

Ammonium removal in drinking water using natural zeolite



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Projectnumber

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This is part of the report of the practical training period of Benoit Boulinguez. This report only contains the materials and methods and results of the experiments with the zeolite of the company Zeolite Products. This report is not publicly available.

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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).

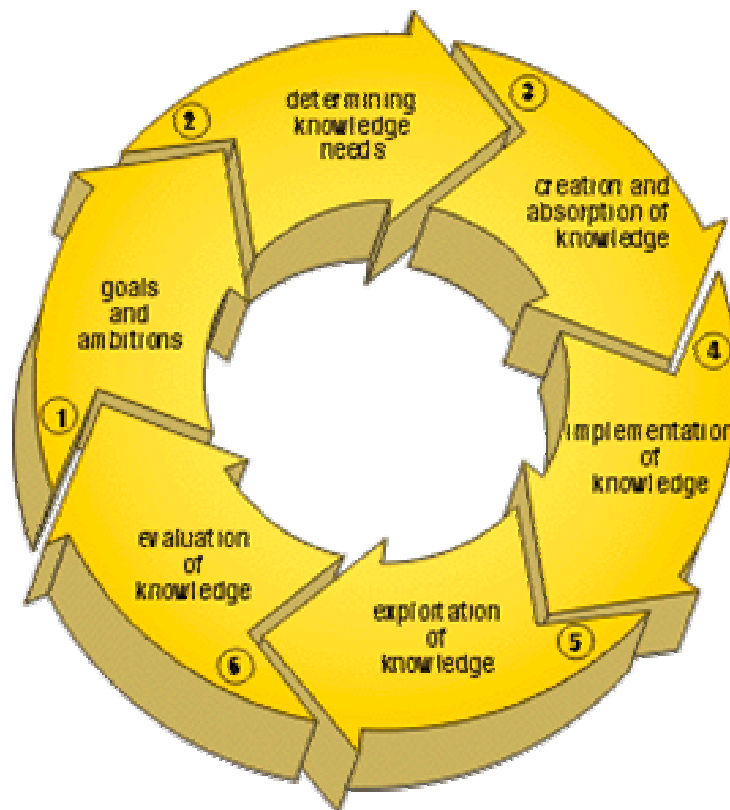


Fig. 1. Knowledge Cycle

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 from 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 samenwerkingsverband Vlaams Water (Belgium), WRc plc (UK), Technologiezentrum Wasser (Germany) and Laboratório 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. In this study batch experiments are performed to determine the removal capacity. This report follows the usual order and presentation of a scientific publication.

2 Materials and methods

2.1 Ammonium measurements

The ammonia gas-sensing electrode used for this study is the ORION 95-12, coupled with the meter ORION 720A. The practical operation is described in the following paragraphs.

2.1.1 Temperature effect

A change in temperature will cause the electrode response to shift and change slope. 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.

2.1.2 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. 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. The alternative procedure is also reliable and has been used for all the measurement. By taking samples 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. 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.

2.1.3 Electrode drift

The daily drift of the electrode is significant, and as a consequence a new calibration is done every day.

2.2 Ammonium titration protocol

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.

2.3 Clinoptilolite samples, preparation and regeneration

Clinoptilolite samples used in this study were received from “Zeolite Products®” a Dutch company. The color of the zeolite is yellow. Sieved samples were received in different size ranges. However, they were sieved into the following standard size ranges: 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.

The following pretreatment or regeneration is applied to condition zeolite fractions 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.

2.4 Experiments

2.4.1 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 the clinoptilolite sample 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.

2.4.2 Experimental

Batch adsorption isotherms and kinetic evolution are determined in the same experiments. Weighted amounts, close to 1 g, of clinoptilolite are introduced into 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%.

3 Results and discussion

3.1 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.

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

where:

Q (mg-N/g) is the amount of ammonium absorbed

C₀ (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.

