^{2+}_4 (H2O)_{24}|$ $[Al_8Si_{28} O_{72}]$-**HEU**
Crystal chemical data	monoclinic, Cm, a = 17.718Å, b = 17.897Å, c = 7.428Å, β = 116.42° {[001] **10** 3.1 x 7.5* + **8** 3.6 x 4.6*} ↔ [100] **8** 2.8x 4.7* (variable due to considerable flexibility of the framework)
Channels	 10-ring viewed along [001] 8-ring viewed along [001]

Table 2. Crystallographic information of Phillipsite
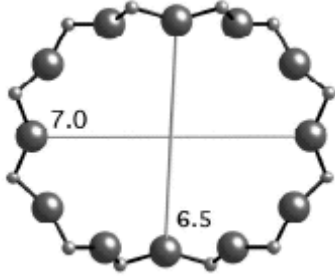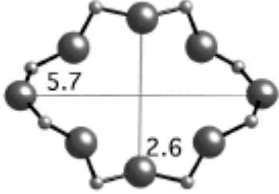
Idealized cell constant	orthorhombic, Cmcm, a = 9.9Å, b = 14.1Å, c = 14.0Å $\|K^+_2(Ca^{2+},Na^+_2)_2 (H_2O)_{12}\|$ $[Al_6Si_{10} O_{32}]$-**PHI**
Crystal chemical data	monoclinic, P121/m1 a = 9.865Å, b = 14.300Å, c = 8.668Å, β = 124.20° [100] **8** 3.8 x 3.8* ↔ [010] **8** 3.0 x 4.3* ↔ [001] **8** 3.2 x 3.3*
Channels	 8-ring viewed along [001] 8-ring viewed along [010] 8-ring viewed along [001]

The three zeolites do not have the same crystal organization, the most regular one is observed for the Phillipsite, because all channels are composed of 8-rings. This regularity involves a more regular diffusion behavior on the whole material because the channels are identical. In the case of clinoptilolite or mordenite, channels are larger, which probably results in a different behave of the diffusion rate in these materials.

Besides, diameters of Phillipsite's ring are smaller than in the both other zeolites, this parameter would explain a better selectivity towards small hydrated cations like ammonium or potassium.

Naturally in the zeolite framework, the ionic exchange sites are occupied by all common alkali metal and alkaline-earth metal ions (Ca, Mg, Na, K), which explains that the chemical formulas may be quite different, even between two samples of identical zeolite. However to get a reliable and higher removal capacity, zeolites are pretreated to be conditioned in a specific form. The common one is the sodium form because sodium ions are easily exchanged with ammonium and in this form zeolites obtain a good selectivity for ammonium.

Table 3. Crystallographic information of Mordenite

Idealized cell constant	orthorhombic, Cmcm, a = 18.3Å, b = 20.5Å, c = 7.5Å
Crystal chemical data	$\vert Na^+_8 (H_2O)_{24}\vert$ $[Al_8Si_{40}O_{96}]$-**MOR** orthorhombic, Cmcm, a = 18.1Å, b = 20.5Å, c = 7.5 Å
Channels	[001] **12** 6.5 x 7.0* ↔ {[010] **8** 3.4 x 4.8 ↔ [001] **8** 2.6 x 5.7}* 12-ring viewed along [001] Limited 8-ring viewed along [001] between 12-ring channels

Klieve & Semmens [2] made an evaluation of these (pre-treated) natural zeolites for ammonium removal. They worked with synthetic water of which the composition is shown in table 4; the results of their measurements are in table 5. Their results were produced in a column study with a grain size of the zeolite of 0.5-0.7 mm.

Table 4. Composition of Klieve & Semmens synthetic water

Element	Concentration
NH_4^+	14 mg/l
Na^+	58 mg/l
K^+	12 mg/l
Mg^{++}	8 mg/l
Ca^{2+}	34 mg/l
pH	7.45

Table 5. Ammonium removal capacity of zeolites

Zeolite	Capacity in meq NH_4^+-N/g of zeolite
Clinoptilolite	0.59
Mordenite	0.44
Phillipsite	1.00

One other zeolite called erionite was studied but the capacity was much lower than that of the three zeolites in table 5, so the results of erionite were not published. According to the results, phillipsite is more efficient than others, it is also more selective and its density is lower than the other ones, confirming the crystallographic overview. However, its structure is very weak and therefore it does not seem likely to be a suitable material in water treatment processes. Clinoptilolite has been selected as the best compromise. After the study of Klieve & Semmens [2] almost all succeeding studies are based on clinoptilolite from different sources.

Also in this study two sources of clinoptilolite (ZEOCEM® and Zeolite Products®) are available. Possible differences between both will be tested during batch experiments.

2.2 Effect of the grain size

The effect of the grain size on ammonium removal is detailed in Sprynskyy [3] et al study. Results are reported in Fig 5.

Ammonium sorption effectiveness and maximum sorption capacity of the clinoptilolite samples increase with decreasing size of the grains until the size of 0.35 mm. For all flow rates this same conclusion can be drawn. They established that the use of a clinoptilolite fraction finer than 0.3 mm is ineffective for ammonium removal under dynamic conditions because of the low water permeation in the zeolite bed. According to publications [2-3-4] which were interested in fraction size, optimal results are obtained with a clinoptilolite fraction of 0.3-0.7 mm. Demir *et al.* [4] also notice that a finer grain size allows a quicker regeneration. Obviously, the regeneration process is an ion-exchange process too.
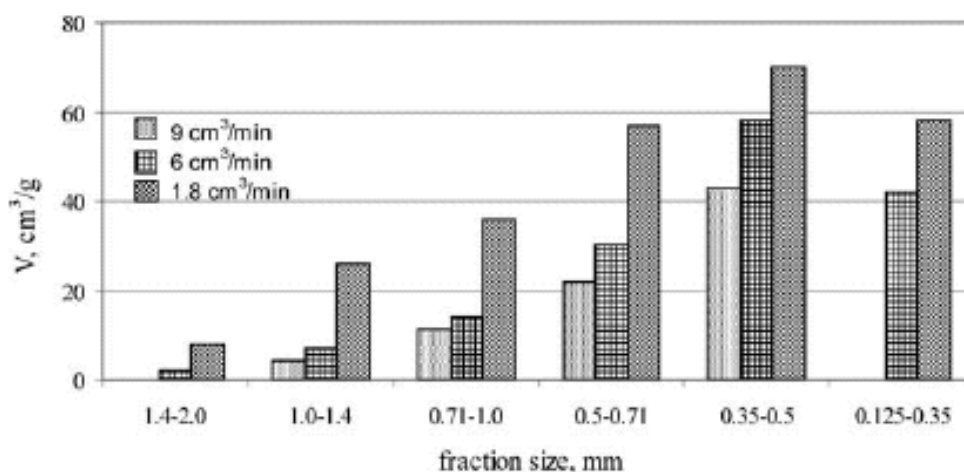
Fig. 5. Solution volume (mL/g) purified to 2 mg/L of ammonium ions per gram of the sorbent (at initial concentration 100 mg-N/L). Sprynskyy got his results in dynamic condition too.

2.3 Pretreatment and regeneration

Pretreatment and regeneration can be considered as the same treatments, since the aim is identical: Pretreatment and regeneration are processes to put the zeolite in the desired form which is usually the sodium one. The only difference is that regeneration removes ammonium ions, while pretreatment removes initial alkali metal and earth-alkaline metal cations included in the raw clinoptilolite.

Murphy *et al.* [5] noticed efficient pretreatment and regeneration of the clinoptilolite mean a constant removal capacity. The best treatment methods increase the removal capacity by up to 20% compared to samples not treated, as shown in Fig. 6. Almost all studies interested in regeneration however results interpretation and conditions have evolved.
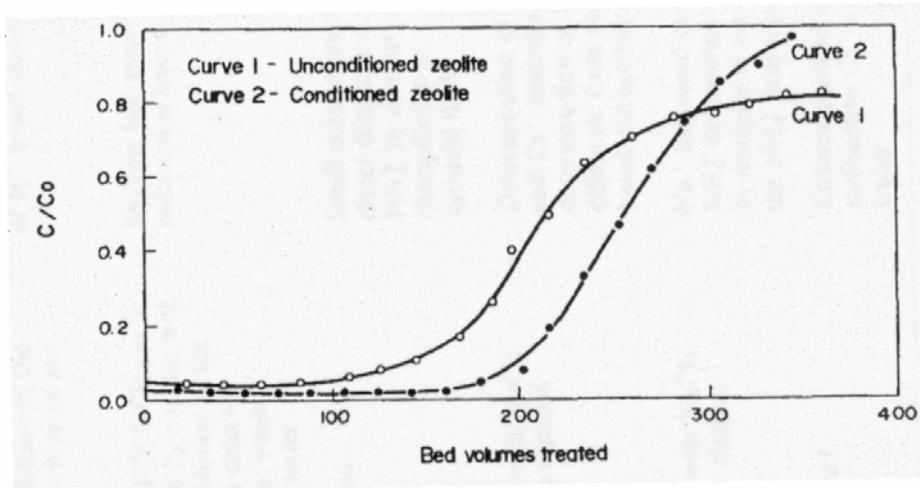
Fig. 6. Impact of conditioning on ammonium breakthrough curves for clinoptilolite (influent 20 mg-N/L, 20 BV/hr)

Murphy *et al.* [5] concluded that pretreatment with acid followed by NaOH and then NaCl resulted in the greatest increase in capacity. However Seyforth [6] investigated on acid and basic conditioning. One portion of samples was activated with 1N NaCl solution at pH 10. The other portion was exposed to 10% HNO_3 for 1h and then to 1N NaCl to convert the zeolite in the sodium form. Conclusion was that the different treatment methods yielded similar capacities.

Jorgensen *et al.* [7] regenerated clinoptilolite with 4% NaOH for 30 min and rinsed samples with deionised water. After repeating this procedure three times, the capacity rose to a constant value around 2.2 meq/g of dry clinoptilolite. They concluded that sodium hydroxide activates the zeolite. Similar results from Seyforth's study [6] suggest that the increase capacity of the zeolite is related to the number of regeneration cycles to which the zeolite is exposed. All later studies concluded the same: after four or five exchange cycles, clinoptilolite reaches its maximum capacity of around 2.2 meq/g of dry clinoptilolite.

Klieve & Semmens [2] demonstrated pretreatment and regeneration with only 1N NaCl are at least as efficient as acid treatment. Samples that received a treatment of sodium hydroxide together with NaCl had the highest observed capacity.

Sarioglu [8] regenerated with 1N NaCl solution and considered the effect of washing the zeolite with acid (0.005M HNO_3) afterwards. He noticed a 31% loss of adsorption capacity after regeneration at pH 10 and an efficiency increase of 22% with acid-activated zeolite samples. His interpretation was that there are amorphous substances in the pores of the zeolite rocks, which prevent ion passage when the zeolite is in contact with a solution.

These results are quite interesting, though, they are in contradiction with the study of Sprynskyy [3], in which a significant decrease of effectiveness was observed

with acid-treated clinoptilolite. Furthermore he also reported that a structural degradation was detectable when a pH below 2 was used.

To conclude with the chemical regeneration, Gaspard *et al.* [9] studied regeneration in a pilot plant. The regeneration solution was at pH 10.5 and 12 g/L of NaCl were added. The set-up is shown in Fig. 7. The system also included a carrousel process between three zeolite filters and regeneration solution. The advantage of working with a high pH is the conversion of ammonium into ammonia, thus maintaining a low ammonium concentration in solution and which allows reusing the regeneration solution in the carrousel system.
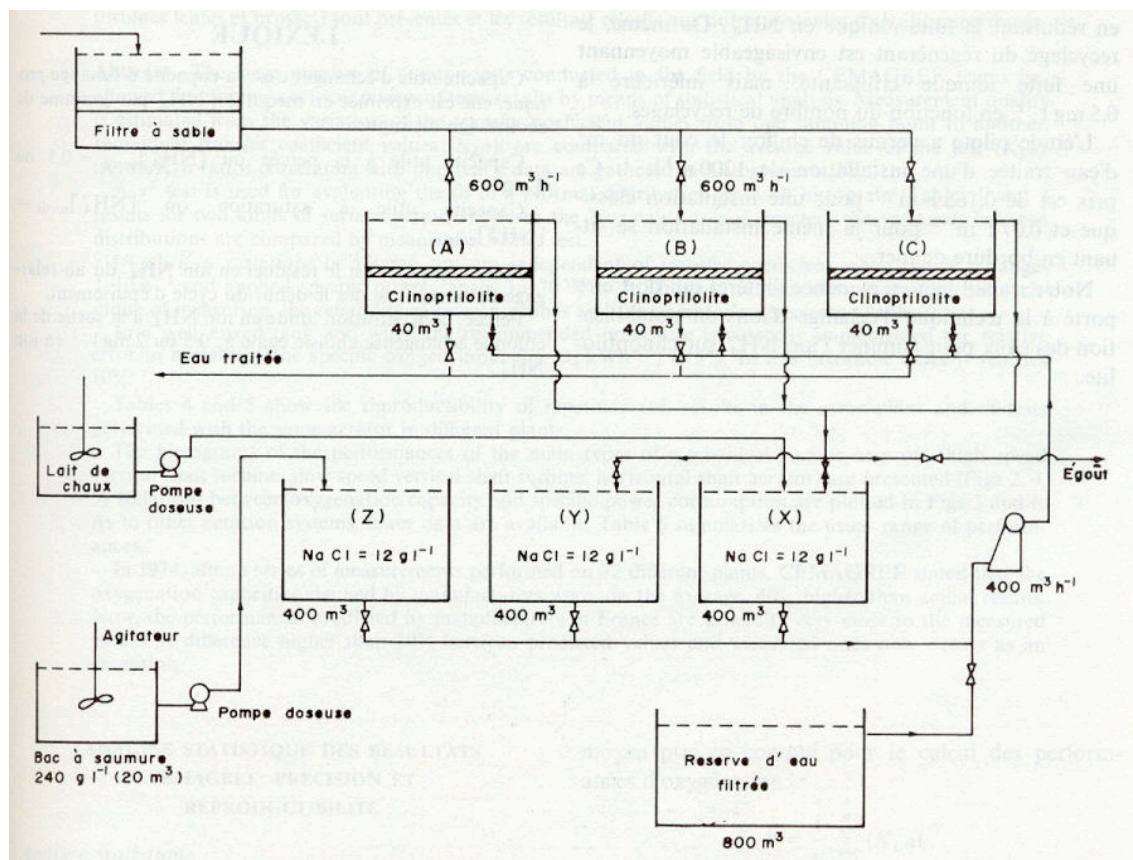
Fig 7. Gaspard *et al.* [9] pilot plant design including carrousel regeneration system.

Heat treatment (600°C over 1h) of the zeolite has been tested by Klieve & Semmens [2]. This treatment does not exhibit an increase of the removal capacity. Nevertheless, a higher selectivity towards ammonium in the presence of other cations was noticed.
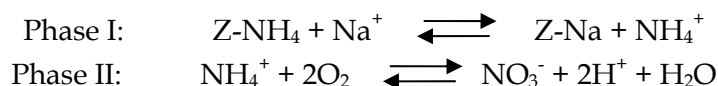
Chemical and physical conditionings presented in previous paragraphs are summed up in table 6.

Table 6. Studied conditionings in literature

Reference	Conditioning
Seyforth [5]	NaCl 1N
Gaspard *et al.* [8]	NaCl and NaOH (pH at level 11)
Sprynsky. [1]	NaCl and NaOH (pH at level 12)
Sarioglu. [7]	NaCl 1N then acid wash (0.005N HNO_3)
Murphy *et al.* [4]	Acid followed by NaOH and then NaCl
Jorgensen. [6]	NaOH 1N
Klieve & Semmens[2]	Heat pretreament (600°C 1h) then NaCl 1N

A few years ago, the possibility of biological regeneration has been pointed out. Bio-regeneration is carried out in two phases. Phase I is desorption of NH_4^+ from the zeolite and phase II is the biological nitrification.

Phase I: $Z\text{-}NH_4 + Na^+ \; \rightleftharpoons \; Z\text{-}Na + NH_4^+$

Phase II: $NH_4^+ + 2O_2 \; \rightleftharpoons \; NO_3^- + 2H^+ + H_2O$

Obviously, the advantage of such a system is the complete removal of ammonium by breakdown, not producing a side stream which is considered as a waste and needs additional treatment. Nevertheless biological treatment required quite specific conditions (pH, temperature, DO, NH_4^+ concentration available to the biomass). It may be necessary to use a pH buffer to prevent high concentrations of hydrogen ions which inhibit the breakdown, and an addition of pressurized oxygen to reach a correct nitrification rate according to Lahav & Green [10]. They also concluded concentrations of above 8g/L as Na^+ are inhibitory to nitrifying populations. However, in the study of Jin Park *et al.* [11] bio-regeneration was achieved completely by supplying air only, without a first step of liberating the ammonium ions into the solution by regeneration. It indicates that the ion exchange sites inside the zeolite are accessible for nitrifying bacteria. This is in contrast with the conclusion of Lahav & Green [10] and Semmens *et al.* [12]. They concluded that the crystalline cages of clinoptilolite are not available for nitrifying bacteria. Both conclusions may be right because they did not use exactly the same clinoptilolite.

All these studies concluded that biofilm formation has little influence on the exchange properties of the minerals. Further, nitrification becomes problematic when the amount of NH_4^+ in the resin is low, which may be a problem in using zeolites in drinking water treatment. Results of these studies are promising but experimental conditions were quite far from ours because concentrations of ammonium were greater than 40 mg/L.

Conney *et al.* [13] have checked reliability and zeolite life in their pilot-scale process for wastewater. Twelve repetitive sewage treatment cycles, under similar conditions, indicated the reproducibility of performance, and no deterioration of the zeolite's ammonium exchange capacity was observed. Fig. 8 shows that the total mass

adsorption of ammonium was closely matched for a series of exhaustion and desorption cycles.
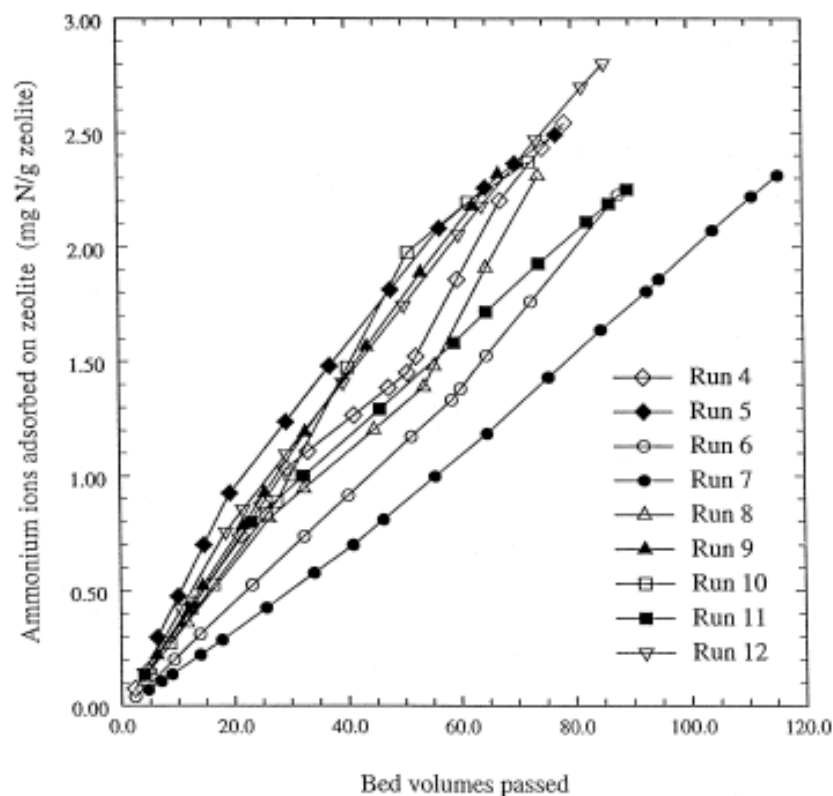
Fig. 8. Zeolite pilot column adsorption of ammonium in Cooney's study. Flow rate is 9.3 BV/ h and filtration rate is 6.9 m /h. Average ammonium feed concentration varies between 31 and 43 mg-N/L

To summarize: the aim of pretreatment and regeneration is to obtain the highest possible ammonium removal capacity. Generally, all ions are replaced by sodium ions. A solution with an excess of NaCl (e.g. 1 M) is efficient, but in addition NaOH may be added to convert ammonium into ammonia. After this treatment some methods were tested to further improve the removal capacity. These methods were heat treatment or an acid wash. In case denitrifying microorganisms are added to the zeolite bed, the ammonium can be removed completely.

