Evaluation of a South African clinoptilolite for the removal of ammonia-nitrogen from secondary sewage effluent for pollution control

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by

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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 ammonia-nitrogen 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 oversees 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^2/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 ammonoia-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 ammonia-nitrogen 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 ammonoia-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^3. 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_3-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 ion-exchange applications. The ammonia-nitrogen capacity at a breakthrough of 2 mg/ℓ NH_3-N is 3,1 g NH_3/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^3/d plants are as follows:

50 m^3/d plant R250 000 without NH_3-N recovery
R290 000 with NH_3-N recovery

100 m^3/d plant R350 000 without NH_3-N recovery
R390 000 with NH_3-N recovery

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

50 m^3/d plant R57,55/d without NH_3-N recovery
R61,75/d with NH_3-N recovery

100 m^3/d plant R85,1/d without NH_3-N recovery
R39,5/d with NH_3-N recover

Note: The value of ammonium sulphate for 50 and 100 m^3/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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The Steering Committee responsible for this project consisted of the following persons:

Dr V Naidoo	Water Research Commission (Chairperson)
Mr GB Saayman	City of Tshwane Metropolitan Municipality (CTMM)
Mr GFJ Horn	Council for GeoSciences (CGS)
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1. INTRODUCTION

Ammonia-nitrogen (NH_3-N) discharged into the water environment accelerates eutrophication of rivers and dams and dissolved oxygen depletion in receiving waters (Rozic et al., 2000; Maranon et al., 2006; Rahmani et al., 2004). Ammonia-nitrogen in its undissociated form is also toxic to fish at low concentration levels (0,2 mg N/ℓ) and its removal can be important for fish farming, particularly where a high proportion of the water is recycled (Maranon et al., 2006). The current discharge requirement of ammonia-nitrogen in secondary effluent is 10 mg/ℓ. This discharge concentration may be reduced to 6 mg/ℓ in future.

Municipal biological treatment plants in South Africa are experiencing difficulties in producing treated effluent containing less than 10 mg/ℓ ammonia-nitrogen during winter months due to slower biological activity and inefficient plant control. Therefore, technologies should be developed that would be able to reduce the ammonia-nitrogen to the desired levels.

The methods of ammonia-nitrogen removal that can be used for the removal of ammonia-nitrogen from wastewaters include (Demir et al., 2002; Jorgensen et al., 1976):

- Biological nitrification and denitrification.
- Liming to pH 11 followed by air (or steam) stripping.
- Breakpoint chlorination, followed by treatment using activated carbon.
- Algae ponds.
- Selective ion-exchange using zeolites (clinoptilolite).

It does not seem possible to apply ammonia stripping and algae ponds effectively due to low temperatures during the winter season. Breakpoint chlorination is very useful for the removal of a few mg ammonia per litre of wastewater, but is too expensive to apply for wastewater with the normal concentrations of 25 to 40 mg of NH_4^+-N/ℓ, since the amount of chlorine required is about ten times the ammonia-nitrogen concentration.

Nitrification and denitrification are biological methods and therefore not applicable for municipal wastewater containing toxic substances. This process seems difficult to control and automise and furthermore takes up a great deal of space. However, the cost of the process is rather moderate and new developments have shown that it is not even necessary to add methanol to the denitrification step. Due to the control and the sensitivity to variations, it seems most useful to apply the method on larger sewage plants.

The ion-exchange process, using the ammonium selective ion-exchanger clinoptilolite, is slightly more expensive than nitrification and denitrification and has the disadvantage that an elution liquid, which must be discharged, is produced. However, this process is not very much dependent on temperature as biological processes and clinoptilolite is also a relatively inexpensive material.

Clinoptilolite is a natural zeolite. Zeolites are a family of alumino-silicates with an unusual crystalline structure enclosing pores occupied by cation and water molecules, both of which have considerable freedom of movement, permitting, within limits, reversible ion exchange and reversible dehydration (Smith, 1963). About 50 species of natural zeolites have been recognized and an equal number synthesized in the laboratory (Sheppard, 1984).

In general, zeolites have an open, infinitely, extended three dimensional framework composed of silica and alumina tetrahedrons. All four corner oxygen atoms of each tetrahedron are shared with adjacent tetrahedrons (Mumpton, 1984). However, there is a net negative charge on the framework because of the substitution of aluminium atoms for silicon atoms. Therefore, the higher the silica: alumina ratio the lower its charge and the lower its cation exchange capacity. This negative charge is balanced by ions found in the interstices of the zeolites, usually alkaline or alkaline-earth cations.

The idealised chemical formula of clinoptilolite is (Pratley Information Sheet, 1977):

$CaNa_4K_4\ (A\ell O_2)_6\ (S_iO_2)_{30}\ .\ 24\ H_2O$

Pratley clinoptilolite has the following formula (Pratley Information Sheet, 1977):

$(Mg\ Ca\ Na\ K_2)_{2,6}\ (A\ell_2O_3)_7\ (S_iO_2)_{30}\ .\ 2\ H_2O$

The cation selectivity of clinoptilolite is:

$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$ (Koon and Kaufman, 1971). Thus, clinoptilolite has a decided preference for larger cations, and its selectivity for NH_4^+ was exploited by Mercer et al. (1970) in the development of an ion-exchange process for the removal of ammonical nitrogen from municipal sewage effluent.

The loading and regeneration of clinoptilolite can be represented as follows (Koon and Kaufman, 1981):

Loading: $NaZ + NH_4^+ \rightarrow NH_4Z + Na^+$

where Z = zeolite

Loading is usually performed under slightly acidic pH conditions to convert any free ammonia to the ammonium ion.

$NH_3 + H^+ \rightarrow NH_4^+$

Regeneration is usually performed with sodium chloride under alkaline conditions (pH 12 to 12,50) to accelerate the regeneration process.

$NH_4Z + NaCl + NaOH \rightarrow NaZ + NH_3 + NaCl + H_2O$

The adsorbed ammonium ions are converted to free ammonia at the high pH and this ammonia diffuses more readily from the tiny pores in the zeolite matrix. Calcium compounds can also be used to regenerate the clinoptilolite.

