

# EXECUTIVE SUMMARY

## Background

Ammonia-nitrogen discharges into the water environment accelerate eutrophication of rivers and dams and dissolved oxygen depletion in receiving waters. Ammonia-nitrogen in its undissociated form is also toxic to fish at low concentration levels (0,2 mg/l) and its removal can be important for fish farming, particularly where a high proportion of the water is recycled.

The current discharge requirement of ammonia-nitrogen in secondary sewage effluent is 10 mg/l. This discharge requirement may be reduced to 6 mg/l in future. It is also experienced at municipal biological treatment plants that it is sometimes difficult to produce treated effluent containing less than 10 mg/l ammonia-nitrogen. Therefore, technologies should be developed that should be able to reduce the ammonia-nitrogen concentration to the desired levels.

Ammonia-nitrogen can be removed from wastewaters by selective ion-exchange using clinoptilolite, biological nitrification and denitrification, liming to pH 11 followed by air (or steam) stripping, breakpoint chlorination followed by treatment with activated carbon and treatment in algae ponds.

Biological nitrification and algae ponds may not be suitable where low temperatures are encountered. Stripping and breakpoint chlorination are considered to be too expensive for the high ammonia-nitrogen concentration levels encountered in secondary effluent. Selective ion-exchange of ammonia-nitrogen using the natural zeolite, clinoptilolite, in the sodium form, which is not very sensitive to temperature fluctuations, and which is a locally occurring mineral, should be a suitable material for ammonia-nitrogen removal from secondary sewage effluent.

Clinoptilolite can be applied as an ion-exchanger in columns or in powder form.

Clinoptilolite should have a low cost in comparison with conventional ion-exchangers. Experimental conditions including laboratory and pilot-scale ammonia-nitrogen removal investigations have been discussed in great detail by many researchers. These investigations, however, have all been performed on foreign clinoptilolites.

Knowledge that is lacking in South Africa is the performance of the local clinoptilolites for the removal of ammonia-nitrogen from secondary effluent. This technology could be an effective low cost technology for the final polishing of secondary sewage effluent for ammonia-nitrogen removal to reduce the ammonia-nitrogen concentration to acceptable levels.

## Aims

The main aim of this investigation is to develop process design criteria and costs for the implementation of a South African clinoptilolite for ammonia-nitrogen removal from secondary effluents for pollution control. Secondary aims are to:

- Characterise the South African clinoptilolites.
- Determine the efficiency of powdered clinoptilolite for ammonia-nitrogen removal from secondary effluent.
- Determine the efficiency of ammonia recovery from the spent regenerant.
- Determine the performance of clinoptilolite on laboratory scale for the removal of ammonia-nitrogen from secondary effluent.
- Determine the performance of clinoptilolite on pilot scale for the removal of ammonia-nitrogen from secondary effluent.

- Derive process design criteria and costs of the process to remove ammonianitrogen from secondary effluent.

## **Conclusions and recommendations**

The following conclusions and recommendations can be made as a result of the investigation:

### Characteristics of the South African clinoptilolites

The South African zeolites (Pratley and Heidelberg) consisted mainly of clinoptilolite with traces of cristobalite low, orthodase high, quartz and muscovite. A relatively high concentration of heavy metals and rare earth elements are also present in the zeolites. The total exchange capacity of the Pratley clinoptilolite is slightly lower (1,3 to 1,4 me/g dry) than that of the well known overseas Hector clinoptilolite (1,6 me/g dry) while the Heidelberg clinoptilolite (1,6 to 1,7 me/g dry) has about the same capacity. The bulk (0,87 to 1,02 g/ml) and particle densities (2,1 to 2,5 g/ml) of the South African clinoptilolites are higher than that of the Hector clinoptilolite (0,67 and 1,66 g/ml, respectively). The surface area of the South African clinoptilolites is low (13 to 17 m<sup>2</sup>/g). However, surface areas of overseas clinoptilolites of the same order have been reported. The Heidelberg and Hector clinoptilolites appear to be more friable than the other clinoptilolites. Attrition losses of the Pratley clinoptilolite (1,1 to 2,2%) were significantly less than that of the Heidelberg (6,2 to 8,0%) and Hector clinoptilolites (9,3%). Higher pH of the regeneration solution affects attrition adversely. Adsorption of ammonium ions on clinoptilolite fit both the Langmuir and Freundlich isotherms to some or other degree. However, it appears that the Langmuir isotherm fits the data the best especially with a particle size of 0,25 to 0,7 mm. Experimental data also correlates well with model calculations.