2.4 The effect of water quality on ammonium removal

2.4.1 pH of the solution

In an aqueous solution, ammonium may be present as NH_3 and/or the ionized form NH_4^+, depending on the pH and the temperature, see *annex 2*. Ammonium ions are removed from aqueous solutions by zeolites via exchange with cations or by adsorption in pores of aluminosilicate systems. Jorgensen *et al.* [7] concluded that ion exchange prevails when the concentration of ammonium is equal to or lower than the

concentration of exchange sites in the zeolite. Thus, only the ion NH_4^+ can be removed by the ion exchange process. Hence, for optimum operation the pH level of the aqueous solution must be at or below 7.5 to favour the ammonium form.

2.4.2 Presence of other cations than ammonium

The ammonium cation-exchange capacity varies depending on the presence of other cations in the aqueous phase. The competition of other ions with ammonium is in particular a point of concern in our study, as the ammonium concentration is relatively low compared to sodium ions and calcium ions in the raw water.

Due to the high selectivity of zeolites for potassium ions, potassium is the main competitor for ammonium removal from an aqueous solution by clinoptilolite [14]. However, not only potassium ions compete with ammonium, Gaspard *et al.* [9] compared breakthrough curves with soft and hard water, respectively 50 and 200 mg/L as Ca^{2+}, shown in Fig. 9. With hard water, the ammonium leakage is higher and the breakthrough point is detected earlier. Thus, the ammonium removal is significantly less efficient with hard water.
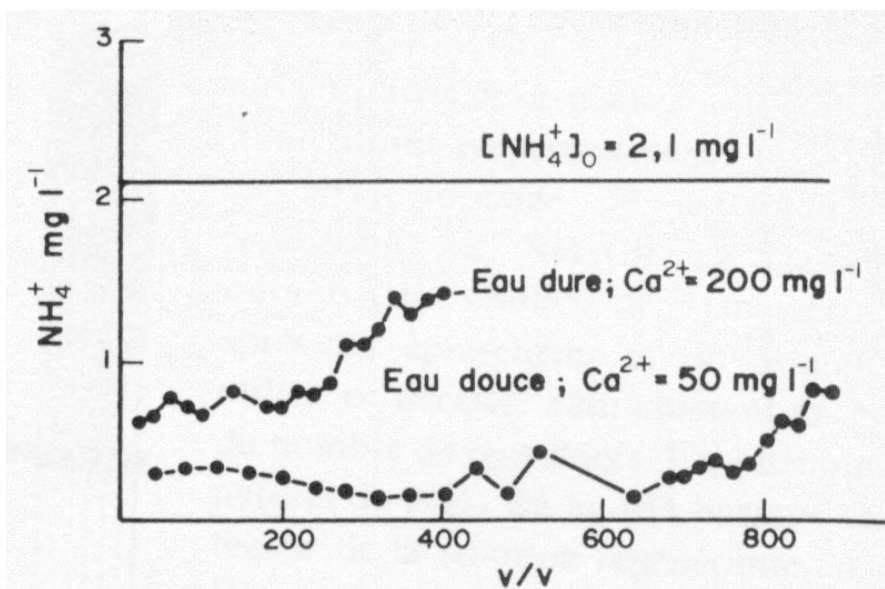
Fig. 9. Comparison of two exhaustions with soft and hard water.

2.4.3 Exchange selectivity

The following selectivity order of ammonium over other cations on clinoptilolite was found by Watanabe *et al.* [15]:

$$Na^+ > K^+ > Ca^{2+} > Mg^{2+}$$
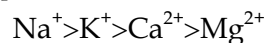
The conclusion of the study of Sprynskyy *et al.* [3] is very similar: sodium ions were observed to be more easily exchanged for both hydrogen and ammonium ions on the zeolite than the other cations. In addition, they found that the exchange of calcium ions increased with increasing ammonium concentration on the zeolite.

Both conclusions indicate that indeed the best regeneration process is to load zeolites with sodium ions.

2.4.4 *Presence of organic contaminants*

The study of Weatherley and Jorgensen [16] has proved contamination of common organic compounds (acid citric and proteins) does not affect the behaviour of the ammonium removal.

2.5 The effect of process conditions on ammonium removal

The flow rate influences ammonium removal [3-4-8]. At lower flow rates more ammonium can be removed. The flow rates applied were lower than 100 BV (bed volumes)/h and the two pilot-scale plants were designed for a flow rate of 10 BV/h.

2.6 Ammonium removal capacity

To conclude this literature review, table 7 summarizes the ion-exchange capacities of clinoptilolite, determined in previous studies. The ammonium removal capacity of clinoptilolite depends on three main parameters:
- The source of the clinoptilolite and mineral treatments
- The water matrix
- The flow rate (in case of a column experiment)

Table 7. Ion-exchange capacities of clinoptilolite

Kind of study	Ion-exchange capacity as mg-N/g zeolite	Ammonium concentration in aqueous solution as mg-N/L	Reference
Column	0.84	1.2 and matrix	Gaspard *et al.* [9]
Column	4.2	20.5	Schoeman [17]
Column	7.42	15-20	Sirkeciolu and Senatlar [18]
Column	7.7	20	Demir *et al.* [4]
Column	8.3	14 and matrix	Klieve and Semmens [2]
Static	8.54	5-25	Ershov *et al.* [19]
Static	8.96	100	Sprynsky *et al.* [3]
Column	9.52	18.8	Koon and Kaufman [20]
Column	19.18	11-13	Sarioglu [8]
Column	21.5	100	Sprynsky *et al.* [3]

3 Materials and methods

3.1 Electrode study

Samples can be analyzed for ammonium by the Nessler method or the Kjedhal nitrogen distillation…. However, this is time consuming and thus costly. Furthermore, data only come available after some time. Therefore, using an electrode, which would be able to follow the evolution and also to determine the ammonium ion concentration in solution, seems to be a more attractive way for this study.

Measuring the conductivity is often applied to follow an ion concentration evolution in dynamic studies. However this technique requires that the molar conductivities between species involved are quite different. Regarding the molar conductivities reported in *annex 1*, the values for calcium, magnesium and sodium are quite close and those for ammonium and potassium too. Thus, direct determination of the ammonium evolution in the case of a competition study with alkali metal and alkaline earth metal ions is not possible by measuring the conductivity. Also none of the different ammonium specific electrodes provided by Orion (model 93-18) or Hach (model 50250) are able to operate correctly with ammonium concentration below 1 mg/L in the presence of interfering ions.

To get round this matter an ammonia specific electrode was used. This gas-sensing electrode is constituted with a gas membrane. Such a membrane prevents interference from components in the water, such as almost all anions, cations, and dissolved species, other than volatile amines. To measurement is based on the transformation of ammonium ions in ammonia with the following acid-base equilibrium:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad pKa = 9.2$$

The equilibrium is shifted to the left using a pH buffer. To transform all ammonium in ammonia, the pH must be higher than 11 (*annex 2*).

The ammonia gas-sensing electrode elected for this study is the ORION 95-12, coupled with the meter ORION 720A. The principle of operation is discussed further in the next paragraph after which the practical operation is described in the following paragraphs.

3.1.1 Electrode theory of operation

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample the partial pressure of ammonia will be proportional to its concentration in the solution by Henry's Law:

$$Kh = \frac{[NH_3]_{aqueous}}{P_{NH_3}} = 56 \text{mol/L} \qquad \text{atm. (25°C)}$$

The Henry's constant, Kh, varies both with temperature and the level of dissolved species. For example, the constant is about 20% lower in 1 M NaCl than in distilled water. Ammonia, diffusing through the membrane, dissolves in the filling solution and, to a small extent, reacts reversibly with water in the filling solution.
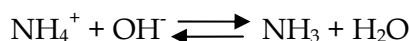
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

The relation between ammonia, ammonium ion and hydroxide concentrations in the filling solution is given by the following equation:

$$\frac{[NH_4][HO^-]}{[NH_3]} = constant$$

The electrode filling solution contains such a high ammonium chloride concentration that the ammonium ion concentration can be considered constant. Thus:

$$[HO^-] = [NH_3] \bullet constant$$

The potential of the electrode sensing element with respect to the internal reference element is described by the Nernst equation:

$$E = E_O - S \log [HO^-]$$

where:

E = measured electrode potential

E_O = reference potential

HO^- = hydroxide concentration in solution

S = electrode slope (-59.2 mV/decade)

Since the hydroxide concentration is proportional to the ammonia concentration, the electrode response to ammonia is also Nernstian.

$$E = E_O - S' \log [NH_3]$$

The reference potential, E_O is partly determined by the internal reference element which responds to the fixed level of chloride in the filling solution.

3.1.2 Electrode characterization

3.1.2.1 Temperature effect

A change in temperature will cause the electrode response to shift and change slope. *Annex 3* lists the variation of the theoretical response with temperature. At 10^{-3} M, a 1 °C temperature change gives rise to a 2% error in the measured mV-signal. Samples and standards should be at the same temperature to get a reliable determination.

3.1.2.2 Analytical procedures

The analytical procedure advised by the manufacturer of the equipment is to take 100 mL of the sample into a 150 mL beaker with the addition of 2 mL of the ISA buffer, an ionic strength and pH buffer for determination of ammonia concentration. However, taking samples with such a volume would interfere with the experiments (e.g. batch experiments were carried out with a volume of 1.6 L). Therefore, this

procedure and a procedure with only 7 mL of sample and 0.2 mL of buffer were compared. According to results in *annex 4*, the alternative procedure is also reliable and has been elected for the batch study. By taking sample of only 7 mL, we can consider the volume of the main solution to be constant during the whole experiment.

The electrode response is relatively slow at low levels of ammonia and is faster with increasing concentration (*annex 3*). Diluting the electrode filling solution with distilled water by a ratio of 1:10 improves the response time at low levels. To speed up the measurement of a sample containing less than 4×10^{-6} M ammonia (0.07 mg/L NH_3 or 0.06 mg/L as N), the electrode is first placed in an ammonia-free pH 4 buffer, then into the sample.

This measurement method is only applied in the first batch experiments, though. In column experiments we noticed a drift f the signal. This drift is caused by a modification of the filling solution during the longer run time of a column experiment. Before the breakthrough, the electrode soaks in a solution with hardly any ammonium ions, resulting in an exchange of ammonia from the filling solution to the system. Even if this leakage is insignificant on measured values, after the end of the run a consequent drift of the electrode answers with the calibrated solution is noticed. The ammonium concentration in the diluted filling solution decreases under these conditions and, as a matter of fact, the ammonium concentration in the filling solution can not be considered as being constant. Thus the regular filling solution will be used for continuous measurements from which the transfer of ammonia to the solution is insignificant.

3.1.2.3 *Effect of cations in solution*

Conditions in this study involve application of different water matrixes, which hardly differ on various cations concentrations. The cation composition of the solutions used in this electrode study is reported in *annex 6*.

In *annex 7*, it is shown that the response of the electrode does not depend on the matrix with the ammonium concentration applied in this study. Thus calibration with synthetic water with only ammonium can be applied for measuring samples with this kind of matrix.

3.1.2.4 *Electrode drift*

The daily drift of the electrode is significant (*annex 8*), and as a consequence a new calibration is done every day for the batch studies. Besides, for the continuous experiments the electrode was calibrated before the run and checked again afterwards.

3.1.2.5 *Buffer test*

Together with the electrode a pH buffer was supplied which is used for lab analyses. For continuous measurements a buffer described in the Handbook of Chemistry and Physics [21] (composition in *annex 9*) is used. The electrode response with this one is compared (*annex 10*). This shows that the buffer could be used for titration of ammonium in solution.

3.1.2.6 *Elecrode answer in dynamic conditions*

Considering the fact that the electrode was not created for online measurements the response time for the system electrode plus its module was checked for increasing and decreasing ammonium concentrations (*annex 11*). The disturbance applied in both cases is a step of 3 mg-N/L at a flow rate of 12 L/h.

The response curves are not similar and the electrode behaviour is quite different when exposed to an increasing to a decreasing concentration. Hence, this system does not seem to be fit for measurements when the ammonium concentration increases and or decreases quickly, as it occurs during the regeneration process. The system is suitable following a slow evolution of the ammonium concentration, like in an ammonium removal process with zeolite. An effective concentration error in dynamic condition of 5% is applicable to every result drawn out from column experiments.

3.2 Meter configuration

The Orion 720A meter is only used in absolute millivolt readout measurements.

In column experiments, the meter is connected to a computer by the RS232 DB9 style port (*annex 12*). Values are sent to the software Microsoft Hyperlink with the information exchange protocol (*annex 12*). Every minute the meter sends the mV value to Hyperlink and the software writes the received value in a text file. At the end of the run, the information in the text file is imported in Excel.

3.3 Ammonium titration protocol

3.3.1 Batch measurements

In a 15 mL plastic test-tube, 0.2 ml of buffer is added to 7 mL of sample or calibration solution. The diameter of the test-tubes is close to that of the electrode to get a small contact area between the aqueous solution and the atmosphere in order to prevent the exchange of ammonia between both phases.

A magnetic stirring bar shakes the solution at 1000 rpm during the measurement, which takes between 1 and 5 minutes (depending on the ammonium concentration).

Between measurements the electrode is rinsed with demineralized water and is stored in a 1 mg-N/L ammonium solution with regular buffer. When it needs to be stored for more than 5 hours, the electrode is soaked in a 1 g-N/L ammonium solution without buffer.

3.3.2 Continuous measurements

A specific electrode module has been set up for column experiments. The module is continuously fed with the water from the and with buffer. The ratio of the flow rate of buffer and the water from the column is 1:35 which is the same as the addition of buffer in batch measurements. The buffer is pumped by a peristaltic pump GISLON minipump_2. The flow rate of the pump is set according to the pump calibration curve in *annex 13*.

Any deposits (e.g. $Ca(OH)_2$) on the electrode are removed by soaking the electrode in a pH 4 buffer during a few minutes while stirring. Between two days electrode soaks in a 1 g-N/L ammonium solution without buffer.

3.4 Clinoptilolite samples

Clinoptilolite samples used in this study were received from two sources, "ZEOCEM®", a German company and "Zeolite Products®" a Dutch one. Despite both samples contain mainly clinoptilolite, colours are quite different, ZEOCEM samples are light green in water and Zeolite Products ones are more yellow, pictures are in *annex 14*. Colour discrepancy could be explained by small differences in purity or composition of the samples. Mineralogical and chemical compositions of both samples are in *annex 15* and the clinoptilolite framework in 3 dimensions is shown in § 2.1.

Of both companies sieved samples were received in different size ranges. For easy comparison between the two samples, each kind of clinoptilolite was sieved into three size groups: 0.5-1.7 mm, 0.18-0.5 mm and 0.063-0.18 mm. Each fraction is washed with demineralized water to remove turbidity and undesirable particles. At first glance Zeolite Products fractions are dustier than ZEOCEM ones.

3.5 Clinoptilolite preparation and regeneration

3.5.1 Batch studies with synthetic water

The following pretreatment or regeneration is applied in this part of the study to condition zeolites into the sodium form. About 30 grams of a sample are added to 800 ml of a 30 g/l solution of NaCl adjusted to pH 10 by NaOH in a 1 l erlenmeyer and a regular agitation is maintained overnight with a magnetic stirring bar. Then the material is washed to remove the regeneration solution and samples are dried at 100°C overnight.

3.5.2 Batch studies with raw water

In this part of study only the sieved ZEOCEM clinoptilolite with a grain size of 0.18-0.5 mm is used. The amount prepared for this study is about 15 g of dried zeolite. Impurities in clinoptilolite sample are removed by an up-flow of demineralized water in column at a flow rate of 450 BV/h until clean water, determined by visible inspection, gets out from column's outlet. Clinoptilolite naturally settles in the column to form a packed bed after stopping the flow.

Conditioning of this material is done in the column with a packed bed of zeolite material. A down-flow of a 20 g/L NaCl solution at pH 11, fixed by NaOH, is maintained during 1h30. This packed bed is then backwashed in up-flow with demineralized water for one hour. Flow rates applied during washing and conditioning are close to 350 BV/h.

3.5.3 Column studies

Material mainly used in this part is the sieved ZEOCEM clinoptilolite with a grain size of 0.18-0.5 mm. One run is done with sieved ZEOCEM clinoptilolite with a grain size bigger than 0.5 mm.

Backwash cleaning with demineralized water is done in the same way that in batch studies with raw water. Besides a backwash is done after each run to prevent biofouling or any fouling in the column.

The reference conditioning consists in using a down-flow with a 20 g/L NaCl solution at pH 11, fixed by NaOH, with a flow rate of 350 BV/h during 1h30. For reconditioning he time interval was not fixed to 1h30 but it was kept running until the ammonium concentration was below 0.02 mg-N/L) in column outlet. After every zeolite conditioning, the packed bed is rinsed by fowling demineralized water during 30 min.

However two other treatments are tested:
- Reference reconditioning followed by heat treatment at 600°C over 1h30 and then followed by backwash cleaning with demineralized water.
- Reference reconditioning followed by an acid-wash (2 L; 0.005 M HNO_3 in the column with a flow rate of 150 BV/h) and then followed by backwash cleaning with demineralized water.

3.6 Raw water samples

This project is sponsored by two companies, WLB Amsterdam and Hydron. Raw water samples are taken from two drinking water plants. WLB Amsterdam's plant is fed with surface water from Loosdrechtse Lake and Hydron's plant treats ground water from Ridderkerk (*annex 16*).

Plastic 20 L jerry cans are used to transport the water samples. The storage time of the samples is less than 2 days.

In the case of Amsterdam's water, the samples for batch studies are taken from the pumps (ref. w1110 plv-sb-001) after the coagulation-flocculation-precipitation process and before the first rapid sand filter. For column studies, samples are taken from the pumps just after the first rapid sand filter. This part of WLB Amsterdam's process is shown in *annex 17* and the compositions of both samples are in *annex 18*.

As the ammonium concentration in the water are currently quite low, ammonium concentrations in the waters before and after the sand filter are respectively raised to 1.5 mg-N/L and 0.16 mg-N/L with NH_4Cl before starting experiments.

Hydron's water samples are taken from the pipe (ref. PRKFC99A) after the first rapid sand filter, part of the process is drawn in *annex 19*. The ammonium level is not raised because the initial concentration in water is around 3 mg-N/L. Composition of the water is in *annex 20.*

3.7 Batch studies with synthetic water

3.7.1 Aim

As results from literature are different as a result of different sources of clinoptilolite, pretreatment and water conditions, the purpose is to quantify the ammonium removal of both clinoptilolite samples and then compare them with values in previous publications.

A kinetic and an equilibrium study are carried out to determine whether clinoptilolite is suitable to remove ammonium at low concentrations and if this is the case, which one of the clinoptilolite samples presents the greatest removal capacity and highest removal rate.

Furthermore two main effects on ammonium removal are checked:
- The grain size of the clinoptilolite.
- The initial ammonium concentration in aqueous solution.

3.7.2 Experimental

Batch adsorption isotherms and kinetic evolution are determined in the same experiments. Weighted amounts, close to 1 g, of clinoptilolite are introduced into six 2 L erlenmeyers, to which 1.6 L of ammonium chloride solutions (in demineralized water) ranging between 0.05 and 10 mg-N/L are added. The solutions are stirred with a magnetic stirring bar at 500 rpm for 300 min and 10 mL samples are taken periodically for measurement of aqueous-phase ammonium concentration. The temperature of work ranges between 19 and 21°C.

As only less than 10 mL of sample is needed for the measurements, we assume that the total volume of the aqueous solution (>1 L) is affected insignificantly by sampling during these batch experiments. Taking 5 samples represents a maximum volume variation of 5%.

In one experiment other cations are added to get an idea of the influence of the water matrix on ammonium adsorption. Concentrations for this experiment are given in table 8.

Table 8. Composition of synthetic water

Element	Concentration
NH_4^+	0.05 to 0.8 mg/l
Na^+	60 mg/l
K+	5 mg/l
Mg^{2+}	15 mg/l
Ca^{2+}	70 mg/l
pH	7.5

The contact time for this experiment is 90 minutes. Only the ZEOCEM clinoptilolite sample with a size range of 0.18-0.5 mm is used.

3.8 Batch studies with raw water

3.8.1 Aim

Ammonium removal behavior with raw water is checked in this part. Besides these experiments represents a possible process application which would be to dose conditioned clinoptilolite between the pumps and the rapid sand filter. A kinetic study is done with different weighted amount of clinoptilolite.

3.8.2 Experimental

Weighted amounts, from 1 g to 4 g, of clinoptilolite are introduced into 2 L erlenmeyers, with 1 L of raw water. The solutions are stirred with a magnetic stirring bar at 500 rpm for 50 min and 7 mL samples are taken periodically for measurement of aqueous-phase ammonium concentration. The temperature ranges between 20 and 22°C.