The performance of clinoptilolite for ammonia-nitrogen removal from polluted waters has been investigated by many researchers the last 35 years. These studies focussed on: (a) The properties of the zeolites (Hedstrom, 2001; Demir et al., 2002; Watanabe et al., 2003; Rozic et al., 2000; Englert and Rubio, 2005; Schoeman, 1986; Leyva-Ramos et al., 2004); (b) Occurrence (Hedstrom, 2001; Wipplinger and Horn, 2000); (c) Factors having an impact on ammonium exchange on zeolites (Hedstrom, 2001; Zie et al., 2006; Rahmani et al., 2004); (d) Chemical and biological regeneration of ammonium saturated zeolites (Semmens et al., 1977; Rahmani et al., 2006).

The ammonium ion-exchange technique has not been extensively used on a commercial scale within the field of domestic wastewater treatment (Hedstrom, 2001). Applying the ammonium ion-exchange technique with the aim to recover nitrogen has not been investigated as much. It was mentioned that the drained nitrified brine might be used as a fertilizer. A combined anion and cation exchange technique was developed where both ammonium and phosphorus ions were separated, desorbed and then precipitated as magnesium ammonium phosphate. This compound is known as a slow release fertilizer. It was also reported that, when ammonia was stripped after an ion-exchange process and then sorbed in sulphuric acid, the formed solution could be used as a fertilizer.

The main aim of this investigation was to develop process design criteria and costs for the implementation of a South African clinoptilolite for ammonia-nitrogen removal from secondary sewage effluent for pollution control. Secondary objectives were to:

a. Determine the efficiency of powdered clinoptilolite for ammonia-nitrogen removal from secondary effluent;

b. Determine the efficiency of ammonia recovery from the spent regenerant;

c. Determine the performance of clinoptilolite on laboratory scale for the removal of ammonia-nitrogen from secondary effluent;

d. Determine the performance of clinoptilolite on pilot plant for the removal of ammonia-nitrogen from secondary effluent; and

e. Derive process design criteria and costs of the process to remove ammonia-nitrogen from secondary effluent.

The first section of this report deals with a background to the study and the second section describes the experimental set-up. The third and fourth sections present the results and discussions and conclusions, respectively. The last section gives the literature references followed by the Appendixes.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Natural Zeolites and Feed solutions used

Three different types of natural zeolites were used for this study. Two of the these natural zeolites (Old Pratley clinoptilolite (Pratley 1) and New Pratley clinoptilolite (Pratley 2) were provided by Pratley Manufacturing and Engineering Company Limited, and identified as mainly clinoptilolite. The Pratley 1 clinoptilolite was supplied in 1986 and the Pratley 2 clinoptilolite was more recently mined. The third natural zeolite (Heidelberg clinoptilolite) was obtained from Heidelberg in Cape Town and was also identified as clinoptilolite. The three different zeolites were crushed and sieved into two different particle sizes (0,25-0,7 mm and 0,5-1,0 mm).

Both secondary sewage effluent and synthetic effluent were used in the laboratory investigation. The wastewater used in this investigation was collected weekly from Sunderland Ridge Sewage treatment plant (activated sludge). The synthetic effluent was prepared by spiking tap water with ammonium chloride.

2.1.2 Reagents and Apparatus used

Reagents

The ammonium chloride, sodium chloride and tri-sodium citrate used were obtained from Promark Chemicals. Phenol was obtained from Merck, and the ethanol 95% ^{V} / v and sodium nitroprusside from Saarchem. The sodium hydroxide pellets were obtained from Radchem. All these chemicals were of analytical reagent grade and all the standard solutions and dilutions of samples were prepared using laboratory deionised water.

2.2 Experimental setup

The experimental setup for the column studies is shown in Figure 1.

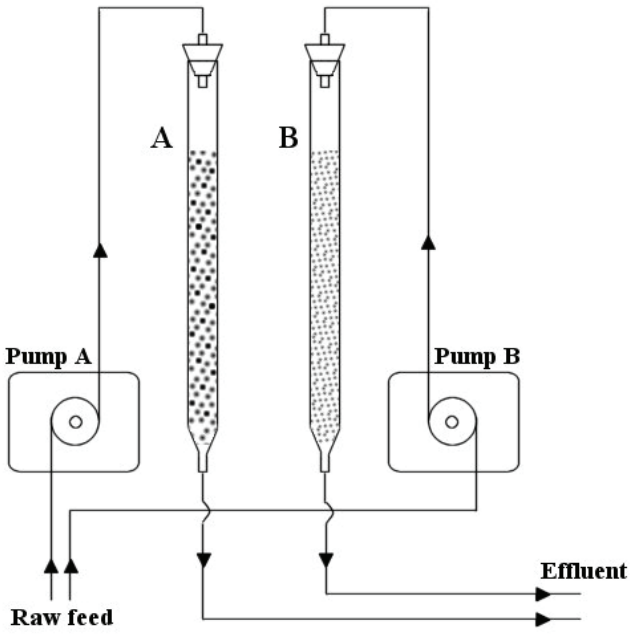


Figure1. Experimental set-up to determine the effect of the different operating parameters on process performance

Column A: clinoptilolite (0,5-1,0 mm particle diameter).
Column B: clinoptilolite (0,25-0,7 mm particle diameter).

Feed from 50-litre containers was pumped with peristaltic pumps through the columns of approximately 25 mm diameter containing 150 mℓ clinoptilolite (1 bed volume (BV) = 150 mℓ). Different loading (5, 10 and 15 BVs/h) and regeneration flow rates were used for the different experiments. The breakthrough point was chosen at 2 mg/ℓ ammonia-nitrogen. Approximately 25 mℓ samples were collected for analysis. The procedure for analysing the samples for NH_3-N is shown in Appendix A.

2.3 Methods

2.3.1 Characterisation of the three natural zeolites

The mineralogical identification of the three clinoptilolites was determined by X-ray diffraction (XRD) analysis. The samples were milled in a swing mill using a WC-milling vessel and then prepared for XRD analysis using a back loading preparation method. The samples were analysed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector with variable divergence and receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore plus software.

Analysis of the major and trace elements was done using X-ray fluorescence (XRF) analysis. The samples were ground to <75 mm in a Tungsten Carbide milling vessel, roasted at 1 000^0C to determine loss on ignition value, and after adding 1 g sample to 6 g Li2B407, fused into a glass bead. Major element analysis was executed on the fused bead using the ARL9400XP and a spectrophotometer. Another aliquot of the sample was pressed in a powder briquette for trace element analysis. Note: Results for elements indicated with an * should be considered to be semi-quantitative.