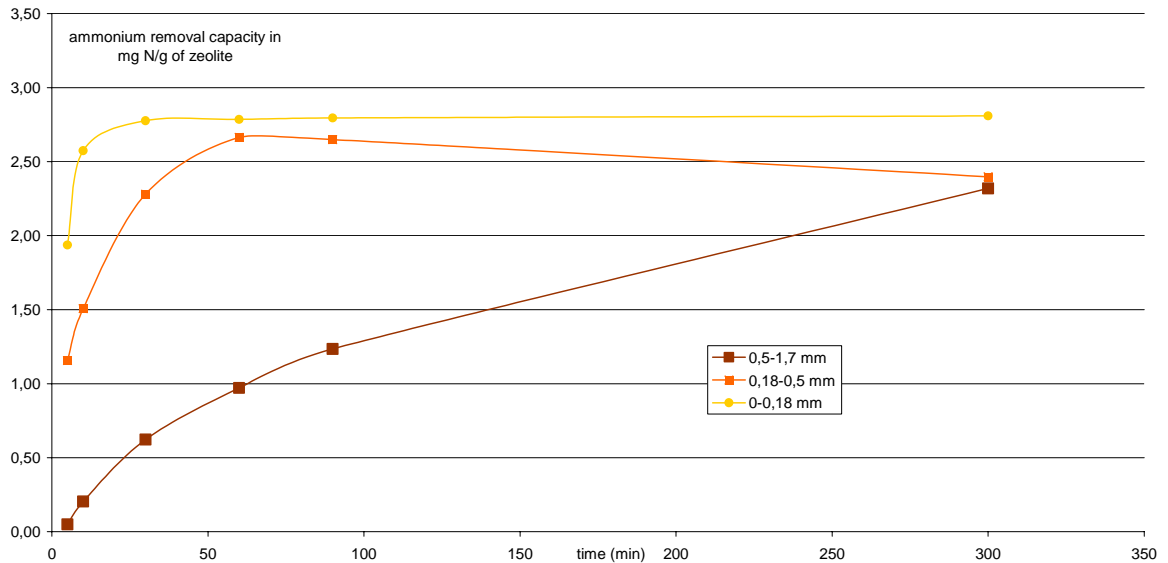


Chart 1. Kinetic of ammonium removal for different grain sizes with initial 2 mg-N/L ammonium concentration in solution.

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.* [1] and Conney *et al.* [2] concluded that intraparticle 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.