3.9 Column studies

3.9.1 Aim

Dynamic studies represent a second step in such a process development. Operation and regeneration parameters are investigated. Ammonium removal with clinoptilolite from raw water and synthetic water is determined and compared to check whether synthetic water with a specific ionic matrix can be used as a model of raw water.

Dynamic studies are also, in a small scale, models of filters which would be a possible process application for ammonium removal with clinoptilolite.

3.9.2 Experimental

For measurement of the adsorption kinetics under dynamic conditions, a glass column, with an inside diameter of 1.8 cm is employed. Fixation system and filters are in stainless steel, the equipment for the column is made of Teflon to resist high or low pH conditions. The top of the column is equipped with a Teflon filter with larger pores (0.3-0.5 mm) to allow fines and undesirable particles to leave when backwashing. The

bottom of the column contains a metal filter (0.06-0.09 mm) on the top of a Teflon one to prevent any zeolite leakage during process.

The zeolite bed weighted amount, height and volume in the column are close to 15 g, 6.5 cm and 16 cm³, respectively. Three diaphragm pumps (Gamma5 - *ProMinent Verder*) feed the column with stock solution. The flow rate is controlled with a "micro oval" flow controller and pumps are controlled by a computer to get a constant flow rate. The temperature is ranges between 20 and 22°C.

After every run the whole system, except the column and the electrode, is rinsed with 0.5 L of 10% HNO_3 solution to clean it. With raw water and synthetic water (with calcium inside), a white deposit of $Ca(OH)_2$ is observed on the inner walls of the system. The system is then rinsed with demineralized water until the pH of the demineralized water is reached at the outlet. Furthermore, this cleaning method prevents biological development in the system.

The scheme of the system is shown in Fig. 10.
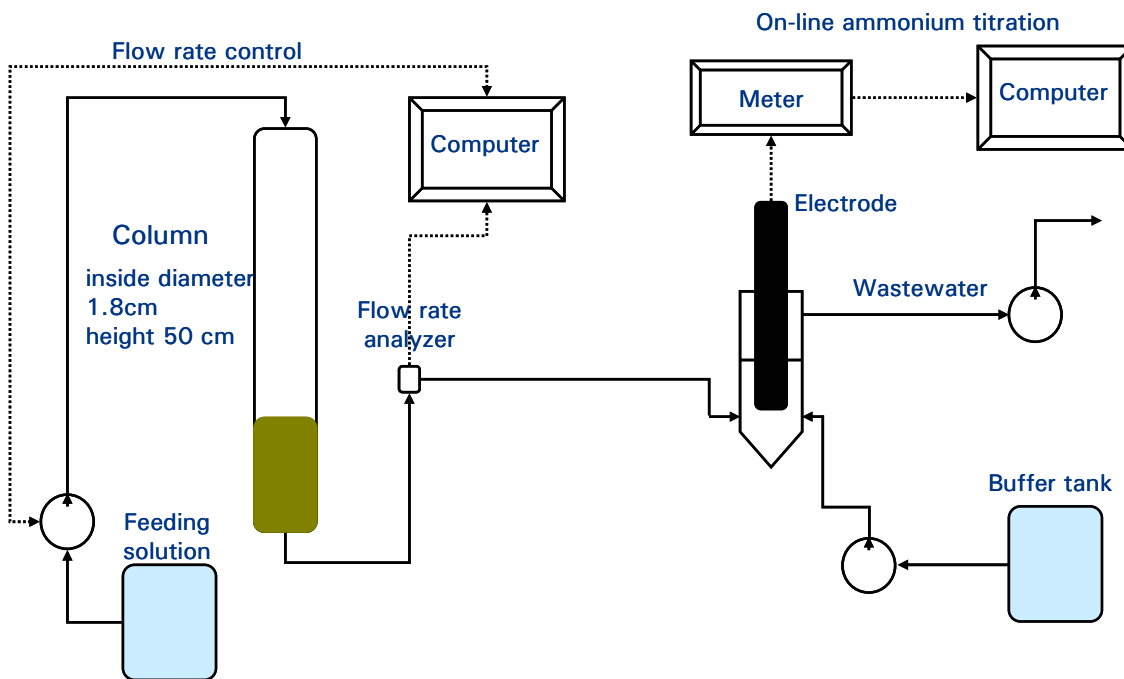
Fig. 10. Scheme of the equipment for the column experiments

3.10 Investigation on regeneration

3.10.1 Aim

Regeneration is not a subject of a deep research in this study, however get an overview of what happening in the first bed volumes of regeneration and also in the whole dynamic regeneration can well orient the ion exchange understanding and also the recommendation for future experiments.

3.10.2 Experimental

Two batch regeneration experiments are done with a packed bed loaded with ammonium. The bed of clinoptilolite is rinsed with 30 mL of demineralized water to remove traces of a previous solution and then dried with a flow of air gas until any

water goes out of the column. The first experiment consists in releasing ammonium from the clinoptilolite by soaking the bed during one hour in 7 mL of the regeneration solution (20 g/L NaCl at pH 12 fixed by NaOH) and repeat it 5 times. The other experiment is to rinse the bed with 7 mL of the regeneration solution and then fill the bed with 7 mL and let the clinoptilolite soak during 24h to check if almost all ammonium ions on the clinoptilolite can be released in such a way.

With such a volume of 7 mL of regeneration solution, clinoptilolite and solution set an homogenous bed without water above the bed. The ammonium concentration is determined in all samples. After every batch regenerations, the bed is completely regenerated in dynamic condition for future experiments.

Although values from the electrode are not accurate to follow precisely a huge variation of the ammonium concentration, the electrode gives an overview of the ammonium released from clinoptilolite during dynamic regeneration. Furthermore the mass balance can be compared with this determined in the run before the regeneration. Regenerations are realized after the runs with Amsterdam's water. After the runs with Amsterdam's water, two dynamic regenerations (one in up-flow and one in down-flow) are done with a flow rate of 350 BV/h and one with a down-flow with a rate of 188 BV/h with a 20g/L NaCl solution and the pH is fixed at 12 by NaOH.

3.11 Summary of experiments

Table 9 Summary of experiments

Kind of experiment	Clinoptilolite	Ammonium concentration as mg-N/L	Water matrix	Process conditions	Results in §
Batch	ZOECEM all sizes	0.05 to 10	None	About 1g of zeolite in 1.6 L; stirring 3h	4.1
Batch	Zeolite Products all sizes	0.05 to 10	None	About 1g of zeolite in 1.6 L; stirring 3h	4.1
Batch	ZEOCEM 0.18-0.5 mm	0.05 to 0.8	Ca = 70 mg/L Na = 60 mg/L K =5mg/L Mg = 15mg/L	About 1g of zeolite in 1.6 L; stirring 90 min	4.1
Batch raw water	ZEOCEM 0.18-0.5 mm	1.5	Amsterdam water see *annex 18*	1g 2g 3g 4g in 1L; stirring 50 min	4.2
Batch raw water	ZEOCEM 0.18-0.5 mm	3	Hydron water see *annex 20*	2g 3g 4g in 1L; stirring 50 min	4.2
Batch regeneration	ZEOCEM 0.18-0.5 mm	None	20 g/L NaCl pH 10 NaOH	7 mL; soaking 1h repeated 5 times	4.4

Batch regeneration	ZEOCEM 0.18-0.5 mm	None	20 g/L NaCl pH 10 NaOH	7 mL; soaking 24h	4.4
Column	ZEOCEM 0.18-0.5 mm	~8	None	15 g of clinoptilolite 5 m/h	4.3.1
Column	ZEOCEM 0.18-0.5 mm	~9	Ca = 100 mg/L Na = 60 mg/L K =5mg/L Mg = 15mg/L	15 g of clinoptilolite 5 m/h	4.3.1
Column	ZEOCEM 0.18-0.5 mm	0.16	Amsterdam water see *annex 18*	15 g of clinoptilolite 5 m/h	4.3.2
Column Regeneration after Amsterdam's run	ZEOCEM 0.18-0.5 mm	None	20 g/L NaCl pH 10 NaOH	15 g of clinoptilolite 2.5 m/h Up-flow	4.4
Column regeneration after Amsterdam's run	ZEOCEM 0.18-0.5 mm	None	20 g/L NaCl pH 10 NaOH	15 g of clinoptilolite 2.5 m/h Down-flow	4.4
Column regeneration after Amsterdam's run	ZEOCEM 0.18-0.5 mm	None	20 g/L NaCl pH 10 NaOH	15 g of clinoptilolite 1.75 m/h Down-flow	4.4
Column	ZEOCEM 0.18-0.5 mm	3	Hydron water see *annex 20*	15 g of clinoptilolite 5 m/h	4.3.2
Column	ZEOCEM 0.18-0.5 mm	3	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	ZEOCEM 0.18-0.5 mm	0.2	Ca = 100 mg/L Na = 60 mg/L K =5mg/L Mg = 15mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	ZEOCEM 0.18-0.5 mm	1.5	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	ZEOCEM 0.5-1 mm	3	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	Acid washed (0.005M HNO₃) ZEOCEM 0.18-0.5 mm	3	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3

Column	Heat treated (600 °C 1h30) ZEOCEM 0.18-0.5 mm	3	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	ZEOCEM 0.18-0.5 mm	3	Ca = 50 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 5 m/h	4.3.3
Column	ZEOCEM 0.18-0.5 mm	3	Ca = 100 mg/L Na = 60 mg/L K =6mg/L Mg = 18mg/L	15 g of clinoptilolite 2.5 m/h	4.3.3

4 Results and discussion

4.1 Batch studies with synthetic water

4.1.1 Kinetic aspect

The amount of ammonium accumulated on the clinoptilolite is calculated by the following expression as the difference between the initial ammonium concentration in solution and that remaining in solution.

$$Q = \frac{(C_0 - C)q}{M.C_0} \qquad (1)$$

where:
Q (mg-N/g) is the amount of ammonium absorbed
C_0 (mg-N/l) represents the initial ammonium concentration
C (mg-N/l) represents the ammonium concentration in solution.
q (mg) is the amount of ammonium added into the solution
M (g) is the mass of zeolite

Results determined by using Eq. (1) are plotted vs. time in chart 1. This chart shows the results for an initial ammonium concentration of 2 mg N/l, but similar curves are obtained for the other concentrations which are reported in *annex 21.*
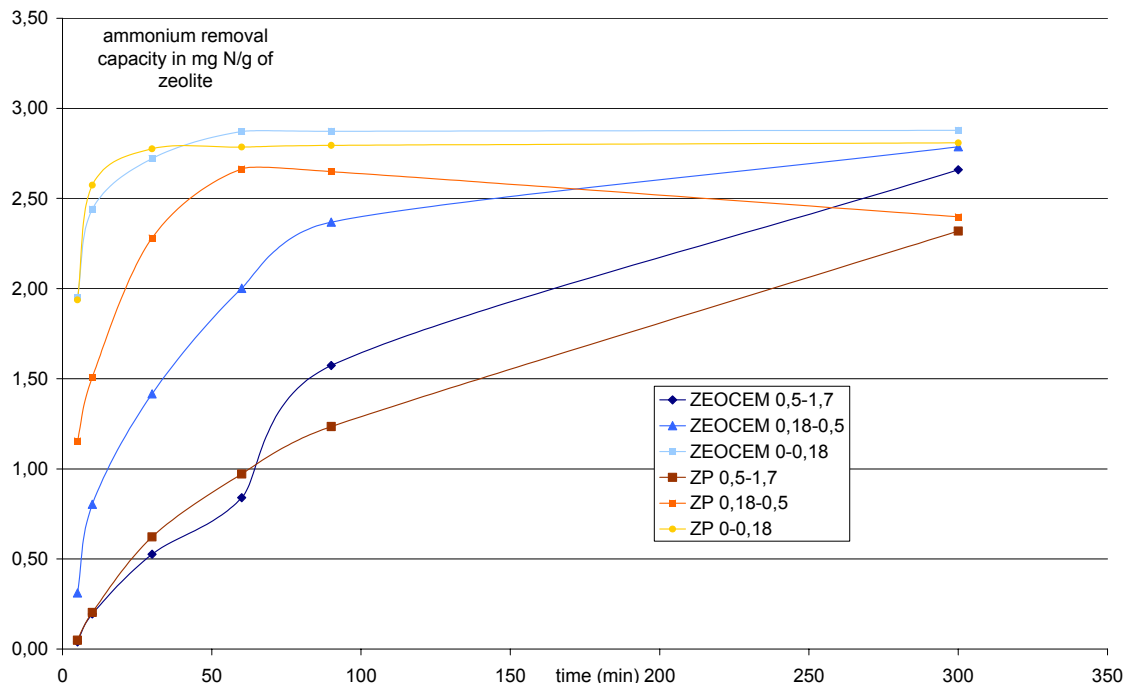

Chart 1. Kinetic of ammonium removal with initial 2 mg-N/L ammonium concentration in solution. (ZP =Zeolite Products)

The curves for the different sizes show that ammonium removal is faster with the smaller grains, and a high removal capacity is obtained quickly. For smaller grain sizes more surface area is available to absorb ammonium.

Apparently equilibrium between the solid and the aqueous phase is not reached, except for the smallest grain size.

Neveu *et al.* [22] and Conney *et al.* [13] concluded that intraparticular diffusion is the mechanism which controls ion exchange onto clinoptilolite. Hence, all parameters influencing film diffusion such as solution stirring, can be neglected. On the other hand contact time between the zeolite and the solution; and the grain size appear as significant parameters for ion exchange effectiveness onto clinoptilolite.

4.1.2 Equilibrium aspect

Results determined by using eq. (1) at t=300 min. are plotted vs. the initial ammonium concentration in solution (chart 2).
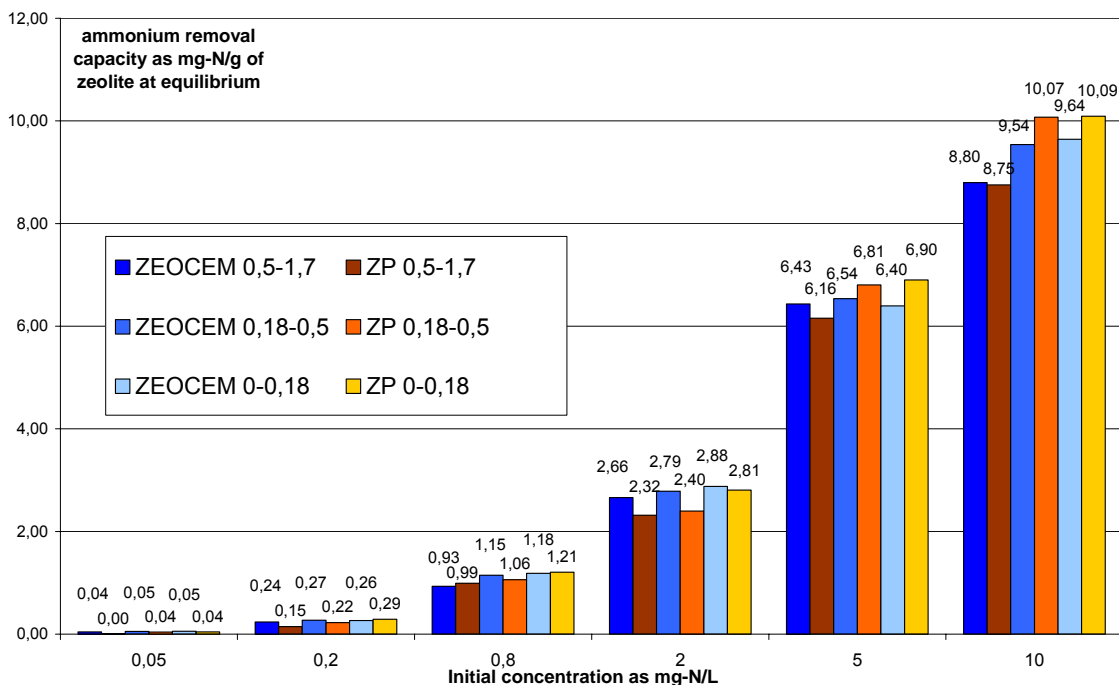

Chart 2. Ammonium removal capacities at t=300 min.

The first conclusion from chart 2 is that an increasing ammonium concentration in the aqueous phase results in an increase of ammonium removal capacity by clinoptilolite.

Except for the highest concentrated solution, where the smallest grains sizes show a higher removal capacity, there are no significant differences between the various sizes and kinds of clinoptilolite for the ammonium removal values after 300 minutes of shaking.

Values obtained for the 10 mg-N/L solution (removal capacity of ammonium: 8.75-10.1 mg N/g) are quite similar to those found in literature related to batch studies: 8.96 mg N/g [3] and 8.54 mg N/g [19].

According to Weatherley and Mildinovic [23] the Langmuir uptake model provides a slightly more consistent fit to the data compared with the Freundlich one. The Langmuir isotherm relates Q_e (mg of ammonia absorbed per gram of clinoptilolite) and C_e (the equilibrium ammonium concentration in solution) as shown in Eq. 2

$$Q_e = \frac{KbC_e}{1+KC_e} \qquad (2)$$

Rearranging the Langmuir equation to get a linear expression, gives Eq. 3

$$\frac{1}{Q_e} = \frac{1}{KbC_e} + \frac{1}{b} \qquad (3)$$

K and b are the Langmuir's parameters. Hence, these parameters can be determined by plotting $1/C_e$ versus $1/Q_e$ (A linear evolution between data is expected to evaluate as accurate as possible the Langmuir's parameters).

The Freundlich model relates the uptake of solute onto exchanger to the solution concentration as shown in Eq. 4. The linear expression is given in Eq. 5.

$$Q_e = kC_e^{1/n} \qquad (4)$$
$$\log(Q_e) = \log(k) + 1/n \log(C_e) \qquad (5)$$

K and n are the Freundlich's parameters.

As for the Langmuir model, data plotted in such a scale should show linearity.

Adsorption isotherms are plotted for the three ZEOCEM® grain sizes in charts 3 and 4. In chart 3 Langmuir's equation 3 and in chart 4 equation 5 of the Freundlich model is used.

Isotherms are absolutely not linear, which means that the Langmuir or Freundlich parameters would be determined with low accuracy.

There may be two explanations for this non linearity:

- The Freundlich and the Langmuir models could be considered as insufficient to describe the system.
- The equilibrium may not be reached between the solid and aqueous phase.