2.3.2 Determination of ion-exchange capacity

Clinoptilolite was loaded into two columns (0,5-1,0 mm and 0,25-0,7 mm) and back washed to remove fines and dried at 105°C overnight. The two columns were equilibrated with 8 litres of 1 M NaCl for one day at a flow rate of 4 mℓ /min. The excess sodium chloride was removed by washing the columns with deionised water (6 litres) and a test for chloride in the effluent was conducted with a few drops of 0,5 M silver nitrate to ensure that all the chlorides had been removed.

The clinoptilolite was then saturated with 16 litres 1 M NH_4Cl for two days at a flow rate of 4 mℓ/min. Excess NH_4Cl was removed by rinsing the columns with deionised water. The ammonium ions were then eluted with 0,5 M NaCl for two days at a flow rate of 4 mℓ/min and the total ammonia-nitrogen capacity was expressed as milli-equivalents (me) NH_3-N/ g dry clinoptilolite.

2.3.3 Determination of densities

Ten gram of washed and pre-dried samples of sizes 0,25-0,7 mm and 0,5-1,0 mm were placed in a 50 mℓ measuring cylinder containing a known volume of water and air bubbles were removed by tapping and the settled clinoptilolite (tapped) and displaced water volumes were determined. The density is expressed as g/mℓ.

2.3.4 Determination of surface areas

Approximately 150 mg of each sample was put into the sample holder of a BET Single Area Meter. Each sample was baked out for 50 min at 150°C in a He/N_2 stream. The sample weight was determined after the drying process. The surface areas were determined using the standard single-point method. Samples were analysed in triplicate.

2.3.5 Determination of attrition losses

Ten grams of the washed and pre-dried clinoptilolites of different sizes (0,25-0,7 mm and 0,5-1,0 mm) were put into 500 mℓ plastic bottles containing 30 BV regenerant (5,9 g NaCl adjusted to pH 12,2 with NaOH) and shaken for three days on a Labotec shaker. The mass loss was determined after fines had been removed by washing at 50 percent bed expansion. The attrition was expressed as the percentage dry mass loss.

2.3.6 Sorption isotherms

The two most commonly used sorption isotherms to determine adsorption behaviour are the Langmuir and Freundlich isotherms. The Langmuir model is based on the assumption that a single monolayer of sorbate accumulates at the solid surface. The

Freundlich model is characterised by sorption that continues as the concentration of sorbate increases in the aqueous phase (Watts, 1997).

The Langmuir isotherm can be modified to account for competitive adsorption by more than one adsorbate and for adsorbents that have sites with different affinities for a given adsorbate.

The Freundlich isotherm showed that adsorption from solutions can be expressed by the following equation:

$$q = KC^{1/n}$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm. Here K is a measure of the capacity of the adsorbent (mass adsorbate/mass adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. When n = 1, the Freundlich isotherm becomes a linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbate(s). Values of n > 1 indicate that affinities decrease with increasing adsorption density. Evaluation of the coefficients K and n can be accomplished using the linearised form of the above equation.

$$\log q = \log K + 1/n \log C$$

The Langmuir isotherm assumes that a single adsorbate binds to a single site on the adsorbent and that all surface sites on the adsorbent have the same affinity for the adsorbate. Surface complexation theory can be used to develop the Langmuir isotherm:

$$q = \frac{x}{m} = q_m \frac{K_{ads} C}{1 + K_{ads} C}$$

where: q = sorbed concentration (mass adsorbate/mass adsorbent)
x = mass of material sorbed on the solid phase
m = mass of sorbate
q_m = maximum capacity of adsorbent for adsorbate (mass adsorbate/mass adsorbent)
C = aqueous concentration of adsorbate (mass/volume)
K_{ads} = measure of affinity of adsorbate for adsorbent

As C gets larger and larger, adsorption sites become filled and q approaches q_m. Evaluation of the coefficients q_m and K_{ads} can be obtained using the linearized form of the above equation.

$$\frac{1}{q} = \frac{1}{q_m K_{ads}} \left(\frac{1}{C}\right) + \frac{1}{q_m}$$

a) Effect of contact time on ammonia-nitrogen removal efficiency using Pratley 1 and Pratley 2 clinoptilolytes (0,25-0,7 mm) (conditioned and unconditioned)

Tap water was spiked with approximately 5; 10 and 20 mg/ℓ ammonia-nitrogen. Then 4 g of pre-washed and dried clinoptilolytes was added into three 500 mℓ bottles, each containing 500 mℓ of the three different concentrations. The bottles were shaken using the Labotec shaker for the following time intervals: 15 min; 30 min; 1 hr; 2 hrs; 3 hrs; 4 hrs; 5 hrs and 6 hrs. Samples were taken and analysed for the remaining ammonia-nitrogen after these time intervals. The removal efficiencies were determined from the results.

b) Batch adsorption for the generation of isotherms

Clinoptilolite samples (Pratley 1: 0,5-1,0 mm; 0,25-0,75; and powdered) were pre-washed to remove fines and dried. The clinoptilolite samples were regenerated with 30 BV 0,1 M NaCl solution by contacting it for 3 hours with the solution. The clinoptilolite samples were then rinsed for 30 minutes with deionized water and dried overnight at 105°C.

Six plastic bottles were filled with 500 mℓ solution containing approximately 10 mg/ℓ NH_3-N each. Clinoptilolite samples of 1; 2; 3; 4; and 5 g were added to five bottles and the bottles were shaken for 3 hours. The sixth bottle was used as a control. The ammonia-nitrogen remaining in solution was determined after 3 hours.

2.4 Performance of clinoptilolite for ammonia-nitrogen removal from tap water and secondary effluent

A number of runs were conducted to evaluate the performance of untreated (unconditioned) as well as regenerated (conditioned) powdered clinoptilolite for ammonia-nitrogen removal from tap water. A number of runs were also conducted to evaluate the performance of powdered clinoptilolite for ammonia-nitrogen removal from secondary effluent. Several column runs were conducted on tap water spiked with ammonia-nitrogen and also on secondary effluent to determine the output capacity of clinoptilolite for ammonia-nitrogen removal. The amount of ammonia-nitrogen removed during elution with the regenerant was determined and regenerant reuse and ammonia removal with air stripping was also investigated.