3.2 Equilibrium aspect

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

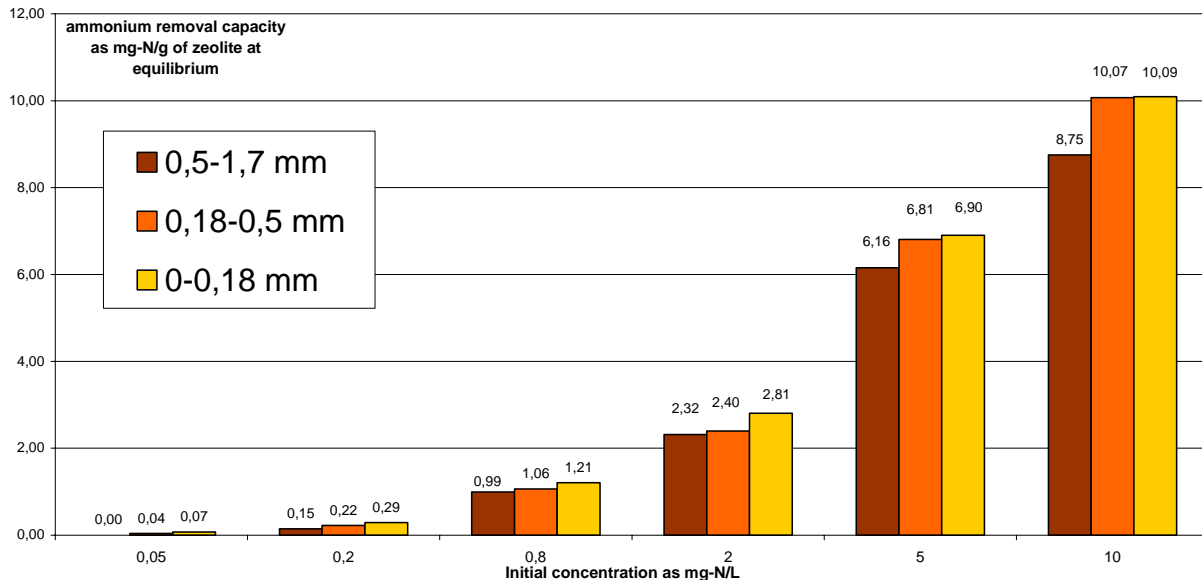


Chart 2. Ammonium removal capacities at $t=300$ min.

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 size shows a higher removal capacity, there are no significant differences between the various sizes 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 [4].

In order to evaluate overall effectiveness of ammonium removal by different clinoptilolite sizes, the percentage of ammonium removed from solution is plotted versus the initial concentration in chart 3.

Chart 3 allows interpretation of the removal capacity for a clinoptilolite sample in a wide range of ammonium concentrations. The clinoptilolite sample with the smallest grain size gives 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.

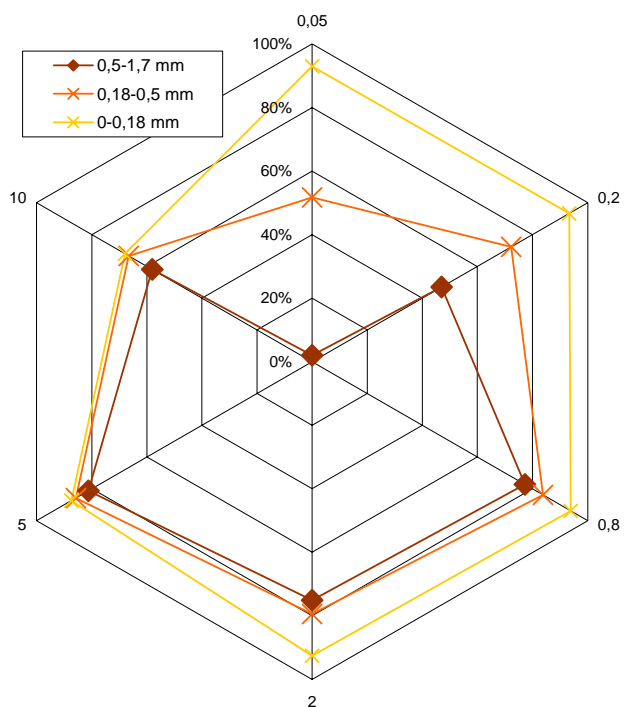


Chart 3. Percentage of ammonium removed from solution with different initial concentrations.

3.3 Conclusion

The aim of this project is to study removal of ammonium by zeolite. From the experiments, carried out in batch, 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 set the pH at 10) and the clinoptilolite samples were a good basis for this project.

4 References

- [1] Neveu A., Gaspard A and Martin G., *Water Res.* 1985, vol 19, p. 611-618.
- [2] Conney E.L, Booker N.A, Shallcross D.C. and Stevens G.W., Ammonium removal from wastewaters using natural Australian zeolite II. Pilot scale study using continuous packed column process. *Separation Sci. and Tech.* 1999, vol 34, p. 2741-2760.
- [3] Sprynskyy M., Lebedynets M., Terzyk A.P, Kowalczyk P., Namiesnik J. and Buszewski B., Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *J. of Colloid and Interface Sci.* 2005, vol 284, p. 408-415.
- [4] Ershov V., *Physical-Chemical Properties and Utilization of Natural Zeolites.* 1985, p. 339.