Kinetic results of batch experiments (§ 4.1.1) show that equilibrium is almost reached in 300 minutes for the smallest grain sizes and for solution with a concentration lower than 5 mg-N/L. Hence, the Langmuir model fits correctly to both isotherms. Results are summarized in table 10 and in charts 5 and 6.
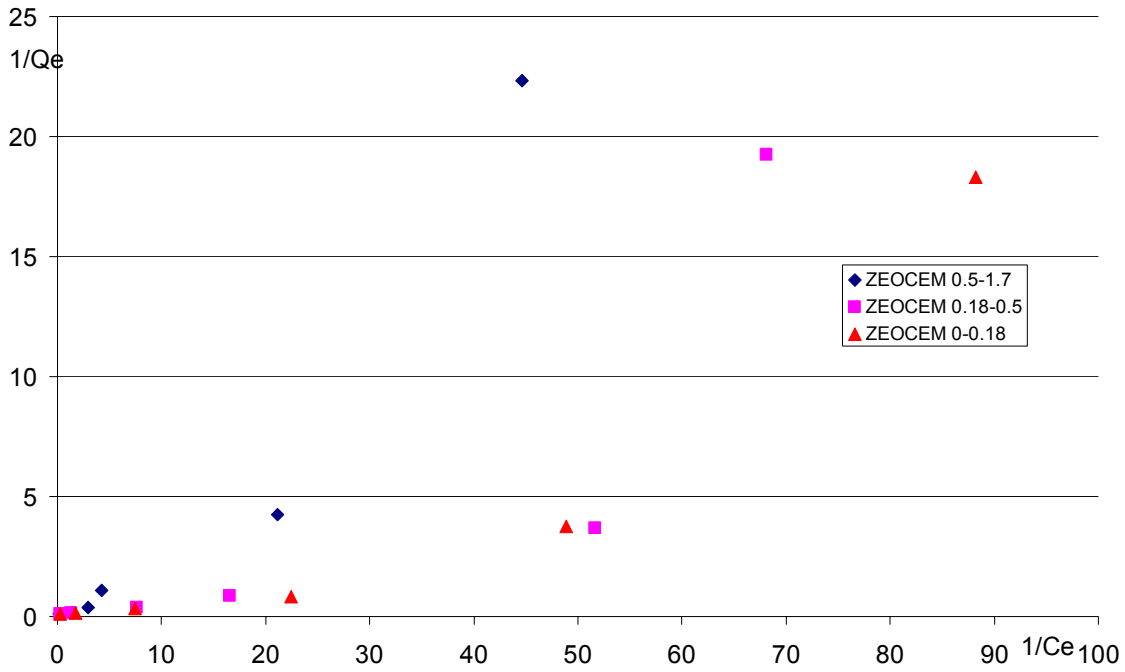
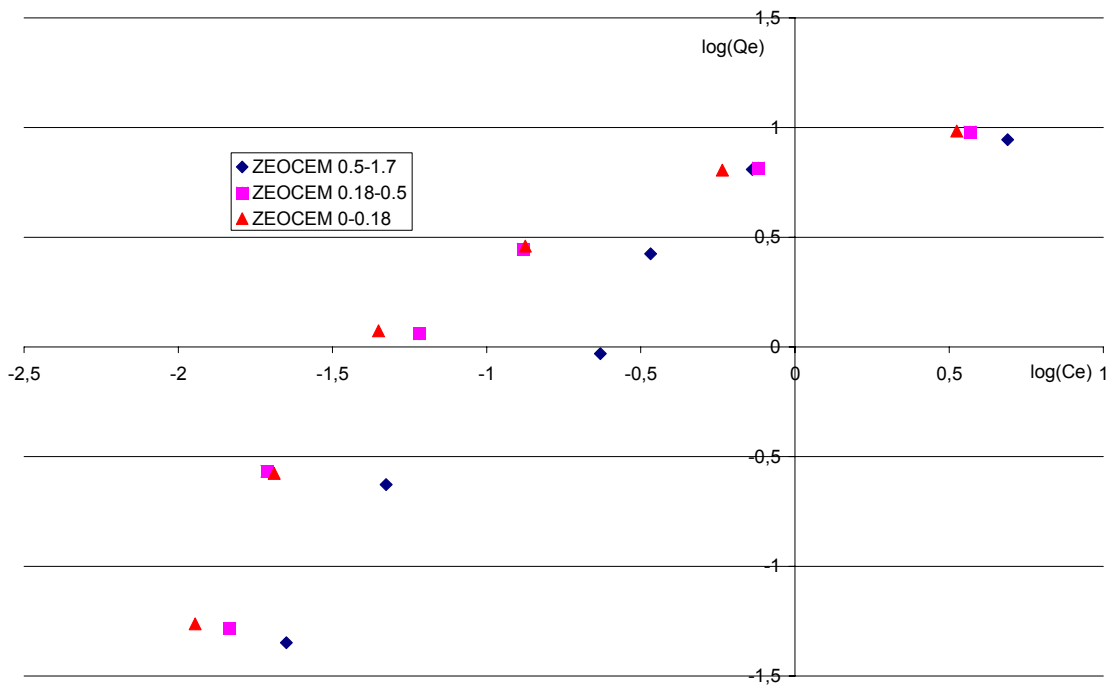Chart 3. Adsorption isotherms for the three ZEOCEM grain sizes, to determine Langmuir parameters.

Chart 4. Adsorption isotherms for the three ZEOCEM grain sizes, to determine Freundlich parameters.
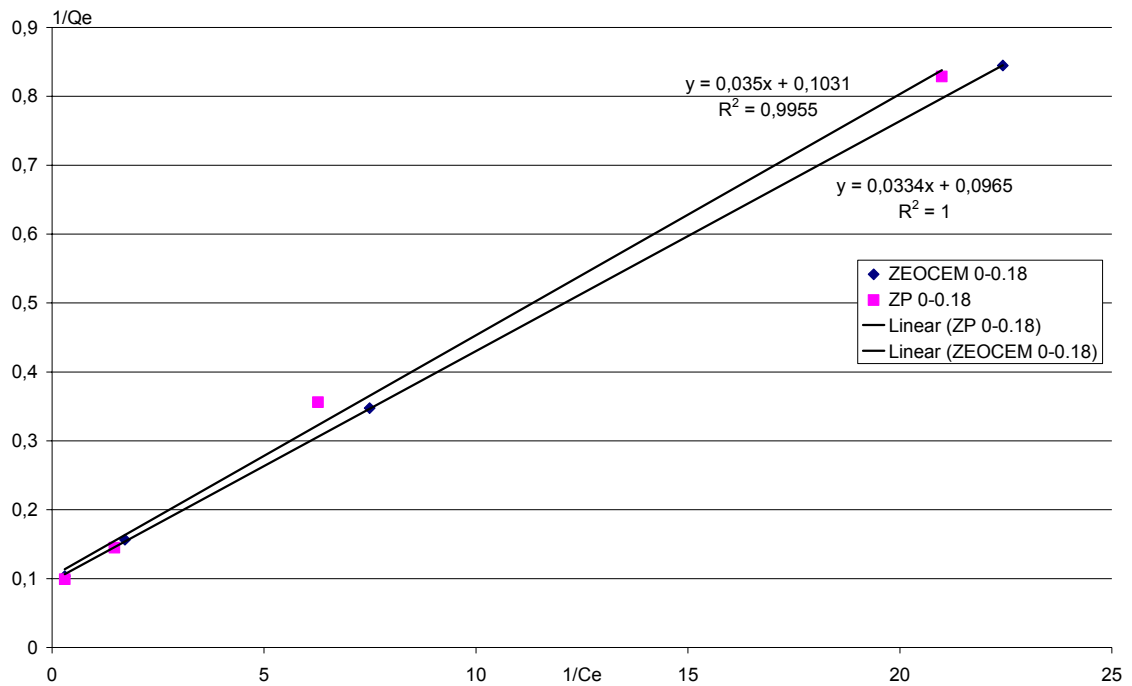
Chart 5. Adsorption isotherms for both clinoptilolite with smaller grain sizes, to determine Langmuir parameters.

Table 10. Values of Langmuir parameters for clinoptilolite smallest grain sizes

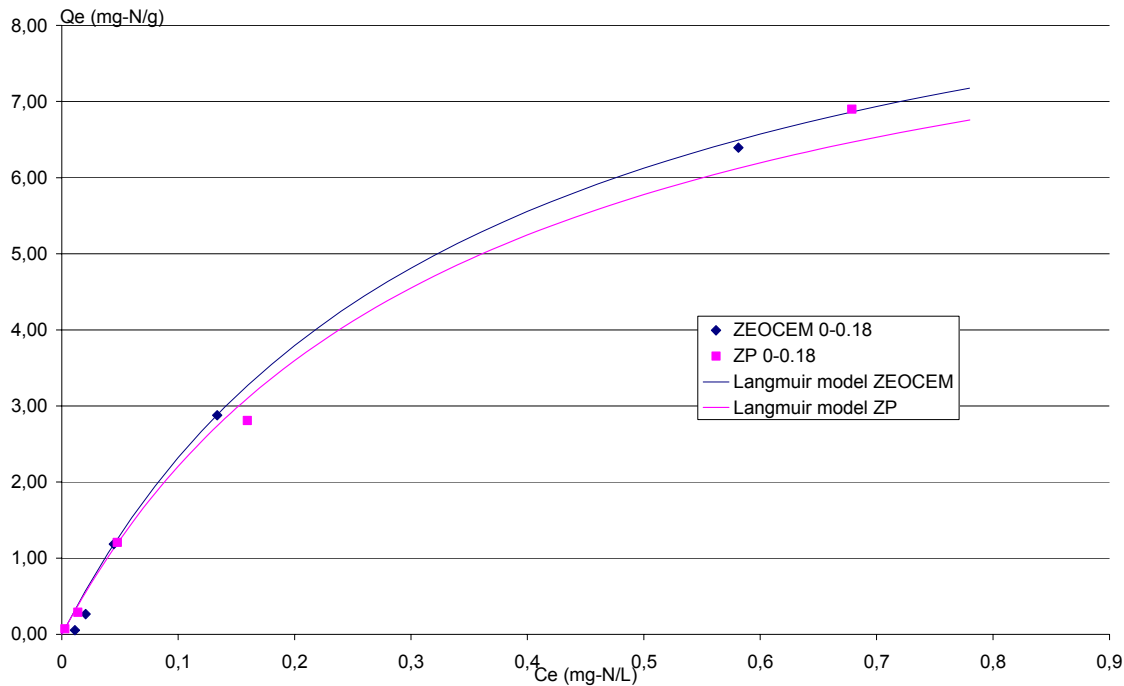| Parameters	ZEOCEM 0-0.18	ZP 0-0.18
b	10.36	9.70
K	2.89	2.94
R^2	~1	0.9955

Chart 6. Adsorption isotherms for both clinoptilolite with smaller grain sizes fitted to the Langmuir uptake model.

The fact than the size of the grains determines whether the model can be used emphasizes that intraparticular diffusion is the limiting factor in ammonium removal. In bigger grains size more time is needed for ammonium ions to reach the farthest pores inside the clinoptilolite, than for smaller grain sizes.

Even though the contact time of 300 minutes was not sufficiently long to reach equilibrium for all clinoptilolite samples, it allows a comparison between sources and sizes of clinoptilolite samples. In any case results are not far from those in previous studies.

In order to evaluate overall effectiveness of ammonium removal by different clinoptilolite samples, the percentage of ammonium removed from solution is plotted versus the initial concentration in chart 7.

Chart 7 allows interpretation of the removal capacity for a clinoptilolite sample in a wide range of ammonium concentrations. The two clinoptilolite samples with the smallest grain size give the widest area in the graph, so they appear as more suitable to work in a wide concentration range. Unfortunately, such small grains cause certain hydraulic problems and are therefore not often used in water treatment. The ZEOCEM sample with a grain size of 0.2-0.5 mm seems to be a good compromise between size and ammonium removal. Therefore almost all following experiments are carried out with this clinoptilolite sample.
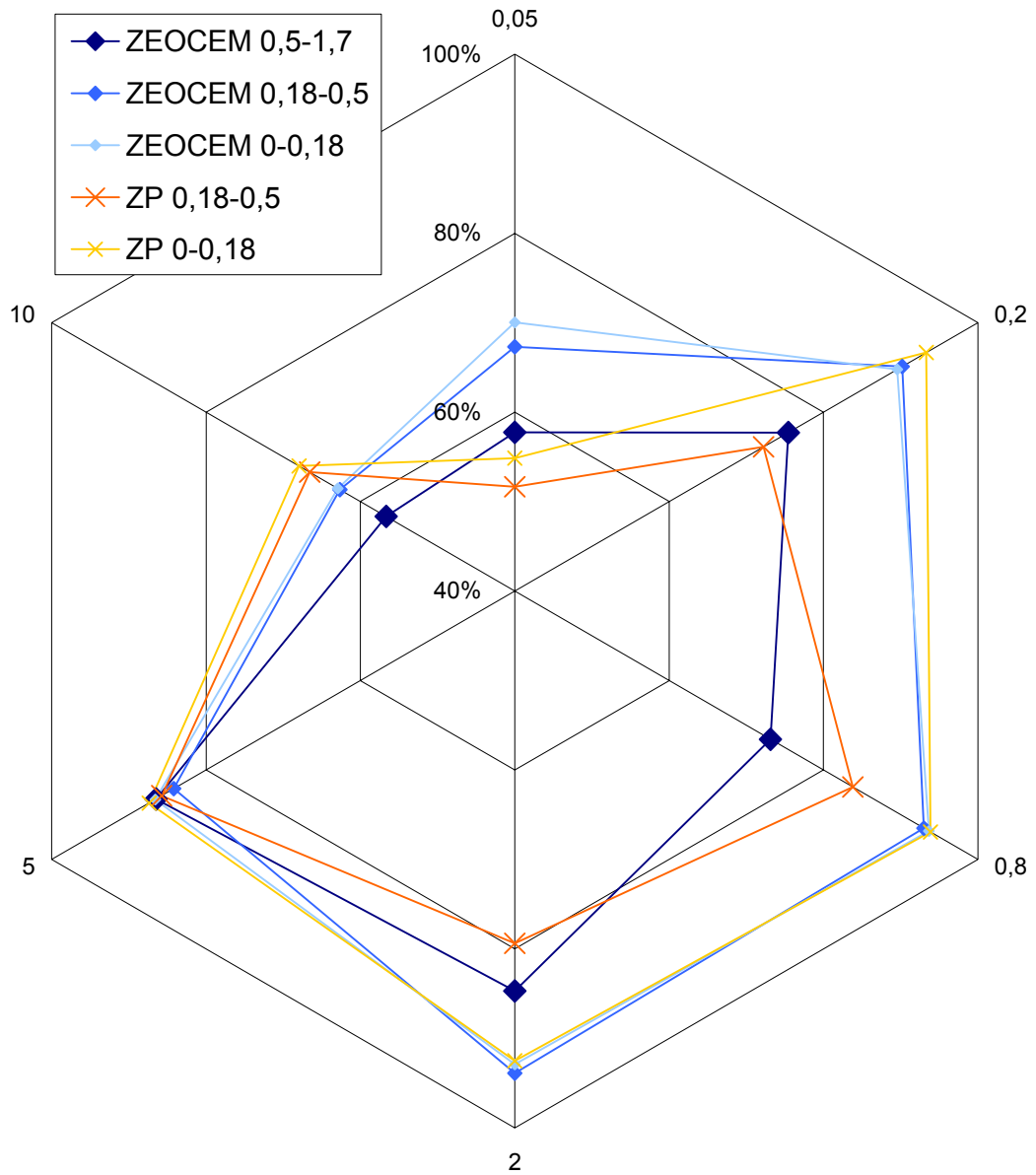
Chart 7. Percentage of ammonium removed from solution with different initial concentrations.

4.1.3 Competition with other cations

Chart 8 reports values of ammonium removal in the experiment with synthetic water (Table 8) in which competition between ammonium and other cations is expected, resulting in a decrease of ammonium removal.
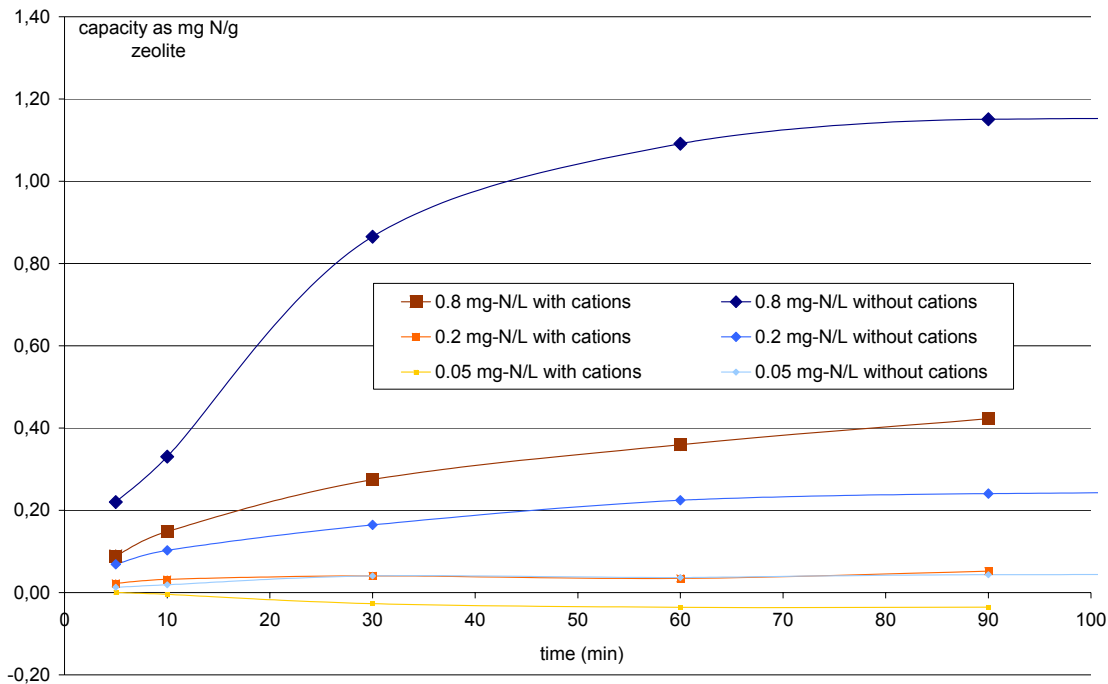
Chart 8. Ammonium uptake in synthetic water with and without ion matrix.

When comparing the results of experiments with and without other cations, the removal of ammonium decreases considerably when other cations are present. For an initial ammonium concentration of 0.8 mg-N/l the capacity is 0.48 mg N/g, a loss of 65% compared with the removal capacity of ammonium without other cations. For 0.2 mg-N/l a capacity of 0.05 mg-N/g is obtained which represents a loss of 80%. For the lowest concentration there is even a release of traces of ammonium held on the zeolites. It raises some questions:

- The activation and regeneration method is not the best one, as traces of ammonium are still adsorbed to the zeolite and will be released when the ammonium concentration is very low compared to concentrations of other cations. This point is explained by the fact that regeneration was done as a batch process, in which some ammonium traces may have remained on the clinoptilolite. Thus, in further experiments the samples were regenerated in a continuous column process (§ 3).
- In previous studies [2-3] the ammonium sorption capacity of the clinoptilolite, estimated under dynamic conditions, is twice that under static conditions. In our case (lower NH_4^+ concentrations), column experiments should reveal whether the effect of other cations is less pronounced in dynamic conditions too. We expect it will be less pronounced, because in static conditions the ammonium concentration decreases while the concentration of alkali and alkaline earth ions remains almost the same while in dynamic conditions the ammonium feed concentration ion is constant.

4.2 Batch studies with raw water

4.2.1 *Results with WLB Amsterdam water*

The results of experiments are shown in chart 9 as the percentage of ammonium removed from solution versus the time.
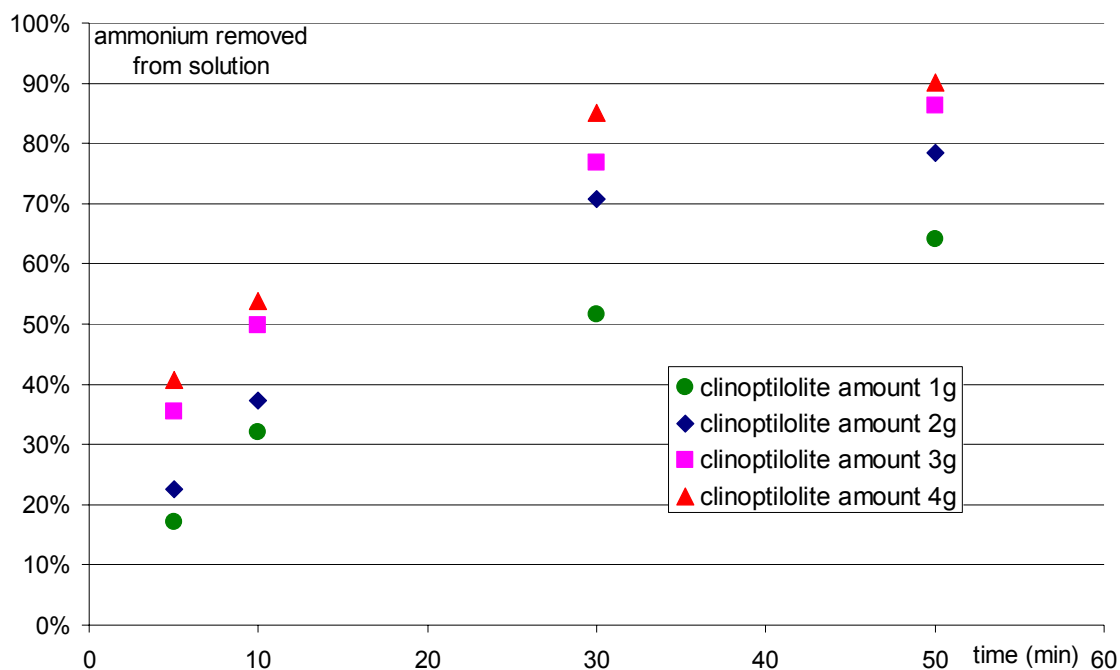

Chart 9. Kinetic of ammonium removed in solution for Amsterdam water with different amounts of clinoptilolite

Obviously equilibrium is not reached between both phases, but that was not the purpose of this experiment. The more clinoptilolite is added to the solution, the more ammonium ions are removed after a certain time interval.

Guideline to a possible soaking application of clinoptilolite in the treatment plant of WLB Amsterdam is to remove 75% of ammonium from solution with a contact time shorter than 10 minutes. Results are far from such a removal efficiency and even if a contact time of 30 minutes could be applied, more than 3 kg of zeolite per cubic meter of water is needed. Knowing that about 4000 m³/h is treated it would mean that 12 000 kg per hour of clinoptilolite or 168 tonnes a day would be needed. Such a process does not appear as a smart possibility.