2.4.1 Determination of ammonia-nitrogen removal from tap water spiked with approximately 10 and 20 mg/ℓ ammonia-nitrogen using unconditioned powdered clinoptilolite (Pratley 1)

Five beakers were filled with 500 mℓ of a solution containing 20 mg/ℓ ammonia-nitrogen (pH 7). Half a gram of powdered clinoptilolite was added to the first beaker, 1 g to the second, 2 g to the third, 4 g to the fourth beaker and 8 g to the fifth beaker. The beakers were stirred for 30 minutes, and the water filtered and the ammonia-nitrogen concentration remaining in the solution was determined. The procedure was also repeated with 10 mg/ℓ ammonia-nitrogen (pH 7).

2.4.2 Determination of ammonia-nitrogen removal from tap water spiked with approximately 10 and 20 mg/ℓ ammonia-nitrogen using conditioned powdered clinoptilolite (Pratley 1)

The powdered clinoptilolite was conditioned and added to approximately 500 mℓ of the 10 and 20 mg/ℓ ammonia-nitrogen solutions, and stirred for 30 minutes. The procedure as described above was then repeated.

2.4.3 Determination of ammonia-nitrogen removal from Sunderland Ridge secondary effluent using powdered clinoptilolite

The efficiency of powdered clinoptilolites (Pratley 1, Pratley 2 and Heidelberg clinoptililites) were determined for ammonia-nitrogen removal from secondary effluent. These experiments were conducted on unconditioned and conditioned powdered clinoptilolites.

Six beakers were filled with 500 mℓ of Sunderland Ridge secondary effluent containing approximately 20 mg/ℓ ammonia-nitrogen (pH 6.9). One gram of powdered clinoptilolite was added to the first beaker, 2 g to the second, 3 g to the third, 4 g to the fourth beaker and 5 g to the fifth beaker. The water was stirred for 15 min, 30 min and 1 hour, filtered and the ammonia-nitrogen concentration remaining in the solution was analysed by the phenate method.

Note: About 40 g of powdered clinoptilolite was added to 30 BV 0.1 M NaCl (1 200 mℓ of 0,1 M NaCl; 1 BV = 40 mℓ) and the mixture was stirred slowly for 30 minutes to prepare the conditioned clinoptilolite. The mixture was allowed to settle, filtered and dried at 105°C for 1 hour.

2.4.4 Establishment of breakthrough curves (tap water spiked with NH_4Cl)

A number of runs were conducted to establish breakthrough curves using tap water spiked with NH_4Cl and secondary effluent from Sunderland Ridge. The pre-washed and dried Pratley 1 clinoptilolite was loaded into a column (0,5-1,0 mm; 1 BV = 150 mℓ). The first run was conducted with unconditioned clinoptilolite and the second run was conducted after regeneration with 30 BV of 0,1 M NaCl solution with the pH adjusted to between 12 and 12,5 with caustic soda (NaOH). Excess NaCl and NaOH were removed by backwashing the column for 30 minutes with tap water. The loading was performed with approximately 20 mg/ℓ ammonia-nitrogen in the feed solution (pH 7) and samples were collected after 20 BV (2 hrs) and analysed for the ammonia-nitrogen by the Phenate method and breakthrough curves were established. The breakthrough point was taken at 2 mg/ℓ ammonia-nitrogen. Runs were also conducted using two different particle sizes of clinoptilolite (0,25-0,7 and 0,5-1,0 mm), different flow rates, different loading rates and different feed pH values to determine the effect of these process variables on process performance. The effect of a number of consecutive runs and regenerant reuse on process performance was also determined.

2.4.5 Establishment of elution curves

During regeneration of the column with 30 BV of 0,1 M NaCl (pH 12), samples were collected from the column outlet at 0 min, 5 min, 10 min, 15 min intervals and continued at time intervals of 15 min until 30 BV were reached. The samples were analysed for ammonia-nitrogen eluted from the clinoptilolite by the Phenate method, and elution curves were plotted.

2.4.6 Regenerant reuse

Several runs were conducted to establish the effect of regenerant reuse on the performance of clinoptilolite when the 0,1 M NaCl regenerant was reused a number of times. The waste regenerant's pH decreased slightly from 12 to 11 and 11,5 during these experiments. The regenerant was air stripped to remove the ammonia. The pH was adjusted back to between 12 and 12,5 with 1 M NaOH and regeneration conducted as previously described.

About 500 mℓ of regenerant solution evaporated during air stripping, decreasing the volume of the solution from 4,5 litres to 4,0 litres. The solution was filled up with fresh 0,1 M NaCl solutions.

2.4.7 Ammonia removal with air stripping from the spent regenerant.

Ammonia removal from the spent regenerant was attempted by two methods. In the one method, spent regenerant was circulated through a column (80 mm diameter) packed with Raschig rings, while air was counter currently passed through the column. In the other experiment air was bubbled through a porous diffuser through the spent regenerant.

2.5 Pilot studies

2.5.1 Methodology

A pilot plant using Pratley clinoptilolite was designed from laboratory column tests (Appendix B).

The following experimental work was conducted:

a. The pilot plant was repeatedly subjected to the treatment cycle to treat secondary effluent, i.e. loading (service run), backwash, regeneration and rinsing. Samples of the treated water were taken at measured intervals (10 BV) to establish breakthrough curves. After breakthrough (2 mg/ℓ NH_3-N) was achieved, the clinoptilolite was backwashed with tap water, regenerated with a 0,1 M NaCl solution at pH 11,4 and rinsed to remove excess caustic soda. This procedure was repeated under similar conditions to establish the repeatability and predictability of the process.

The treated water from these cycles was discharged into a product water tank. The sole purpose of the tank was to accurately control the flow rate

and sampling intervals. Sampling intervals were determined volumetrically instead of on the basis of time and flow rate. During these tests all the operational parameters were maintained as constant as possible.