### Efficiency of powdered and granular clinoptilolite for ammonioia-nitrogen removal

Powdered clinoptilolite functions effectively for ammonia-nitrogen removal from tap water spiked with ammonia and from secondary effluent. Ammonia-nitrogen could be reduced from approximately 20 mg/l (tap water) to approximately 6 mg/l with unconditioned clinoptilolite at a dosage of 16 g/l, whereas a dosage of only 4 g/l was required to reduce the ammonia-nitrogen concentration to 6 mg/l in the case of the conditioned clinoptilolite (Pratley 1). Ammonia-nitrogen could be reduced from approximately 13 mg/l in secondary effluent to approximately 6 mg/l with a dosage of 10 g/l (unconditioned) and 6 g/l (conditioned) clinoptilolite (Pratley 1). Ammonia nitrogen could be reduced from approximately 12 mg/l in secondary effluent to approximately 4 mg/l (unconditioned) with a dosage of 4 g/l (Pratley 2). A dosage of less than 2 g/l would be required to reduce the ammonia-nitrogen of 9 mg/l in secondary effluent to less than 6,0 mg/l (conditioned; Pratley 1). Ammonia-nitrogen could be reduced from 10 mg/l in secondary effluent to 6 mg/l at a dosage of 2 g/l (conditioned and unconditioned) (Heidelberg). However, dosages are high and this will make the process uneconomical.

The removal efficiencies of ammonia-nitrogen with clinoptilolite (0,25 to 0,7 mm particle size) decreased with increasing feed concentration. Removal efficiencies decreased from about 80 percent (4,0 mg/l feed) to approximately 60 percent (20,1

mg/l feed) for unconditioned clinoptilolite. Removal efficiencies decreased from about 87,5 percent (5,2 mg/l feed) to about 63 percent (20,5 mg/l feed) for conditioned clinoptilolite. Therefore, significant quantities of ammonia-nitrogen could be removed with unconditioned as well as with conditioned granular clinoptilolite.

#### Performance of clinoptilolite on laboratory scale for the removal of ammonia-nitrogen

The output of treated water in column studies increased with decreasing flow rate (5 to 15 BV/h). Smaller particle size (0,25 to 0,7 mm) performed better for ammonianitrogen removal than coarser (0,5 to 1,0 mm) particles. Output of treated water also increased with decreasing feed concentration from 43 to 10 mg/l. The breakthrough capacity to 2 mg/l ammonia-nitrogen increased with increasing feed concentration in the feed range of 10 to 43 mg/l. The pH of the feed also affects output of treated water. The highest output was achieved at a pH of 7. Lower and higher pH affects output adversely as a result of competing ions. Almost all the ammonioia-nitrogen loaded onto the clinoptilolite could be removed with 30 BV 0,1 M solution chloride at high pH (pH 11 to 12).

The output capacity for ammonia-nitrogen removal from tap water spiked with ammonia-nitrogen should not significantly decrease with consecutive loading and regeneration cycles. Output capacity remained at about 130 BV after five loading/regeneration cycles. However, the unconditioned clinoptilolite performed poorly in column studies for ammonia-nitrogen removal.

The output capacity for ammonia-nitrogen removal from secondary sewage effluent also remained more or less the same after a number of loading/regeneration cycles. However, it was observed that the leakage of ammonia-nitrogen was the highest during the last run. Therefore, a reduction in output could be expected with an increasing number of runs.

A poor performance of ammonia-nitrogen removal was observed in column studies with the 0,5 to 1,0 mm particle size when the regenerant was reused. Decreasing output was observed and the leakage of ammonia-nitrogen was also high during the last run. Output of treated water was about 80 BV. However, it was demonstrated that output could be increased to about 220 BV by regenerating with a stronger regenerant solution (1,0 M sodium chloride solution). However, output again decreased when 0,1 M sodium chloride was used as regenerant.

Ammonia-nitrogen could be effectively removed from the spent regenerant with counter-current air-stripping using Raschig rings. Ammonia-nitrogen could be removed in one case from 65 mg/l in the spent regenerant to approximately 1,0 mg/l (98,5% removal). In another case the ammonia-nitrogen could be removed from 120 to 10 mg/l (91,7% removal).

It appears that it should be possible to conduct approximately 6 to 8 regenerant reuses without a reduction in output capacity when using the 0,2 to 0,5 mm Pratley clinoptilolites. It also appears that there is very little difference in the performance of Pratley 1 and Pratley 2 clinoptilolites for ammonia-nitrogen removal.