The ammonium removal by the solid phase is plotted versus time in Chart 10.

A loss of 63% is observed due to competition in raw water in comparison to results determined with synthetic water without competition for an initial ammonium concentration ranging between 1.5 and 2 mg-N/L.
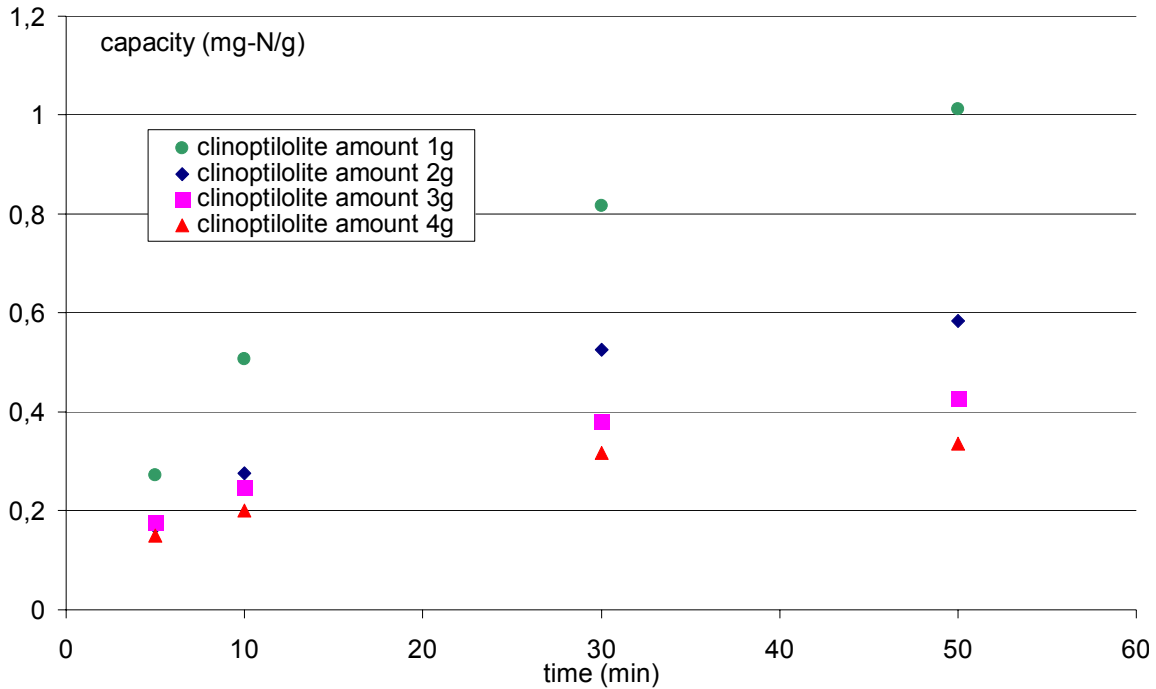
Chart 10. Evolution of removal capacities with Amsterdam water

4.2.2 Results with Hydron water

The results of the experiments are plotted in Chart 11 as the percentage of ammonium removed from solution versus the time.
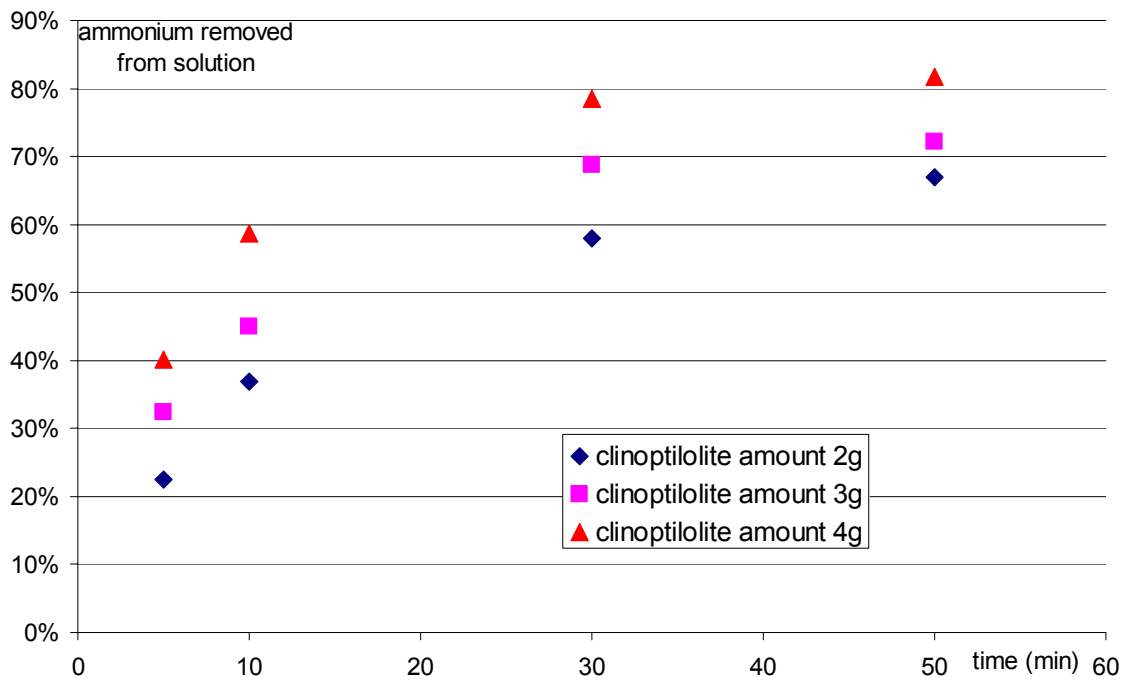

Chart 11. Kinetic of ammonium removed in solution for Hydron water with different amounts of clinoptilolite

Conclusions drawn from chart 11 for Hydron water are similar than the conclusion for Amsterdam water; more than 3 g of clinoptilolite is needed to reach an ammonium decrease in solution of 75%, with a contact time of 30 minutes. The efficiency loss is around 60% in comparison to water without competition.

4.3 Column studies

4.3.1 First column experiments

Two runs are done with synthetic water prepared with only NH_4Cl. The aim is to check the stability of the measurement system and further to expose the zeolite bed to two cycles (run and regeneration) to prevent changing removal capacity due to first cycles in next experiments. The results are plotted in Chart 12.
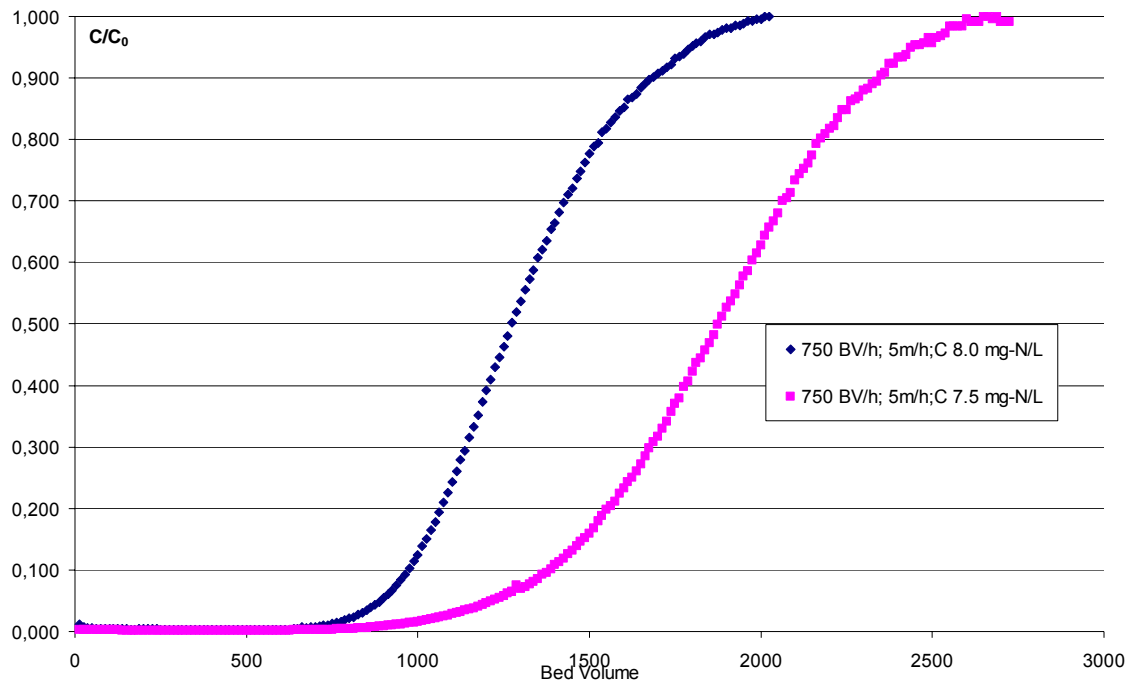
Chart 12. Breakthrough curves of ammonium removal in synthetic water without competition

From these breakthrough curves the amount of ammonium adsorbed on clinoptilolite during the two experiments is calculated with the following equation 6:

$$Q_{\Delta t} = \frac{C_{t+\Delta t} - C_t}{M} \Delta t.F \qquad (6)$$

where:

$Q_{\Delta t}$ (mg-N/g) is the amount of ammonium adsorbed during a time interval

C_t (mg-N/L) is the ammonium concentration at time equals t

$C_{t+\Delta t}$ (mg-N/L) is the ammonium concentration in solution at time t plus a time interval Δt

F (L/h) is the flow rate of solution

M (g) is the mass of zeolite in the packed bed

Δt (h) is the time interval

Considering the whole zeolite bed is loaded with ammonium at the end of the run, the maximum removal capacity can be calculated by integration of equation 6 over the whole duration of the experiment. It can be considered that the zeolite bed is maximally loaded with ammonium when the outlet concentration is equal to the feed concentration. Values determined for 8.0 mg-N/L inlet and 7.5 mg-N/L inlet are respectively 10.9 mg-N/g of clinoptilolite and 14.8 mg-N/g of clinoptilolite. The increase of removal capacity between both runs is interpreted as the effect of the first cycles of clinoptilolite as in [2,4,8,13] .The possible effect of the concentration difference between the two feed concentrations is opposite to the evolution noticed here. Increasing the ammonium concentration involves an increase of the ammonium removal capacity (§ 4.1.2).

During the first bed volumes the maximum ammonium sorption by the clinoptilolite is reached when the minimum of ammonium concentration is observed in the column outlet. Between both runs the sorption effectiveness is at the same level until the breakthrough occurs.

Then experiments with the same zeolite bed are done with synthetic water including an ion matrix, to evaluate the loss of removal capacity due to such a matrix. Ammonium concentrations are close to those in the experiments described above and the water matrix is described in table 11. Breakthrough curves are shown in Chart 13.

Table 11. Composition of synthetic water

Parameter	Value
NH_4^+	9 or 8.7 mg/l
Na^+	60 mg/l
K+	5 mg/l
Mg^{2+}	15 mg/l
Ca^{2+}	100 mg/l
pH	7.3

Maximum sorption capacities determined for the feed concentrations of 9 mg-N/L and 8.7 mg-N/L are respectively 1.6 mg-N/g and 1.8 mg-N/g. Still, it seems that the zeolite bed has not reached stable removal capacity after 3 cycles, because the lower feed concentration (8.7 mg-N/L) gives the highest removal (1.6 mg-N/g). However the noticed difference is lower than previously and allows, with a certain approximation, to draw up some conclusions.

The decrease of removal capacity due to the water matrix is shown in table 12

The matrix effect leads to a reduction of the three parameters of ammonium removal in dynamic conditions:
- the number of bed volumes before the breakthrough;
- the slope of the curve;
- the ammonium removal capacity;

Obviously the ammonium feed concentration or the ratio of ammonium and other cations influences also ammonium removal and is checked further (§ 4.3.2 and § 4.3.3.1).
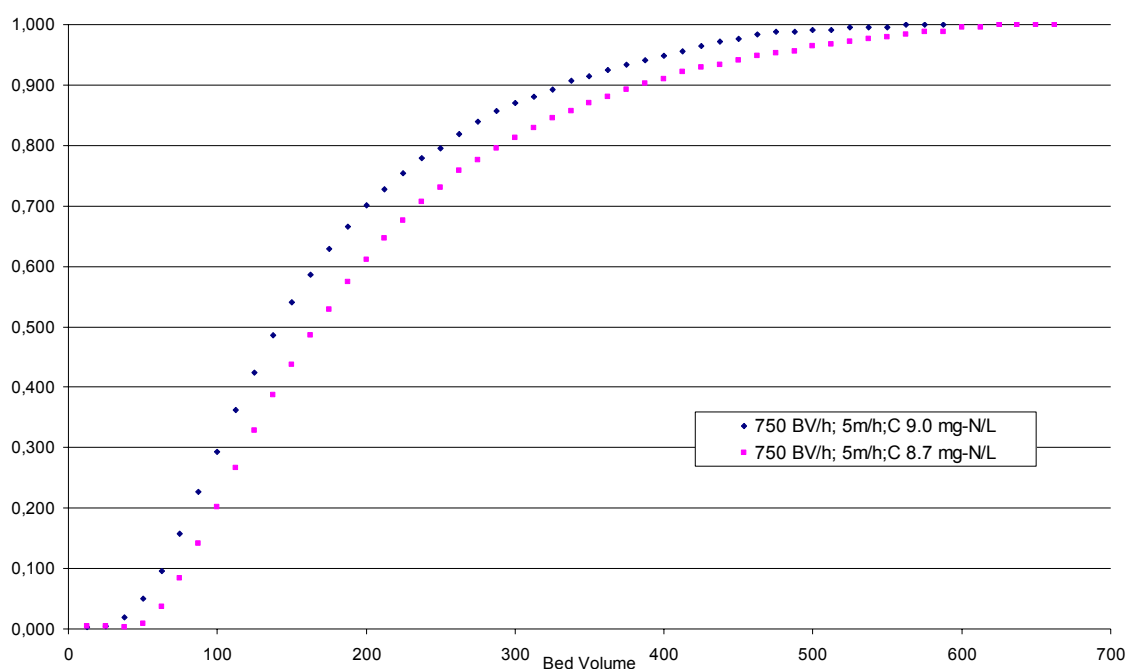
Chart 13. Breakthrough curves of ammonium removal in synthetic water with competition

Table 12. Decreases due to the matrix application

Parameter	Without competition	With competition	Loss
BV before breakthrough (0.1 mg-N/L)	960 BV	60 BV	93%
Number of BV to reach the feeding concentration after breakthrough	1600 BV	600 BV	63%
Global removal capacity	14.8	1.8	93%

4.3.2 Results with raw water

The composition of the raw water from WLB Amsterdam and from Hydron Zuid Holland are shown in *annex 18 and 20*. The concentration of ammonium is higher in water from Hydron. Also the concentration of others cations is higher in this water

A small variation of the ammonium concentration was done with both waters to observe how it influences the ammonium removal, and Hydron water has been also used as a comparison point to synthetic water with the same ion matrix. The dynamic conditions are the same as in the experiments described in § 4.3.1., 5 m/h (around 800 BV/h) and the temperature ranged between 21 and 23 °C

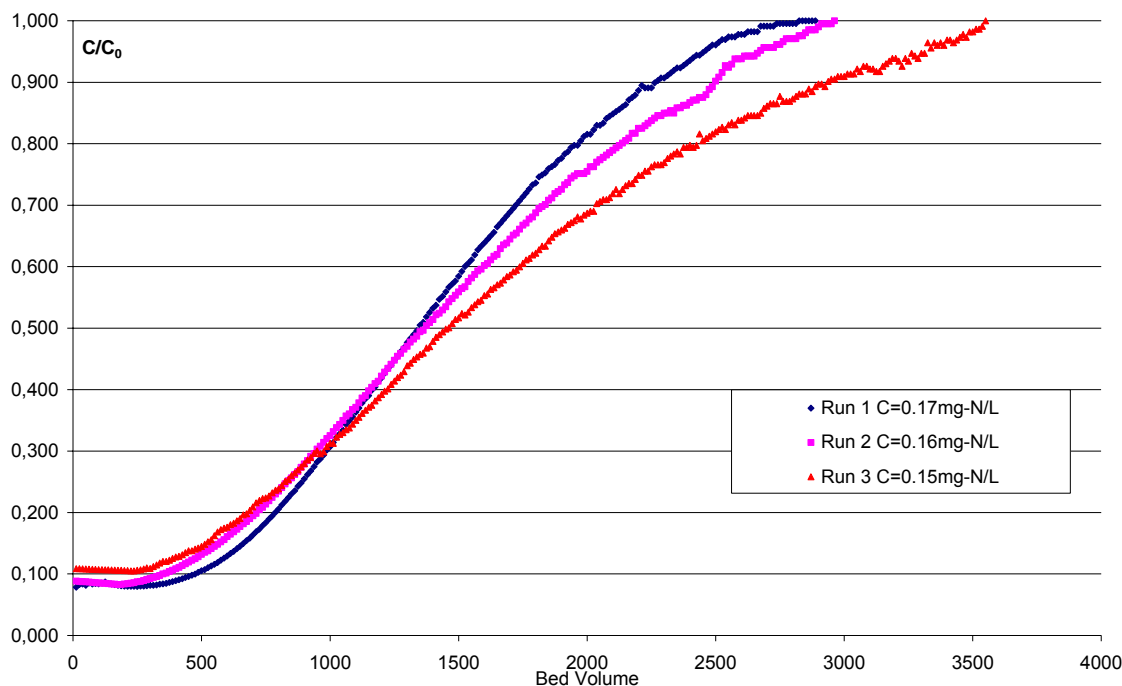Results with Amsterdam water's run are shown in chart 14 and table 13.

Chart 14. Breakthrough curves of ammonium removal with Amsterdam water.

Table 13. Amsterdam water results

Parameter	Run 1 0.17 mg-N/L	Run 1 0.16 mg-N/L	Run 1 0.15 mg-N/L
BV before breakthrough (0.04 mg-N/L)	1050 BV	1100 BV	1215 BV
Removal capacity at breakthrough	0.17 mg-N/g	0.16 mg-N/g	0.16 mg-N/g
Number of BV to reach the feed concentration after breakthrough	1840 BV	1860 BV	2375 BV
Total removal capacity	0.25 mg-N/g	0.24 mg-N/g	0.25 mg-N/g

The curves start at C/C_0 = 0.1%. These values, noticed during the first minutes before the concentration starts to increase, are lower than 0.02 mg-N/L. This is the lowest value detectable with the electrode. Actually the same behaviour occurred in previous dynamic studies (§ 4.3.1). But because the ammonium is now lower, the observation of this leakage is more clearly. However, this leakage can be considered as traces of ammonium in solution and not as a significant leakage.

With a lower ammonium concentration, the number of BV before the breakthrough increases, as well as the total number of BV increases. The removal capacity at the breakthrough and the total removal capacity do not depend on a small variation of the ammonium concentration.

When these results of capacities are compared to those reached with raw water from Hydron, reported in chart 15 and table 14, a removal factor of 10 in favour of Hydron water is calculated.
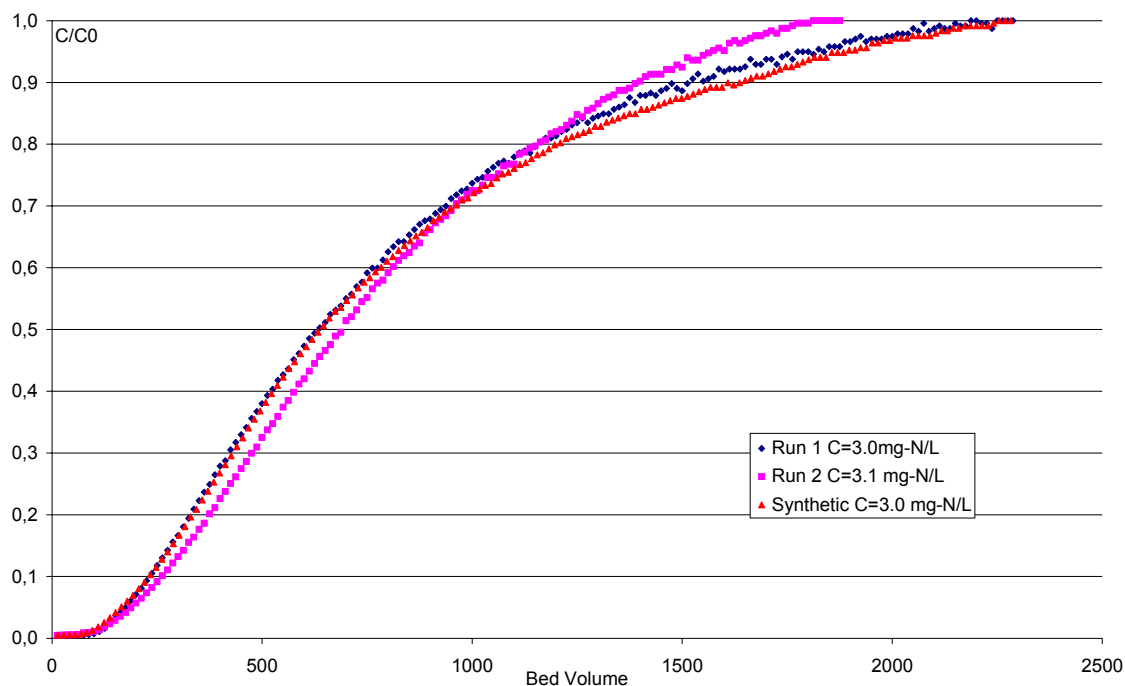
Chart 15. Breakthrough curves of ammonium removal with Hydron water.