The treated secondary effluent was discharged back into the main effluent stream on completion of the service run and the spent regenerant was either returned to a holding tank for conditioning and reuse or discharged back into the main effluent stream.

b. Samples of the spent regenerant were collected from the column outlet and analysed for ammonia-nitrogen eluted from the clinoptilolite bed to establish elution curves.

c. The loading cycle was repeated with lower and higher flow rates to investigate the effect of feed flow rate on process performance.

d. A biological restoration process was introduced to restore the spent regenerant utilising the concept of nitrification. The concept is discussed in more detail in the pilot experimental set up below but in brief, the regenerant consisting of 0,4 M NaCl solution at approximately neutral pH is pumped through the exhausted clinoptilolite to displace the ammonium ions. The regenerant is drawn from a storage tank and passed through the column to strip the ammonia from the clinoptilolite. The ammonium rich regenerant is returned to a storage tank from which it is fed to an aeration tank where the ammonium is oxidised to nitrate by nitrifying bacteria. The sodium content of the regenerant solution is maintained by the addition of NaOH which also serves to maintain a neutral pH in the aeration tank. It is well documented that nitrifying bacteria operate at maximum efficiency in the range $7.0 < pH < 8.5$. Secondary effluent was used as make-up and top up water to provide the necessary nutrients to support the growth and reproduction of the nitrifiers. Three runs were conducted as proof of concept. Breakthrough and elution curves were established from the biologically restored regenerant.

2.5.2 Experimental set-up

a. Location of the pilot plant

The pilot plant was commissioned at the 4,0 Mℓ/d Thaba Tshwane Wastewater Treatment Works which is owned and operated by the Department of Public Works. The facility is situated about 8 km south of Pretoria in the military area of Thaba Tshwane.

The influent to the works originates from the Thaba Tshwane military complex consisting of residential areas, military training areas, sporting facilities, hospitals, commercial business and light industries.

The sewage is characterised as a typical low strength domestic sewerage. The low strength can be attributed to the poor state of the plumbing in the buildings of the area served which results in significant infiltration of fresh water into the system. This observation is substantiated by the high volume of night flow measured on the water supply system and the treatment works alike.

Typical characteristics of the raw water that enters the works are:

TSS 287 mg/ℓ; COD 448 mg/ℓ; NH_3-N 18,2 mg/ℓ; NO_3-N 0 mg/ℓ;
EC 50,6 mS/m; pH 7,1.

The treatment works comprises of a conventional bio-filter configuration consisting of primary treatment (screens, grit removal, primary settling) followed by secondary treatment (biofiltration, humus tanks, chlorination and rapid sand filtration). The secondary effluent is split into two streams and is disposed of by irrigation. Vegetable crops are irrigated at the Thaba Tshwane prison with the first stream and the sport fields and golf course are irrigated with the second stream.

A suitable position for the pilot plant was selected on top of the effluent pumping station adjacent to the rapid gravity sand filters. This position was selected because it:

i. provides a stable, sheltered platform for the pilot plant;

ii. provides a convenient position to abstract treated filtered effluent from the works under gravity;

iii. is in close proximity to a power supply point for the supply of power to the pilot plant; and

iv. is adjacent to a large effluent sump into which the product, rinse and backwash water from the pilot plant could be discharged.

b. Pilot plant

The design of the pilot plant was based on the process design criteria established in the laboratory experiments (Appendix B). The laboratory experiments provided information on the ion-exchange and adsorption characteristics of the clinoptilolite in terms of the ammonia-nitrogen capacity at varying feed concentrations, loading flow rates, regeneration concentrations, regeneration flow rates and regeneration times. The suggested optimum loading flow rate of 10 BV/h was used for testing and include experiments with higher and lower (5 BV/h and 15 BV/h) flow rates. The pilot plant set-up worked very well and was robust, flexible and easy to operate.

In addition to the scaling up of the laboratory experimental set-up, a nitrification step was provided to verify the concept of biological restoration of the regenerant for reuse.

Design criteria for the pilot plant are shown in Table 1 (from Appendix B).

The clinoptilolite used in the pilot plant is referred to as "Pratley 2" in the laboratory experiments and was obtained from Pratley Manufacturing and Engineering Company Limited. It was supplied in 50 kg bags and had a size grading of 0,1-3,0 mm. The clinoptilolite was crushed and sieved at a commercial soil laboratory to obtain the required grading of 0,25 to 0,7 mm on which the pilot column design was based.

A 150 mm diameter 2,1 m long column was fabricated from a transparent Perspex tube and closed off on either end with strained end caps (Appendix B). The top strainer prevents the loss of media during the backwash cycle and the bottom strainer provides the support platform for the media. The transparent column allowed the various cycle flows through the clinoptilolite to be observed for any operational peculiarities. The column was filled with 23 litres (1 BV) of graded clinoptilolite for the continuous adsorption of ammonia-nitrogen from the effluent. The clinoptilolite occupied 1,3 m of the 2,1 m column leaving 0,8 m (50%) for bed expansion during the backwash cycle.

Table 1: Process design criteria for the design of the pilot plant

Criterion	Value / Comment
Flow	1 m^3/d; 7 m^3/week
Particle size	0,25 to 0,7 mm
NH_3-N exchange capacity	0,22 me/ℓ or 3,08 g/ℓ
Bed volume (BV)	23 ℓ
Loading flow rate	10 BV/h (230 ℓ/h)
Loading time	Until breakthrough (approx. 15 h)
Treated water	Approximately 150 BV
Regeneration flow rate	10 BV/h (230 ℓ/h)
Regenerant usage	30 BV of 0,1 M NaCl adjusted to pH 11,4 with NaOH solution
Regeneration time	3 h
Rinsing time	10 min.
Total cycle time	Approximately 20 h
Cycles per day	1
Attrition losses	2%/a (guestimated)
Water recovery	98%
Waste regenerant	3,3%
Backwash flow rate	40-50 BV/h
Backwash time	10 min.
Flow volume	1 m^3/d; 7 m^3/week; Design based on two runs of 3,5 m^3/week

A typical operational cycle consisted of:

i. **Loading**: 15 to 20 h @ 10 BV/h; feed water 15 to 20 mg/ℓ NH_3-N; column operated in down-flow mode.

ii. **Backwashing**: 10 min @ 40 to 50 BV/h with tap water; column operated in up-flow mode at a flow rate resulting in 50% bed expansion.

iii. **Regeneration**: 3 h with 0,1 M NaCl at pH 11,4; column operated in down-flow mode.

iv. **Rinsing**: 10 min @ 10 BV/h with tap water; column operated in down-flow mode.