The breakthrough capacity for Pratley 2 clinoptilolite remained at approximately 0,22 me/ml when six regenerant reuses were applied and when 30 BV 0,1 M sodium chloride was used as regenerant. A deteriorating performance for ammonia-nitrogen removal was observed when 15 bedvolumes 0,1 M NaCl was used for regenerant reuse. It is further important to note that the amount of caustic soda required to raise the pH increased significantly with increasing regenerant reuse cycles.

Chemical cost for ammonia-nitrogen removal from secondary effluent (column studies)

is estimated at R0,76/m<sup>3</sup>. However, this cost should be reduced with regenerant reuse and ammonia recovery. Chemical cost with powdered clinoptilolite is very high and it appears not to be an option for the removal of ammonia-nitrogen from secondary effluent.

### Performance of clinoptilolite on pilot scale for the removal of ammonia-nitrogen

Pilot studies have shown that between 165 and 175 bedvolumes of product water could be produced when the feed ammonia-nitrogen concentration was approximately 16 mg/l. No significant reduction in output capacity was experienced. Therefore, fouling of the clinoptilolite surface should not be a big issue during ammonia-nitrogen removal from secondary effluent. Most of the ammonia-nitrogen could be removed from the clinoptilolite with approximately 15 to 20 bedvolumes of regenerant. Potassium, calcium and magnesium ions that are removed with the ammonia-nitrogen in secondary effluent could also be effectively removed from the clinoptilolite during regeneration. A backwash flow rate of 700 l/h would be required for the successful backwash of the clinoptilolite prior to regeneration. Ammonia-nitrogen speciation as a function of pH has shown that the ammonia-nitrogen should be successfully removed from the feed up to a pH of approximately 7.5. It has been shown that output of product water remained constant after three consecutive biological regenerations. Therefore, it appears that biological regeneration should not adversely affect the surface of the clinoptilolite. However, more consecutive regenerations would be required to prove this point.

### Process design criteria and costs

Process design criteria for a full-scale plant have been successfully derived from pilot studies. A loading flow rate (15 to 20 mg/l NH<sub>3</sub>-N in feed) of 10 bedvolumes per hour is suggested because the retention time in the column is in the same order as that of ionexchange applications. The ammonia-nitrogen capacity at a breakthrough of 2 mg/l NH<sub>3</sub>-N is 3,1 g NH<sub>3</sub>/l. Between 120 and 170 bedvolumes of product water should be produced.

Design options for ammonia-nitrogen removal are suggested. Effluent from the secondary clarifiers (< 10 NTU) can be filtered through a sandfilter (< 1 NTU) to protect the clinoptilolite bed from plugging. Feed water containing 15 to 20 mg/l ammonia-nitrogen can be passed through the clinoptilolite bed and the treated water should have an ammonia-nitrogen concentration of less than 6 mg/l which can be discharged back into the water environment. The spent regenerant can either be chemically/physically or biologically treated for ammonia removal to recover the regenerant for reuse. This will reduce the volume of the spent regenerant for disposal. However, only a few biological regenerations have been conducted but the results look promising. More work should be conducted to determine the efficiency of biological regeneration. Chemical/physical treatment of the spent regenerant on the other hand has been well researched and ammonia-nitrogen can be recovered as a fertilizer in the process.

The estimated capital costs for 50 and 100 m<sup>3</sup>/d plants are as follows:

**50 m<sup>3</sup>/d plant** R250 000 without NH<sub>3</sub>-N recovery

R290 000 with NH<sub>3</sub>-N recovery

**100 m<sup>3</sup>/d plant** R350 000 without NH<sub>3</sub>-N recovery

R390 000 with NH<sub>3</sub>-N recovery

The estimated operational costs for 50 and 100 m<sup>3</sup>/d plants are as follows:

**50 m<sup>3</sup>/d plant** R57,55/d without NH<sub>3</sub>-N recovery

R61,75/d with NH<sub>3</sub>-N recovery

**100 m<sup>3</sup>/d plant** R85,1/d without NH<sub>3</sub>-N recovery

R39,5/d with NH<sub>3</sub>-N recover

**Note:** The value of ammonium sulphate for 50 and 100 m<sup>3</sup>/d plants are estimated at R19,50 and R39/d, respectively. The typical life-time of an ion-exchange plant is approximately 15 years.

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