Table 14. Hydron water results

Parameter	Run 1 C=3.0 mg-N/L	Run 2 C=3.1 mg-N/L
BV before breakthrough (0.8 mg-N/L)	425 BV	435 BV
Removal capacity at breakthrough	1.23 mg-N/g	1.29 mg-N/g
Number of BV to reach the feed concentration after breakthrough	1800 BV	1430 BV
Total removal capacity	2.40 mg-N/g	2.46 mg-N/g

In the two runs similar removal capacities were found. Synthetic water is a good model for raw water, according to comparison of curves. This is a relevant fact for the rest of this study, involving that experiments can be done with synthetic water and the results can be applied to real water.

Comparison of the results of both water types shows a large effect of the ammonium concentration on the removal capacity. The removal capacities with the water of Hydron are ten times as much as that with the water from Amsterdam, even though the water of Hydron is harder.

A small increase of the hardness of the water modifies the ammonium removal capacities which is shown by results (table 15) of a run with synthetic water with a higher ammonium concentration and higher hardness (60 mg Ca^{2+}/L; 50 mg Na^+/L; 5 mg K^+/L; 15 mg Mg^{2+}/L) than water of Amsterdam.

Table 15. Matrix effect on removal capacities

Parameter	Amsterdam C=0.17 mg-N/L	Synthetic C=0.22 mg-N/L
Removal capacity at breakthrough (20% of entry concentration)	0.12 mg-N/g	0.10 mg-N/g
Total removal capacity	0.25 mg-N/g	0.20 mg-N/g

Removal capacities are lower in the case of synthetic water, even though the ammonium concentration in the water is higher than in Amsterdam water.

4.3.3 Modification of parameters

4.3.3.1 Prediction of ammonium removal according to the ammonium concentration

The ammonium removal capacity is linked to the ammonium concentration in the feed solution. Results extracted from three runs, with the same ion matrix (Ca^{2+}=100 mg/L; Na^{+}=60 mg/L; K^{+}=6 mg/L; Mg^{2+}=18 mg/L) and process conditions (velocity of 5 m/h and the same bed of clinoptilolite) but with different concentrations of ammonium are shown in table 16. Chart 16 describes the evolution and the prediction of ammonium removal according to the ammonium concentration of the feed solution in the range of 0.2 to 3 mg-N/L

Table 16. Ammonium removal evolution in function of ammonium concentration in the feeding solution

Concentration	Removal capacity when concentration in outlet=20% of feeding concentration	Removal capacity at the end
3.08 mg-N/L	1.02 mg-N/g	2.49 mg-N/g
1.54 mg-N/L	0.53 mg-N/g	1.26 mg-N/g
0.23	0.09 mg-N/g	0.02 mg-N/g

The removal capacity is linear with the ammonium concentration in the inlet. With this approach, a removal capacity for a specific ammonium concentration in a water with an ionic composition close to the one used here, can be determined. However, this model does not evaluate the evolution and the level of the ammonium concentration in the outlet as a function of the feed concentration.
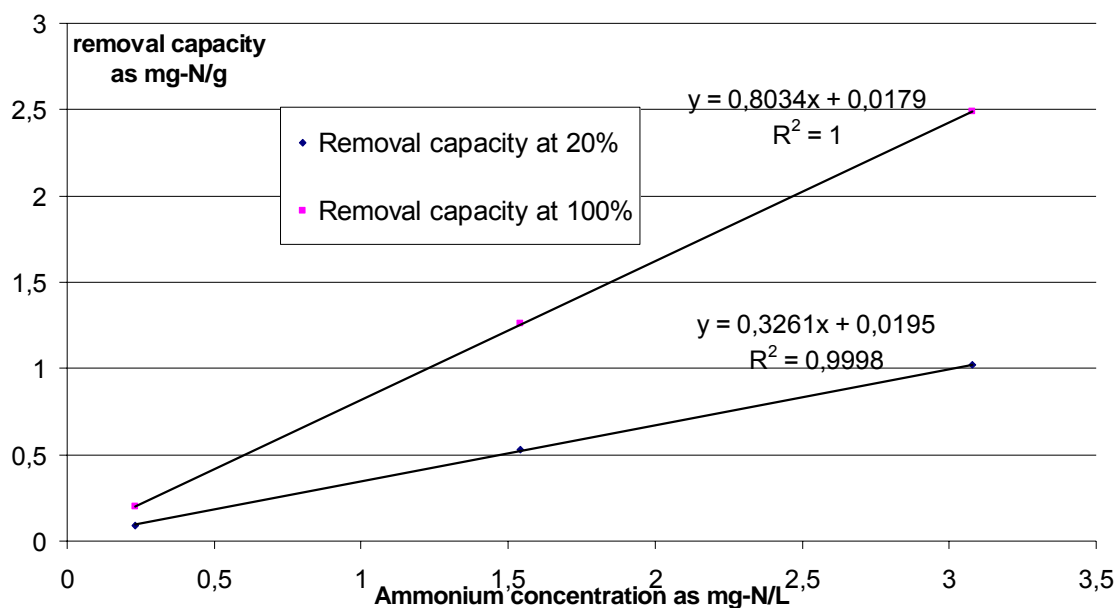
Chart 16. Evolution of the ammonium removal capacity as a function of the ammonium concentration in the feed solution.

4.3.3.2 *Influence on ammonium removal of various parameters*

In following results some parameters have been modified to check their influences on zeolite removal in dynamic conditions. For each run only the described parameters is changed. The ammonium concentration is always around 3 mg-N/L.

A reference run is done in the following conditions:

- Ammonium concentration equals of 3.1 mg-N/L
- Zeolite sample: ZEOCEM with grain size of 0.18-0.5 mm
- Bed velocity: 5m/h
- Superficial velocity close to 800 BV/h
- Ion matrix: 100 mg Ca^{2+}/L; 60 mg Na^+/L; 6 mg K^+/L; 18 mg Mg^{2+}/L
- Bed height and volume 6.5 cm and 15.5 cm^3

Table 17 and Chart 17 show the effect of modifying the parameters on ammonium removal.

An accurate interpretation between the grain sizes can not be done because the contact time is too low to get reliable results with the biggest grains. The regular contact time applied in an industrial treatment is around 10 min and here it is around 5 sec. However with the conditions applied for these experiments, biggest grains are less efficient than smallest grains.

The run after the acid wash of the bed with a 0.005M solution of HNO_3 does not increase the removal capacity. Actually a slight decrease is noticed. This treatment is not relevant to increase the removal capacity as Sarioglu [7] mentioned it.

Table 17. Evolution of removal behaviour according modification of some parameters

| Modified parameter	Removal capacity at 20% of the feed concentration	Total removal capacity	Number of BV before the breakthrough (20 % of C_0)
Reference [NH$_4$]=3.1 mg-N/L	1.02 mg-N/g	2.49 mg-N/g	350
ZEOCEM with grain size 0.5-1 mm [NH$_4$]=3.0 mg-N/L	0.18 mg-N/g	0.80 mg-N/g	75
Acid wash (0.005 HNO$_3$ 2L) after conditioning and before the run [NH$_4$]=3.1 mg-N/L	0.73 mg-N/g	2.24 mg-N/g	250
Heat pretreated zeolite (600°C over 1h30) [NH$_4$]=2.9 mg-N/L	0.78 mg-N/g	2.38 mg-N/g	275
Calcium concentration divided by 2 to reach 50 mg/L [NH$_4$]=3.2 mg-N/L	1.14 mg-N/g	2.68 mg-N/g	370
Velocity = 2.5 m/h [NH$_4$]= 3.1 mg-N/L	1.11 mg-N/g	2.16 mg-N/g	370
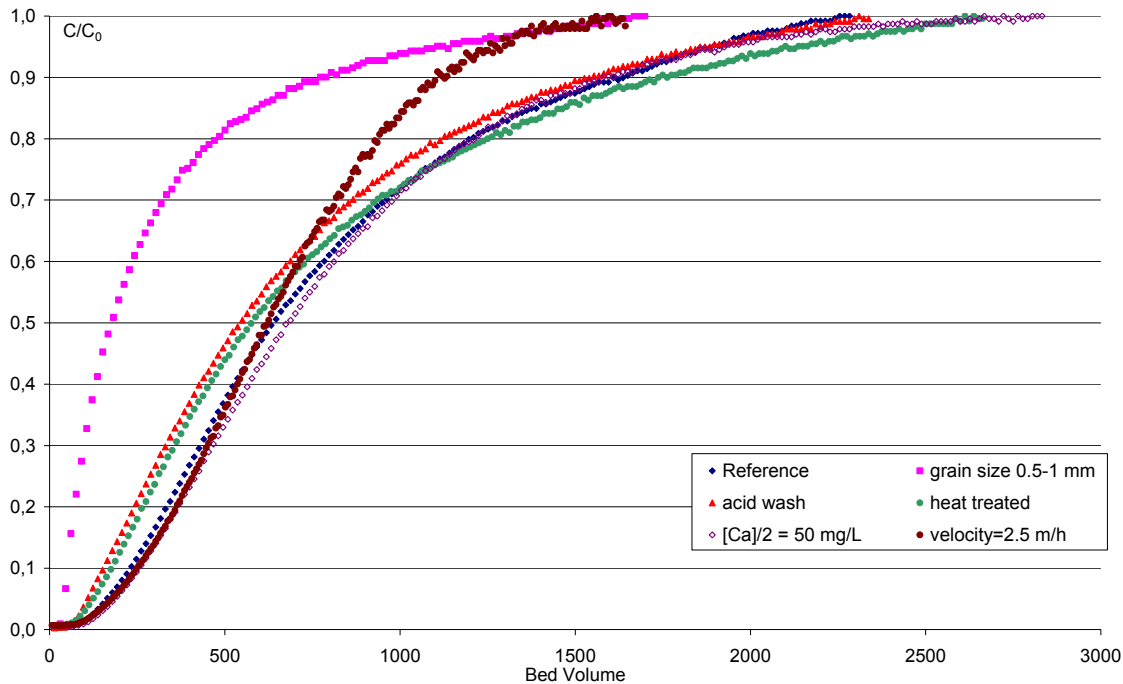
Chart 17. Breakthrough curves with parameters modification

The run after the heat activation is more interesting, although values of removal capacity are lower than the reference one. The bed was composed with clinoptilolite which had not been exposed to any cycles before the run, only a conditioning had been made. So the effect of first cycles must be considered in this case. If a 20% increase of the removal capacity is assumed due to effect of first exposition, this treatment may improve ammonium uptake in hard water. The effect can be explained as a modification of the clinoptilolite framework. Phillipsite with its smaller rings is more selective than regular clinoptilolite. Perhaps heat activation contracts the rings of clinoptilolite, which then tend toward smaller rings as present in phillipsite, which may make clinoptilolite more selective. This hypothesis on the ring modification may be confirmed with X-ray diffraction studies of clinoptilolite before and after the heat treatment. More consecutive runs with this bed can confirm the increase of the ammonium removal and also check if this treatment is a long life treatment.

The experiment with the calcium concentration equal to 50 mg/L shows a slightly higher removal capacity. This experiment confirms that a clinoptilolite column is more efficient when it is placed after a softening treatment, although the increase in efficiency is below 10%.

The last experiment, with the velocity in the bed equal to 2.5 m/h reveals a different dynamic of adsorption. Velocity in the bed is proportional with the contact time. The contact time in the reference is 4.5 sec and in this run it reaches 9 sec. Over the first 500 bed volumes, ammonium uptake is slightly better than in the reference run, however the evolution of ammonium removal after 500 BV is worse in comparison with the reference. It means that the other cations (Ca; Na; K; Mg) are more competitive when the bed is highly loaded. Considering that ammonium ions are removed more easily from the solution than the competitive cations, increasing the contact time involves a higher adsorption of competitive cations and as a consequence a decrease of exchange sites available for ammonium ion. However this interpretation needs to be confirmed with a more thorough study. It is important to notice that if the bed is not completely loaded, the removal capacity is higher at lower velocity.

4.4 Investigation on regeneration

A bed of clinoptilolite, loaded with 17.5 mg-N of ammonium, was exposed 5 times to 7 mL of the regeneration solution. Results are shown in table 18.

Table 18. Batch regeneration with 5 volumes of 7 mL of the regeneration solution

	1st	2nd	3rd	4th	5th	Total
[NH$_4$] as mg-N/L	13.99	41.88	53.29	54.68	53.52	
NH$_4$ released as mg-N	0.098	0.293	0.373	0.328	0.375	1.426

According to these results, the first bed volumes of regeneration solution do not release as much ammonium as the next ones. These first volumes change the film solution around the clinoptilolite grains and do not completely act as a regeneration solution. Then next volumes are really used to release ammonium from the clinoptilolite. Concentrations in the 3rd, 4th and 5th volumes are similar, but the total amount of ammonium desorbed during these 5 BV is only 10% of the total amount of ammonium on the clinoptilolite. This means that much more than 35 mL of regeneration solution is needed to get a conditioned clinoptilolite. This regularity of the ammonium desorption from the clinoptilolite can be linked to the following

parameters: the contact time, the ammonium concentration in the solution and the ammonium concentration on the clinoptilolite.

In order to know whether more than 10 % can be removed with only a few volumes of regeneration solution, a clinoptilolite bed, loaded with 30.2 mg-N of ammonium ions, was soaked during 24h in 7 mL of the same regeneration solution. Results are shown in table 19.

Table 19. Batch regeneration with 7 mL of the regeneration solution

	1st
[NH$_4$] as mg-N/L	77.15
NH$_4$ released as mg-N	0.54

The amount desorbed after 24h represents only 2% of the total amount of ammonium on the clinoptilolite, this kind of regeneration is absolutely not a good way. The parameter which controls the amount desorbed from the material is mainly the equilibrium between the ammonium concentration in the aqueous phase and that in the solid phase. The time appears as a less significant factor of desorption for this time scale.

Results extracted from the dynamic regeneration with the electrode are shown in table 20 and chart 18.

Table 20. Dynamic regeneration after the runs with Amsterdam's water

	375 BV/h and up-flow	375 BV/h and down-flow	188 BV/h and down-flow
Max [NH$_4$] as mg-N/L	16.10	23.01	14.81
NH$_4$ released as mg-N/g of clinoptilolite	0.38	0.33	0.24
NH$_4$ removed in the run before as mg-N/g of clinoptilolite	0.25	0.24	0.25
Error between the removal and the released amount of ammonium	34%	27%	<5%

As in the batch regeneration experiments, the first volumes of the solution do not release the ammonium from the clinoptilolite, they just change the film solution around the clinoptilolite grains. Then a peak of ammonium, released from the material, is observed, followed by a decrease of ammonium desorption. The electrode is known as unsuitable to follow a quick evolution of the ammonium concentration, and especially to come back to low values of ammonium concentration. Nevertheless with a flow rate of 188 BV/h the evolution is slow enough to get a correct mass balance. Whatever the conditions, the maximum concentration determined with the electrode gives an idea of the real maximum concentration of ammonium released from the bed because the error on the mass balance is due to a longer time to come back to low ammonium concentration (§ 3.1.2.6).
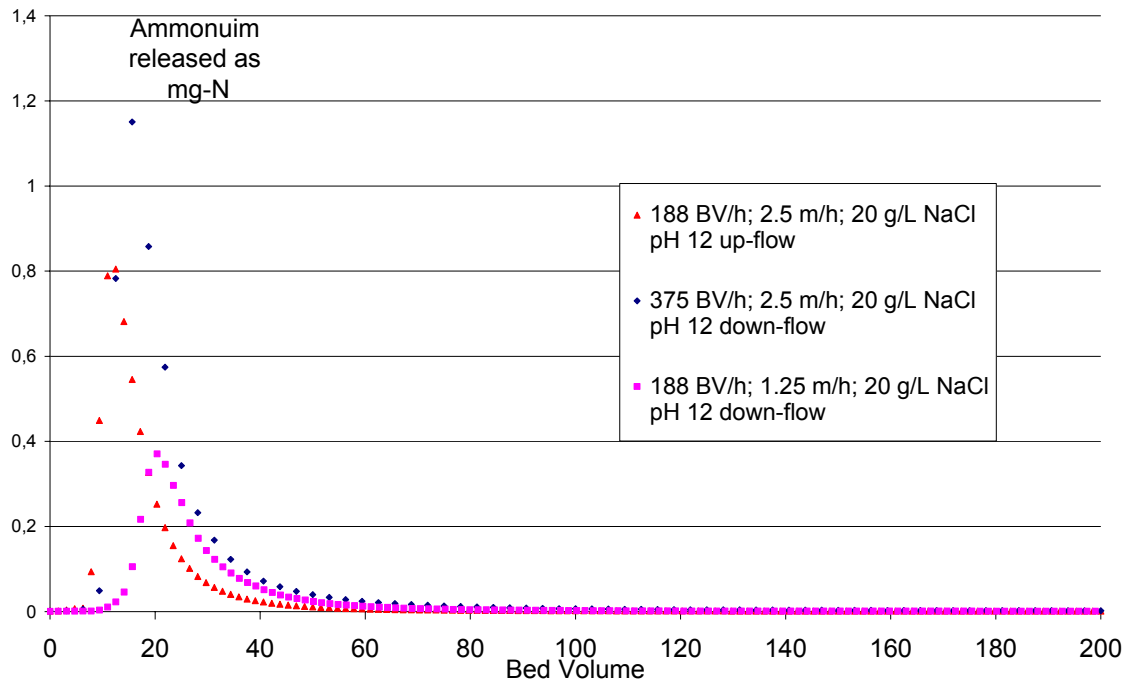
Chart 18. Dynamic regeneration of the packed bed after the runs with the water from Amsterdam.

According to these curves, up-flow regeneration is more efficient than down-flow when we consider the number of bed volumes (due to the expansion of the bed by a factor 2) however the volume of regeneration solution needed is more important.

These three beds had the same quantity of ammonium before their regeneration so the equilibrium between the two phases can not explain the difference noticed with these experiments. The down-flow experiment, with a high velocity, shows a highly concentration of ammonium released than with a lower velocity. This means that more ammonium is released from the clinoptilolite bed, with the same quantity of the regeneration solution. This increase is explained by a better hydraulic exchange between the film solution and the regeneration solution in the column. However a better release of ammonium from the clinoptilolite is possible, only if the kinetic exchange between sodium and ammonium is sufficiently high to be not considered as a limiting factor.

Thus, the exchange velocity between sodium and ammonium ions can be considered high and thus regeneration can be performed with a high flow rate.

With all the flow rates applied, between 30 and 100 BV of fresh regeneration solution is needed to condition the clinoptilolite correctly.

5 Conclusion and recommendations

The aim of this project is to study removal of ammonium in two different raw waters by zeolites. The treatment plant of WLB Amsterdam sometimes experiences a problem during the cold season, because the efficiency of its biological treatment for ammonium is reduced. For the plant of Hydron Zuid Holland, the ammonium concentration in the influent water before the first rapid sand filter increases sometimes, due to an increase of the concentration in the ground water, involving a difficult control of the biological treatment .The current treatment of ammonium is realized in the first rapid sand filter. Two possibilities of zeolites application are checked. The first is to soak a certain quantity of the mineral in the water before the rapid sand filter and during a certain time to reduce the ammonium concentration by 75% (initial concentration = 1.5 mg-N/L). The second one is to apply a zeolite column after the rapid sand filter to reduce the ammonium concentration down to 0.04 mg-N/L (initial concentration = 0.16 mg-N/L). The water from WLB Amsterdam has the following ionic matrix: 80 mg-Ca^{2+}/L; 25 mg-Na^+/L; 7 mg-Mg^{2+}/L; 4 mg-K^+/L. For the plant of Hydron Zuid Holland, the water contains a higher ammonium concentration, around 3 mg-N/L, before the dry sand filter. Furthermore the ion composition in the water is also higher: 100 mg-Ca^{2+}/L; 60 mg-Na^+/L; 18 mg-Mg^{2+}/L; 6 mg-K^+/L. The guideline for this plant is to reduce the ammonium concentration to 1 mg-N/L in the inlet of the rapid sand filter. The same processes as described above are tested to reduce the ammonium concentration.