The pilot plant was designed with a single pump receiving water from one of three sources depending on the operational cycle, i.e.:

filtered effluent for the loading cycle;
tap water for the backwash and rinse cycles; and
0,1 M NaCl for regeneration of the clinoptilolite.

A system of valves and pipes were installed so that the flow direction (up-flow or down-flow) through the column could be selected by the operator. The configuration makes provision for any possible combination of flow pattern allowing the necessary flexibility in operation.

c. Pre-treatment procedure

Column pre-treatment was applied by backwashing the clinoptilolite with tap water until all the fine particles (fines) entrapped in the column were released and the wash water was visibly clear. Pre-treatment was continued by passing 30 BV of a 0,1 M NaCl at pH 11,4 through the column at a flow rate of 10 BV/h followed by a rinsing cycle. This procedure was repeated.

The flow diagram and layout of the pilot plant are shown in Figure 2.

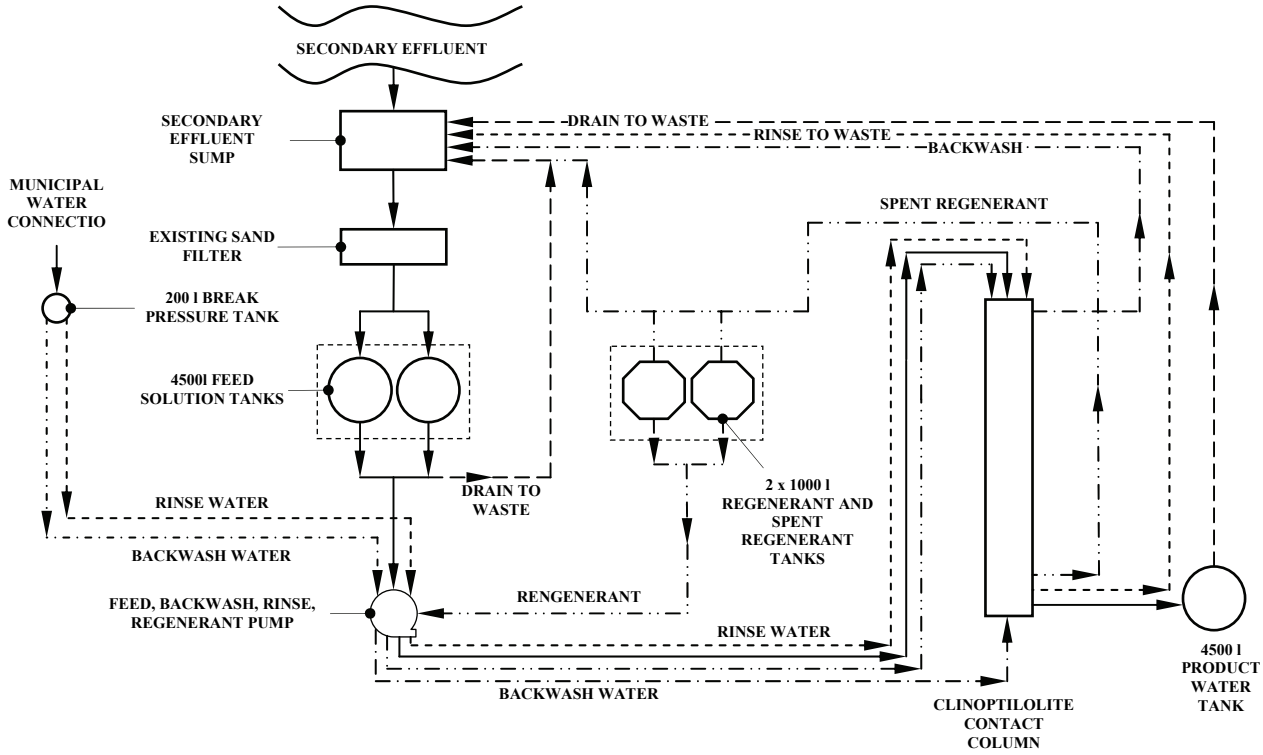


Figure 2: Flow diagram of pilot plant set-up.

Feed water was sourced from one of two 4 500 litre tanks that was filled under gravity with filtered effluent from the rapid gravity filters. The filtered effluent had the advantage of restricting the contamination of the clinoptilolite bed. From these tanks (one at a time) the effluent was pumped through the column at the selected flow rate in either the up-flow or down-flow directions and onward to a 4 500 litre treated water tank.

The 4 500 litre tanks were selected because they each represented 200 BV (4 600 ℓ) if filled to the brim which volume was shown to be the upper limit of the volume required to achieve breakthrough at the target initial feed concentration of 15 to 20 mg/ℓ NH_3-N.

One of the feed water tanks was filled and spiked with NH_4Cl to raise the ammonia-nitrogen concentration to the target value of between 15 and 20 mg/ℓ while the other one was in operation (loading cycle). The tanks were used alternatively.

A 20 mm transparent PVC pipe was installed on the outside of the 4 500 litre product water tank and marked off at intervals of 10 BV. This was found to be a convenient method of measuring the depth (volume) of effluent passing through the column during the feed cycle.

Conversion of the clinoptilolite bed back to the sodium form was conducted with a 0,1 M NaCl solution which was adjusted to a pH of 11,4 with NaOH prior to passing through the exhausted clinoptilolite. The regenerant was made up in a 1 000 litre PVC tank with tap water and was pumped through the column at the set flow rate. Two 1 000 litre tanks were provided so that the spent regenerant could be captured and reused. The regenerant was fed from the one tank through the column and into the second tank. The tanks were used alternatively as feed and storage tanks.

A 1 000 litre aeration tank was added to the system for the nitrification of the spent regenerant. This tank was piped in series with the two existing regenerant tanks and the three tanks were operated in a feed water (spent regenerant) aeration and settling tank (batch mode) and restored regenerant tank.

Backwash and rinse water was obtained from the municipal system. Water was laid onto the pilot plant from a garden tap and was discharged into a small 200 litre PVC tank to break the municipal water pressure. From this tank the water was pumped through the column in the selected direction and discharged to waste.

A flow meter was installed at the feeder pipe to give a real time indication of the flow rate. This type of flow measuring device only measures the flow rate and not the total flow. Given the nature of the pump and varying pressure in the system (dropping inlet pressure and rising outlet pressure), it was accepted that the flow rate would have to be controlled on a continuous basis. The product water tank was used to verify the total flow and to ensure that the sampling intervals were based on volume and not strictly according to a time schedule.

Samples were taken at volumetric intervals of 20 BV, 40 BV, etc., for ammonia-nitrogen determinations.

A variable speed drive was installed on the feed pump to control the pumped flow rate. The drive worked on the principle of dropping the power frequently but proved to be unreliable and susceptible to Eskom's power outages. An alternative hydraulically controlled arrangement was introduced by changing the pipework to recirculate some of the water from the delivery side of the pump to the suction side of the pump. The hydraulically controlled mode proved to be robust and reliable.

d. Analytical procedure

Test samples for ammonia-nitrogen were initially analysed at the Department of Public Works' water laboratory using the Hach Nessler method but long delays were experienced in getting the results. These delays severely retarded the momentum of the experiments and an alternative more direct method of measuring the ammonia-nitrogen concentration was required to get quick but relatively accurate results.

An Orion 93-18 Ammonium Ion-Selective Electrode was then used to measure the ammonium concentration directly. Drift problems common with these types of measuring devices were overcome by the regular analysis of standards and recalibration of the electrode. Random samples were also submitted to the laboratory for testing and confirmation of the results obtained with the selective electrode. Good correlation between the results obtained using the electrode and the results obtained by the laboratory could be obtained if the electrode measurements in the electrode testing procedure were undertaken strictly in accordance with the operation manual.

3. RESULTS AND DISCUSSION (LABORATORY STUDIES)

3.1 XRD and XRF analyses

3.1.1 XRD patterns of the zeolites

The XRD patterns of the different zeolites samples are shown in Appendix C.

Pratley 1 and 2 clinoptilolite samples consisted mainly of clinoptilolite with traces of cristobalite low, orthodase and albite high. The Heidelberg clinoptilolite sample consisted mainly of clinoptilolite with traces of quartz and muscovite.

3.1.2 XRF analysis

The XRF analysis of the zeolites are shown in Tables 2 and 3. The most abundant elements for all samples apart from the structural elements (Al, Si, Fe, and O) were potassium, calcium, sodium and magnesium (Table 1). The XRF analysis of the well known Hector clinoptilolite and of a clinoptilolite from Hungary are also shown in Table 2 for comparison purposes. These clinoptilolites differ somewhat regarding their monovalent and divalent contents.

The South African clinoptilolites also differ somewhat regarding the presence of their trace element concentrations (Table 3). These differences, however, are not very significant.

Table 2. X-ray fluorescence analysis (major elements) of the three clinoptilolites (Pratley 1, Pratley 2 and Heidelberg)

Name of Element %	PRATLEY 1	PRATLEY 2	HEIDELBURG	U.S. HECTOR[2]	HUNGARY[3]
SiO_2	70.91	70.28	70.35	66,21	69,12
TiO_2	0.12	0.17	0.13	0,10	0,39
Al_2O_3	11.84	12.36	12.10	12,91	11,60
Fe_2O_3	1.17	1.23	1.16	0,84	1,59
MnO	0.02	0.02	0.03	-	0,01
MgO	0.85	0.74	0.72	0,39	0,18
CaO	1.61	1.29	1.56	1,33	1,27
Na_2O	1.04	1.77	0.62	5,82	0,17
K_2O	4.00	3.53	4.08	1,04	5,50
P_2O_5	0.02	0.02	0.03		
Cr_2O_3	0.01	0.01	0.01		
NiO	0.01	0.02	0.01		
V_2O_5	0.01	0.01	0.01		
ZrO_2	0.00	0.01	0.01		
LOI [1]	8.20	8.46			
TOTAL %	99.82	99.92			

(1): LOI: loss on ignition.
(2): Chmielewska et al. (2002).
(3): Jorgensen et al. (1975).

Table3. X-ray fluorescence analysis (trace elements) of the three clinoptilolites (Pratley 1, Pratley 2 and Heidelberg)

Element (ppm)	PRATLEY 1	PRATLEY 2	HEIDELBURG
As	5	3	3
Cu	17	13	19
Ga	16	15	15
Mo	1	1	1
Nb	26	27	11
Ni	6	6	8
Pb	4	8	13
Rb	107	98	36
Sr	1012	703	953
Th	7	7	6
U	3	3	3
W*	164	113	239
Y	20	23	25
Zn	49	40	47
Zr	150	151	122
Cl*	290	395	692
Co	33	23	42
Cr	7	7	7
F*	1107	1220	851
S*	343	142	1252
Sc	2	2	5
V	17	17	17
Cs	9	10	9
Ba	580	385	3269
La	52	56	37
Ce	98	105	78

3.2 The total ion-exchange capacities and densities of the zeolites

The densities and total ion-exchange capacities of the zeolites are shown in Table 4.

Table 4: Total NH_3-N exchange capacities, bulk densities and specific gravities of Pratley 1, Pratley 2 and Heidelberg clinoptilolites (0,25-0,7 and 0,5-1,0 mm)

Type of Clinoptilolite and particle size	Total NH_3-N capacity (me/g dry)	Bulk density (g/mℓ)	Particle density (g/mℓ)
Pratley 1 0,25-0,7 mm	1,44	1,02	2,22
Pratley 1 0,5-1,0 mm	1,38	1,0	2,08
Pratley 2 0,25-0,7 mm	1,27	0,87	2,22
Pratley 2 0,5-1,0 mm	1,42	0,91	2,08
Heidelberg 0,25-0,7 mm	1,68	1,0	2,22
Heidelberg 0,5-1,0 mm	1,63	0,95	2,5

The total exchange capacities of the Pratley clinoptilolites vary between approximately 1,3 and 1,4 me/g dry. The Heidelberg clinoptilolite appears to have a slightly higher capacity of 1,6 and 1,7 me/g dry. The capacity of the well known Hector clinoptilolite is about 1,6 me/g dry which is of the same order as that of the Heidelberg clinoptilolite and slightly higher than that of the Pratley clinoptilolite (Schoeman, 1986; Dryden and Weatherley, 1987).