The soaking process is evaluated with the batch experiments and the column process is evaluated with column experiments. In these experiments the influence of some parameters (flow rate; grain size; pretreatment of the clinoptilolite) on the ammonium removal are investigated.

From the batch experiments we conclude that the removal of ammonium is comparable to that found in literature for synthetic water without others cations than NH_4^+ (removal capacity = 9 mg/g zeolite with a 10 mg-N/L solution). Thus, the regeneration method used (NaCl 20 g/L and NaOH to stet the pH at 10) and the clinoptilolite samples were a good basis to start this project.

The batch experiments with the two raw waters show that more than 4 g/L of zeolite would require a contact time of 30 min to reduce the ammonium concentration as described above. This treatment does not appear as a smart possibility. The column experiments seem to be more relevant to design an ammonium removal process. The conditions for the column experiments with the raw waters are: a 15 g packed bed of clinoptilolite with a height of 6 cm and a velocity of the water in the bed close to 5 m/h.

For Amsterdam water, 1000 BV of water can be treated before the outlet concentration is higher than 0.04 mg-N/L. At this point the ammonium removal capacity of the bed is 0.16 mg-N/g of clinoptilolite. With the water of Hydron, 430 BV of water can be treated before the outlet concentration is higher than 1 mg-N/L, in that case the capacity of the bed is 1.3 mg-N/g.

For Hydron, ammonium directly in the raw anaerobic water is also an option. The lack of oxygen does not seem to be as a parameter that affects ammonium removal, but in that part of the treatment the concentration of iron and manganese are

high, which would probably reduce the efficiency of the ammonium removal. Further experiments can show the feasibility of such a process.

As the results are worse for the water of Hydron (less BV treated), some parameters are varied in the column experiments with a synthetic water, known to be a good model of this raw water. The most relevant options for the ammonium removal are

- The heat activated clinoptilolite, which seems to be more selective towards ammonium than a non heat activated clinoptilolite;
- The grain size ranged between 0.2-0.5 mm to reach the equilibrium between the solid and the liquid phase quickly.

Furthermore a predictive model was fitted to the removal capacities as a function of the feed ammonium concentration. The model reveals a linear evolution of the removal capacity as a function of the feed ammonium concentration, but may only be applied for the water of Hydron. Such a model can be used with the parameters of Langmuir to build a model of some columns in series or a higher packed bed than that used for the column experiments.

About the heat activation of clinoptilolite: it may be studied further to understand the effect of the heat treatment on the framework of the clinoptilolite. X-ray diffraction of the material could help to understand the heat activation. The durability of the activation and the increase of the capacity after applying several cycles should be tested too. If this activation appears as persisting, perhaps bigger grain size with this activation can show a better efficiency of the removal capacity and can then be used. It would be better from a hydraulic point of view to work with bigger grains. It would decrease the hydraulic resistance of the bed.

Concerning the regeneration, a contact time of one hour with the regeneration solution is enough to approach the equilibrium between the solid phase and the equilibrium phase. However, dynamic regeneration shows that more than 40 BV are needed to regenerate correctly the clinoptilolite bed. The possibility to reuse the regeneration solution can be tested in further column experiments, for instance in a carousel system. But some matters can occur:

- The precipitation of the $Ca(OH)_2$ in the solution;
- The accumulation of the competitive cations;
- The decrease of the ammonium removal efficiency by reusing the solution.

To avoid the accumulation of ammonium in the regeneration solution, the stripping of ammoniac could be a possibility, but it means that the pH of the solution must be above 10 to transform ammonium in ammoniac. Another possibility would be to treat the ammonium in solution by a biological treatment, but in that case the sodium concentration may be a problem for the bacteria.

6 References

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7 Annexes

Annex 1

<div align="center">

Table 1. Equivalent ionic conductivity at infinite dilution

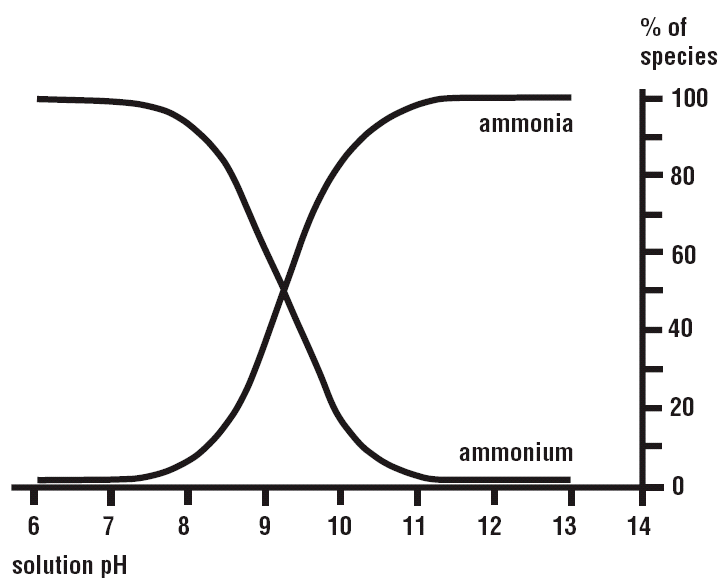| Ion	Λ_0 (10^{-4} m^2 S mol^{-1})
$1/2Ca^{++}$	59.47
$1/2Mg^{++}$	53
K^+	73.48
Na^+	50.08
NH_4^+	73.5

</div>

Annex 2

Chart 1. Predomination form of the ammonia in solution according to the solution pH level at 20°C.

Annex 3

<div align="center">

Table 2. Temperature effects on ORION 95-12 electrode

Temperature (°C)	Slope (mV)
10	-56.18
15	-57.17
20	-58.16
25	-59.16
30	-60.15

</div>

Annex 4
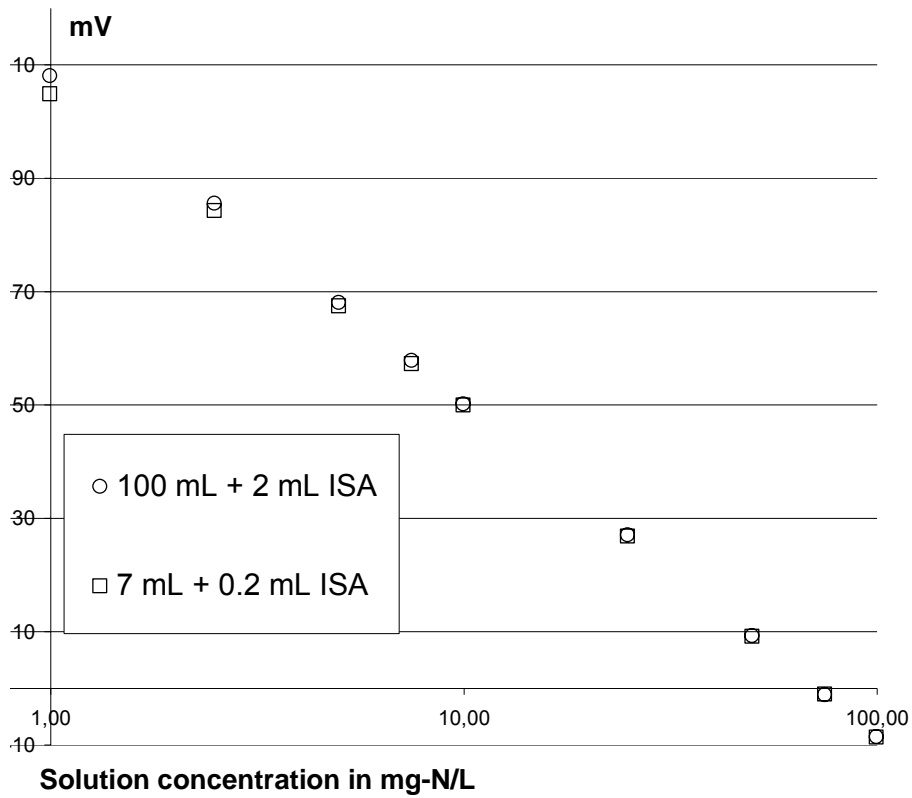
Chart 2. Comparison of both analytical procedures for ammonium determination.
T= 20°C stirring 1000 rpm

Table 3. Student's t test between both analytical procedures

Values with a sample of 100 mL	Values with a sample of 7 mL
-8,5	-8,6
-1,1	-1
9,3	9,2
27,1	26,9
50,2	50
57,9	57,3
68,1	67,5
85,6	84,3
108,1	104,9

Probability of the Student's t test returned	0.08

A value lower than 0.05 points out a significant
difference between both series.

Annex 5
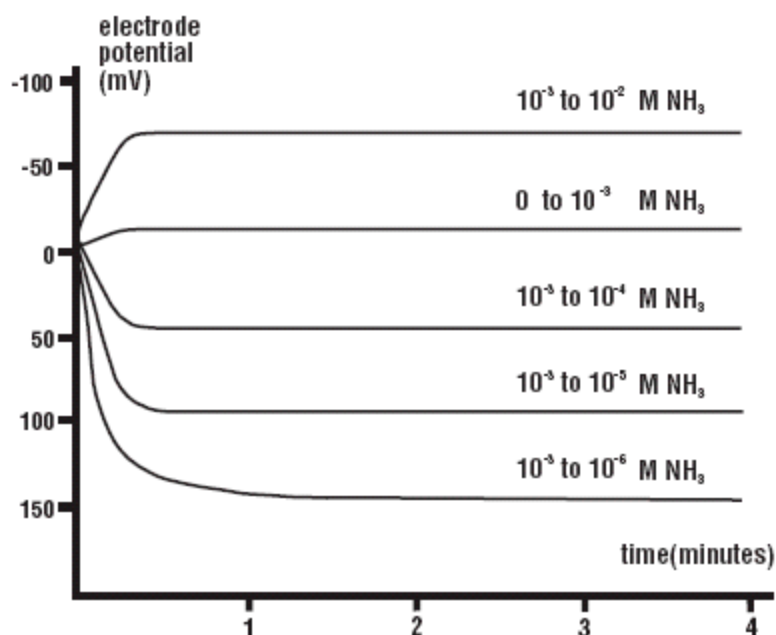
Chart 3. Typical Electrode Response to step changes in ammonia concentration

Annex 6

Table 4. Cations concentrations in calibration samples with cations

Ion	Concentration (mg/L)
Ca^{++}	70
Mg^{++}	15
K^+	5
Na^+	60

Annex 7

Table 5. Student's t test between calibration samples with and without others cations

Only ammonium	With cations	
-17,3	-17,9	
-5,2	-5,5	
22,5	22,5	
60,8	57,9	
73,8	81	
Probability of the Student's t test returned		0.71

A value lower than 0.05 points out a significant difference between both series.

Annex 8

Table 6. Student's t test between two days of calibration with the same procedure

Values for day 1	Values for day 2
-9,6	-8,6
8	9,2
25,6	26,9
48,8	50
66,2	67,5
83,6	84,3
104,4	104,9

Probability of the Student's t test returned	0.01

A value lower than 0.05 points out a significant difference between both series.

Annex 9

Table 7. pH buffer composition

pH	13
0.2 molar KCl solution	25 mL
0.2 molar NaOH solution	66 mL
Final volume of mixtures	100 mL

Annex 10
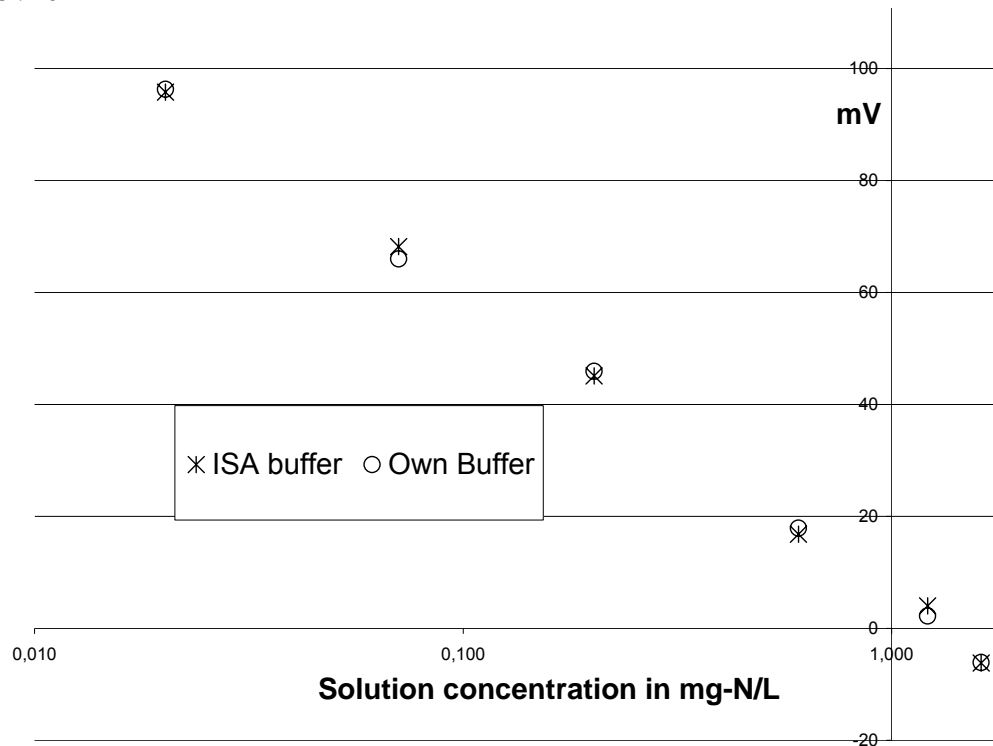
Chart 4. Comparison of the electrode answer with the both buffer

Table 8. Student's t test between both buffers calibration

ISA buffer	Our buffer
95,8	96,3
68,2	66
45,1	45,9
16,8	17,9
4	2,2
-6,2	-6,1

Probability of the Student's t test returned	0.68

A value lower than 0.05 points out a significant difference between both series.

Annex 11
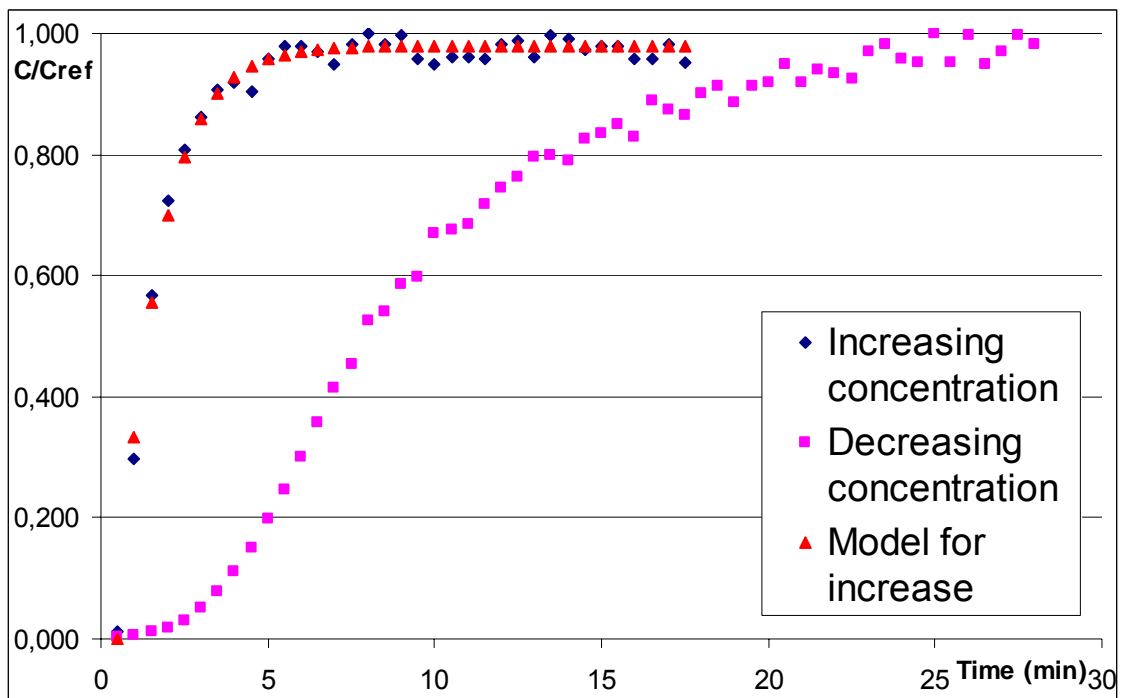
Chart 5. Modelling of the electrode response under dynamic condition.

The following system's transfer function is determined for an increasing ammonium concentration.

$$X \quad \boxed{G(s) = \frac{K}{1 + \tau(s + t_0)}} \quad Y$$

- The time constant τ equals 1.2 min
- The delay factor t_0 equals 0.5 min
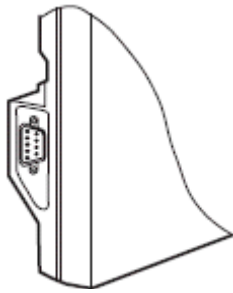- K factor, which can be considered as the right value approximation, equals to 0.98

Annex 12

Table 9. Connection configuration between Hyperlink and the meter

Parameter	Value
Baud rate	1200
Data bits	8
Parity	No
Start Bit	1
End Bit	1

Picture 1. RS232 DB9 style port picture

Annex 13
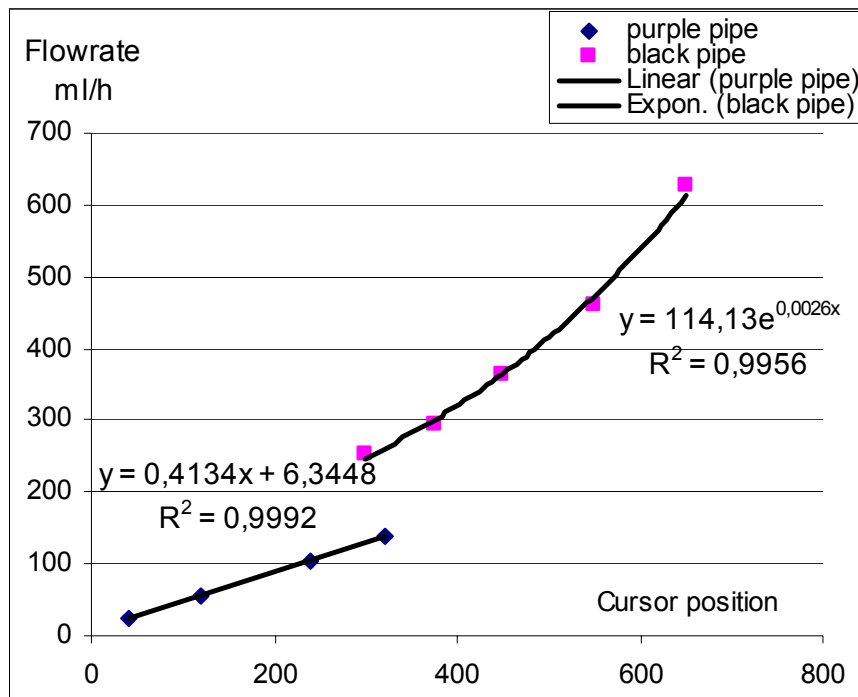
Chart 6. Calibration curves for the Gilson minipump_2

In the chart:
- Legend: purple pipe, black pipe, Linear (purple pipe), Expon. (black pipe)
- Y-axis: Flowrate ml/h
- X-axis: Cursor position
- $y = 114{,}13e^{0{,}0026x}$, $R^2 = 0{,}9956$
- $y = 0{,}4134x + 6{,}3448$, $R^2 = 0{,}9992$
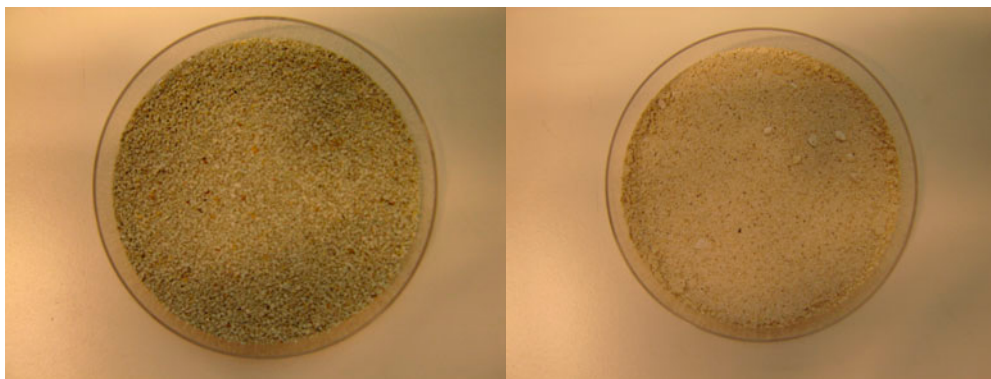
Annex 14

Picture 2. Pictures of ZEOCEM (left) and Zeolite Products (right) samples.

Annex 15

Table 10. Mineralogical and chemical composition of natural ZEOCEM samples
according to provider

Mineralogical		Chemical	
Clinoptilolite	84%	SiO_2	65-71.3%
Cristobalite	8%	Al_2O_3	11.5-13.1%
Feldspat	3-4%	CaO	2.7-5.2%
Illite	4%	K_2O	.2-3.4%
Quartz	Traces	Fe_2O_3	0.7-1.9%
Carbonates	< 0.5%	MgO	0.6-1.2%
		Na_2O	0.2-1.3%
		TiO_2	0.1-0.3%

Table 11. Mineralogical and chemical composition of natural Zeolite Products samples
according to provider

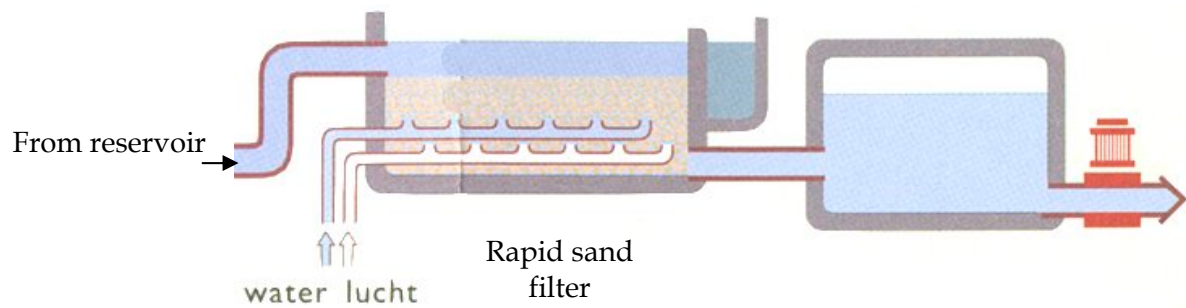| Mineralogical		Chemical	
Clinoptilolite	95%	SiO_2	62.8%
		Al_2O_3	10.66%
		CaO	2.37%
		Na_2O	0.35%
		K_2O	0.74%
		MgO	1.10%
		H_2O	6.92%
		Other	9.76%

Annex 16

Picture 3. Position of plants in The Netherlands

Annex 17
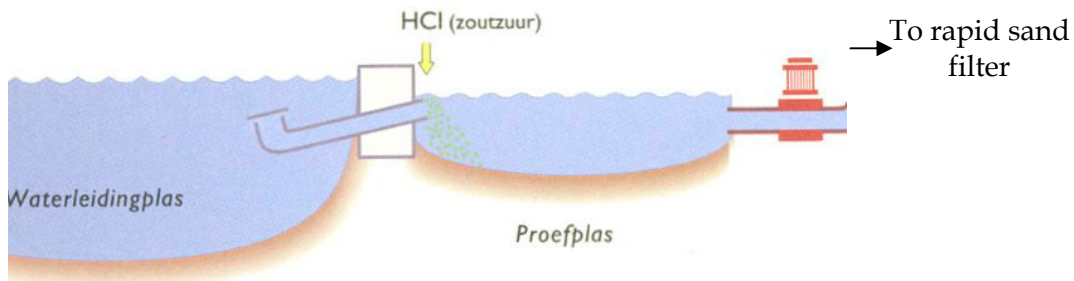
Picture 4. WLB Amsterdam drinking water treatment plant, point of samples before the rapid sand filter (pumps are in red).

From reservoir

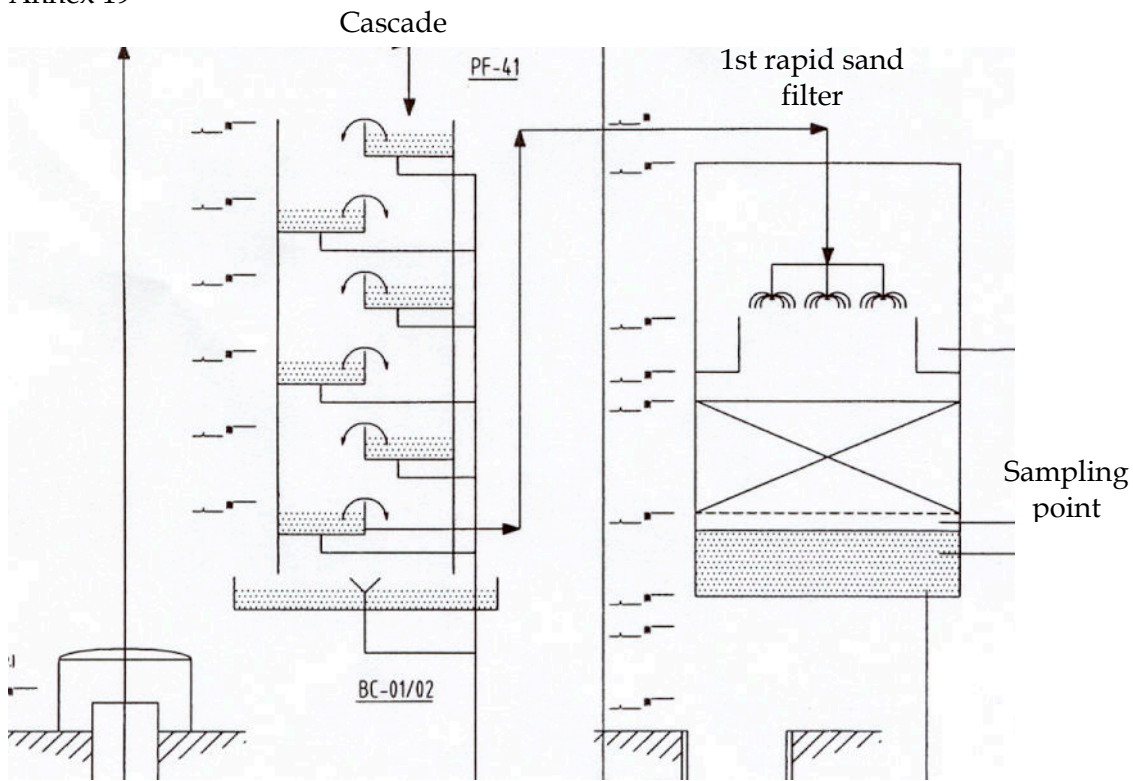Rapid sand filter

water lucht

Picture 5. WLB Amsterdam drinking water treatment plant, point of samples after the rapid sand filter (pumps are in red).

Annex 18

Table 12. WLB Amsterdam samples matrix

Component	Concentration as mg/L before rapid sand filter	Concentration as mg/L after rapid sand filter
HCO_3	210	204
CO_3	< 0.5	< 0.5
Cl	74	75
SO_4	7	7
Na	24	24
K	3.2	3.2
Ca	81	80
Mg	6.5	6.5
Fe	0.09	< 0.05
Al	< 3	< 3
pH	7.2	7.2

Annex 19

Cascade

PF-41

1st rapid sand filter

Picture 6. Part of Hydron's plant.

BC-01/02

Sampling point

Ground water

Annex 20

Table 12. Hydron samples matrix

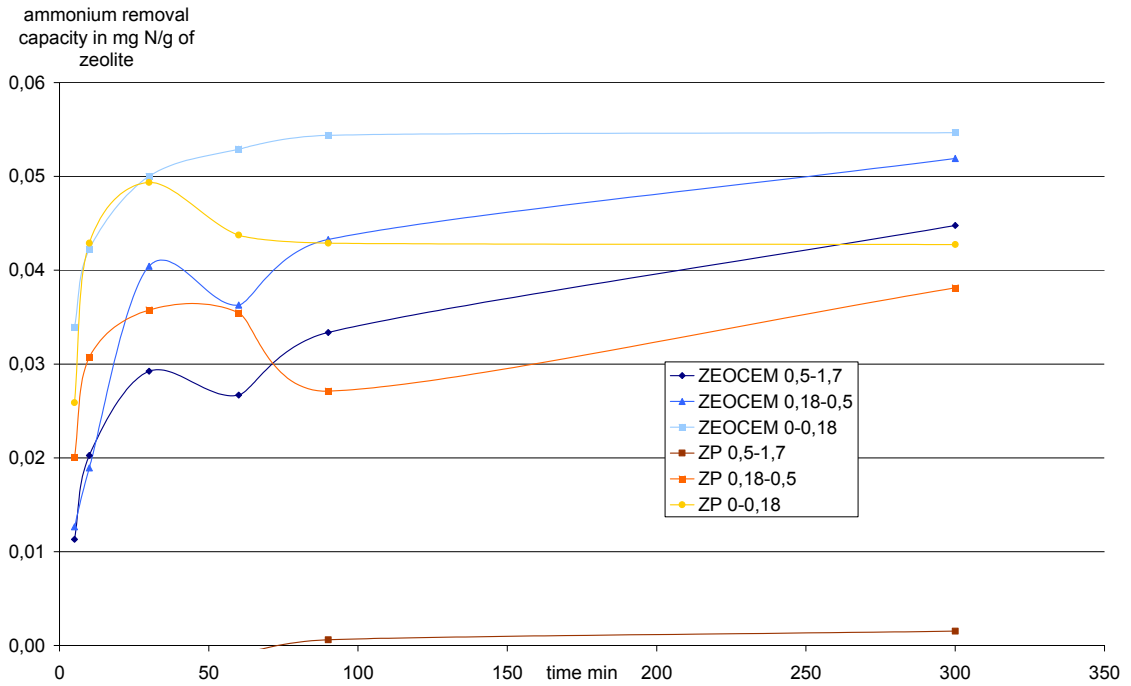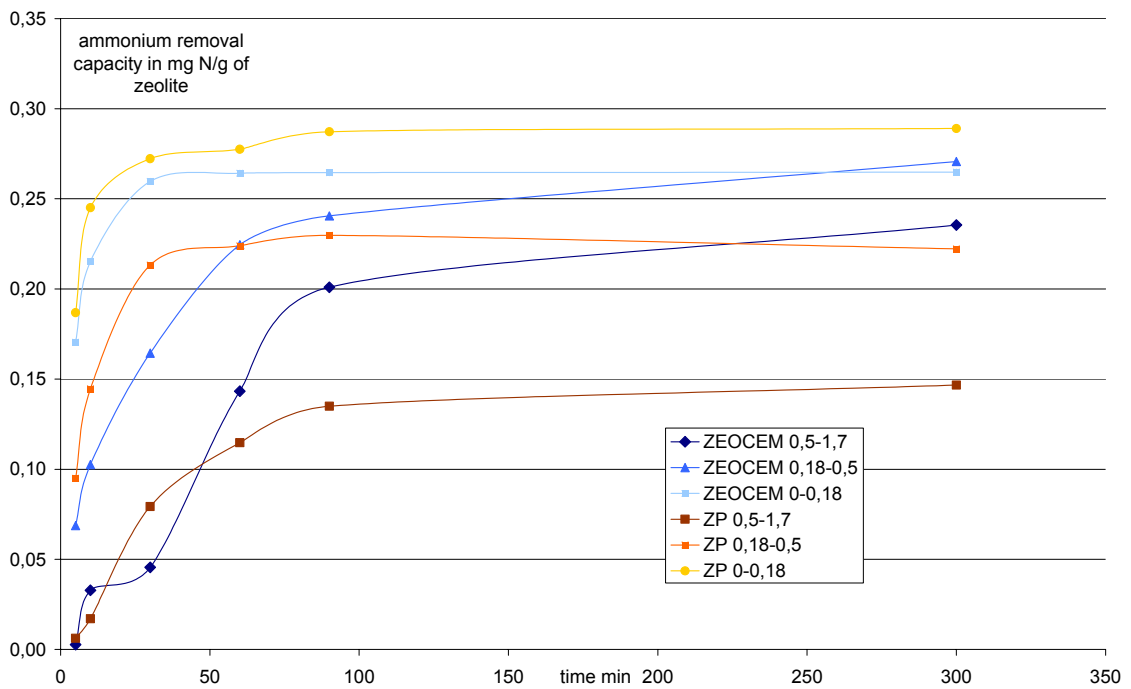| Component	Concentration as mg/L after rapid sand filter
Na	60
K	5
Ca	102
Mg	17
Fe	< 0.05
Mn	< 0.09
pH	7.3

Annex 21

Chart 7. Kinetic of ammonium removal with initial 0.05 mg-N/L ammonium concentration in solution.

Chart 8. Kinetic of ammonium removal with initial 0.2 mg-N/L ammonium concentration in solution.
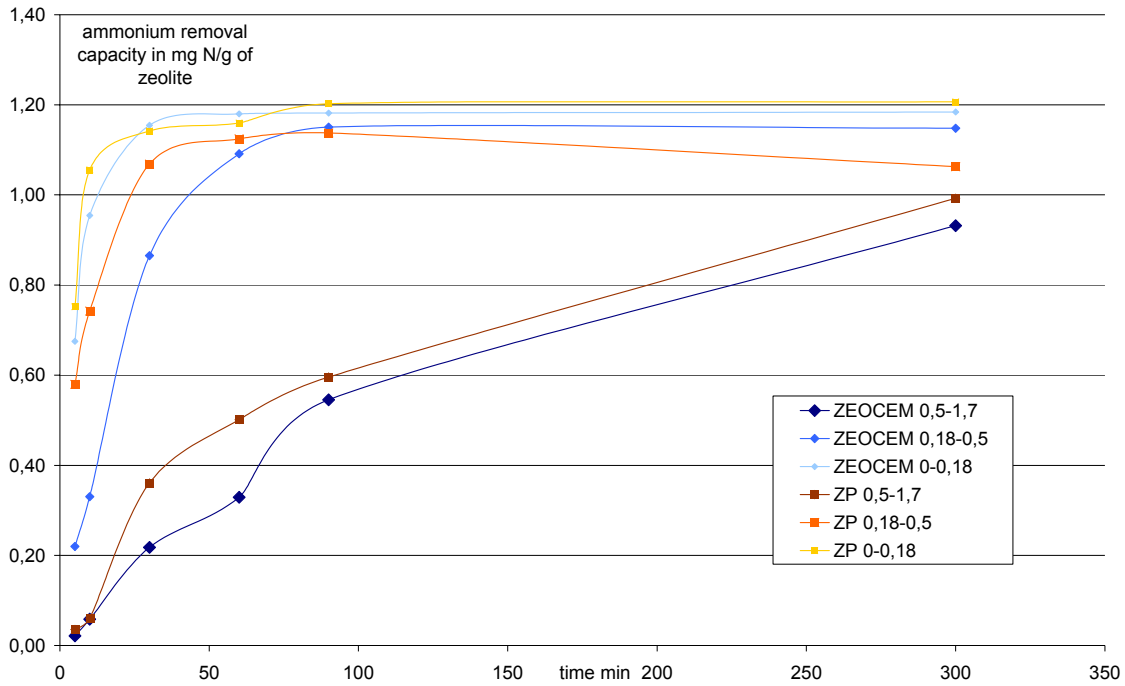
Chart 9. Kinetic of ammonium removal with initial 0.8 mg-N/L ammonium
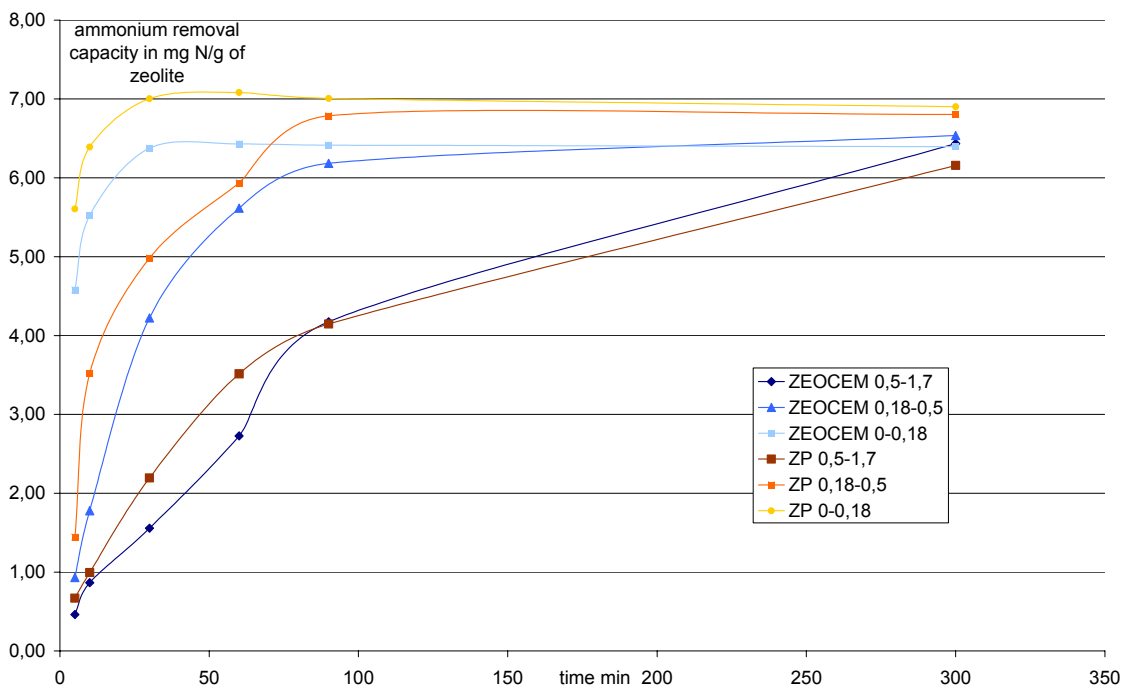concentration in solution.

Chart 10. Kinetic of ammonium removal with initial 5 mg-N/L ammonium
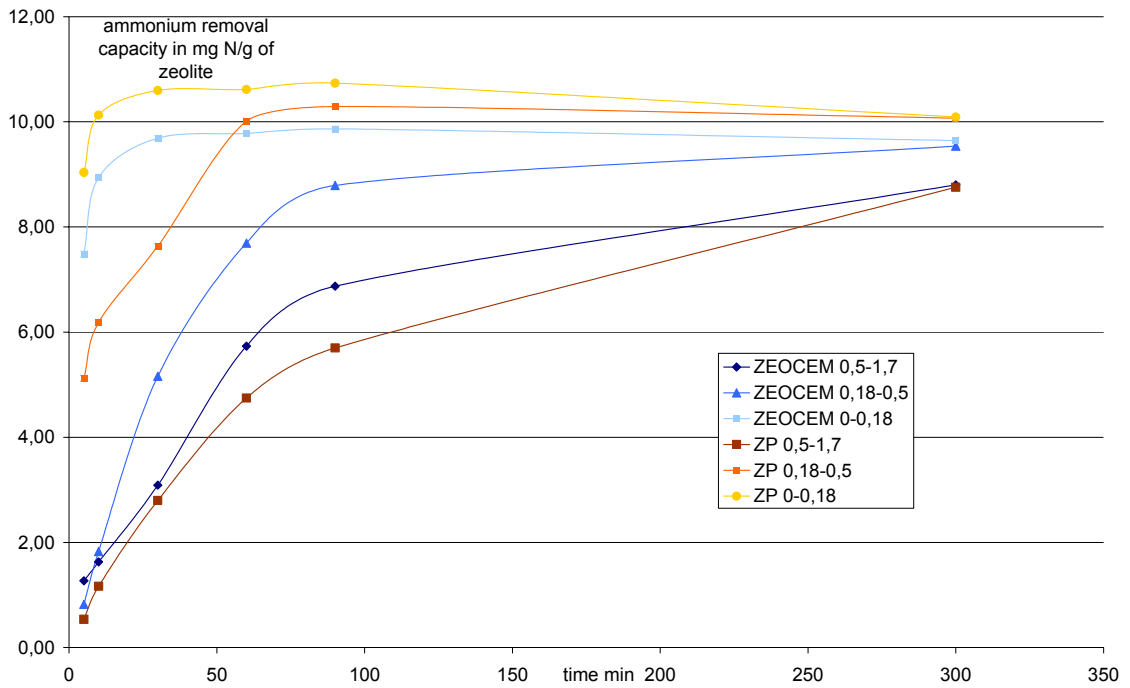concentration in solution.

Chart 11. Kinetic of ammonium removal with initial 10 mg-N/L ammonium concentration in solution.