The bulk densities of the Pratley clinoptilolites vary between 0,87 and 1,02 and that of the Heidelberg clinoptilolite between 0,95 and 1,0. The particle densities of the Pratley clinoptilolites very between 2,08 and 2,25 and that of the Heidelberg clinoptilolite between 2,22 and 2,15. The high particle densities is indicative of the internal pore structure of the zeolites. The bulk and particle densities of the Hector clinoptilolite are 0,67 and 1,66, respectively.

3.3 Surface areas of the zeolites

The total surface areas of the zeolites are shown in Table 5.

Table 5: Surface areas of the Pratley and Heidelberg clinoptilolites

Sample and size	Surface area (m^2/g)
Pratley 1 (0,25-0,7 mm)	15,2
Pratley 1 (0,5-1,0 mm)	16,9
Pratley 2 (0,25-0,7 mm)	14,8
Pratley 2 (0,5-1,0 mm)	17,6
Heidelberg (0,25-0,7 mm)	16,6
Heidelberg (0,5-1,0 mm)	13,3

The surface areas of the Pratley clinoptilolites vary between 14,8 and 17,6 m^2/g while the areas of the Heidelberg clinoptilolite vary between 13,3 and 16,6 m^2/g. Clinoptilolites from Mexico show surface areas that vary from 5,15 to 22,2 m^2/g (Leyva-Ramos et al., 2004). Clinoptilolite surface areas of 15 to 20 m^2/g have also been reported (Ouki and Kavannagh, 1999).

3.4 Attrition losses of the zeolites

The attrition losses of the zeolites are shown in Table 6.

Table 6: Attrition losses of the Pratley and Heidelberg clinoptilolites

Sample and size	Initial mass	Final mass	% Dry mass loss
Pratley 1 (0,25-0,7 mm)	10 g	9.78 g	2,2
Pratley 1 (0,5-1,0 mm)	10 g	9.78 g	2,2
Pratley 2 (0,25-0,7 mm)	10 g	9.80 g	2,0
Pratley 2 (0,5-1,0 mm)	10 g	9.89 g	1,1
Heidelberg (0,25-0,7 mm)	10 g	9.209 g	8,0
Heidelberg (0,5-1,0 mm)	10 g	9.377 g	6,2

The attrition losses of the Heidelberg clinoptilolite (6,2 to 8,0%) are significantly higher than that of the Pratley clinoptilolites (1,1 to 2,2%). Attrition losses for the Hector clinoptilolite were reported to be 9,3% (Schoeman, 1986). Koon and Kaufmann (1975) found that caustic regeneration solutions seemed to cause an attrition of zeolites because the caustic solution attacked the clinoptilolite frame structure. There was also a significant decrease in the zeolite mass when the pH of the regeneration solution was increased from 11,5 to 12,5. Attrition rates were 0,15; 0,25; and 0,4 percent/cycle for exposure to pH 11,5; 12,0; and 12,5 solutions, respectively.

3.5 Sorption Isotherms (Langmuir and Freundlich plots)

3.5.1 Effect of contact time on ammonia-nitrogen removal (Pratley 1 and 2 clinoptilolites)

The effect of the contact time on the removal of different concentrations of ammonia-nitrogen with clinoptilolite are shown in Figures 3a (unconditioned) and 3b (conditioned). The removal efficiencies are shown in Figures 4a (unconditioned) and 4b (conditioned). The detailed results are shown in Appendix D.

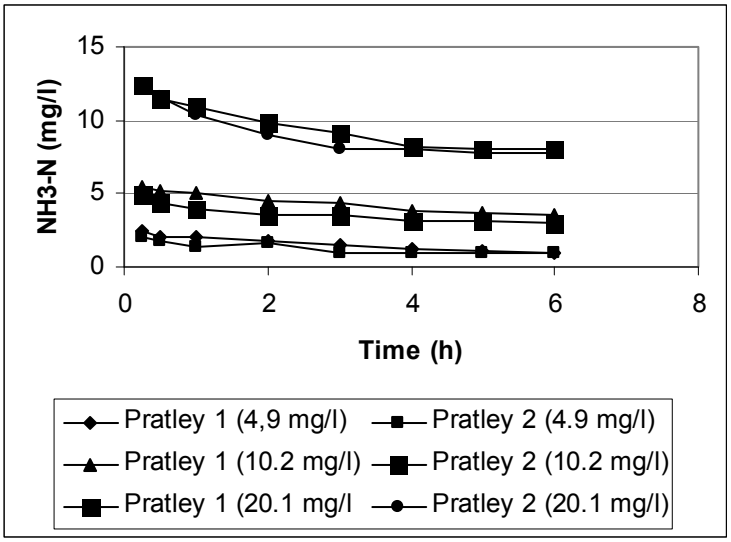


Figure 3a: The effect of contact time on ammonia-nitrogen removal for the unconditioned clinoptilolite (0,25-0,7 mm)

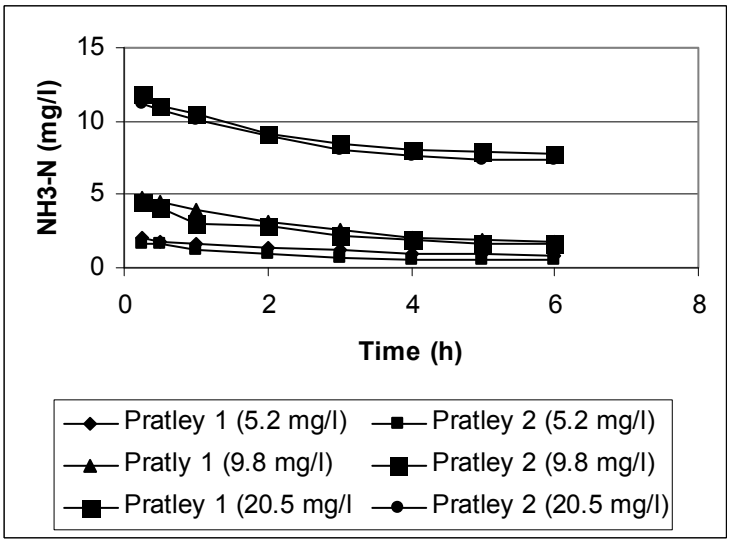


Figure 3b: The effect of contact time on ammonia-nitrogen removal for the conditioned clinoptilolite (0,25-0,7 mm)

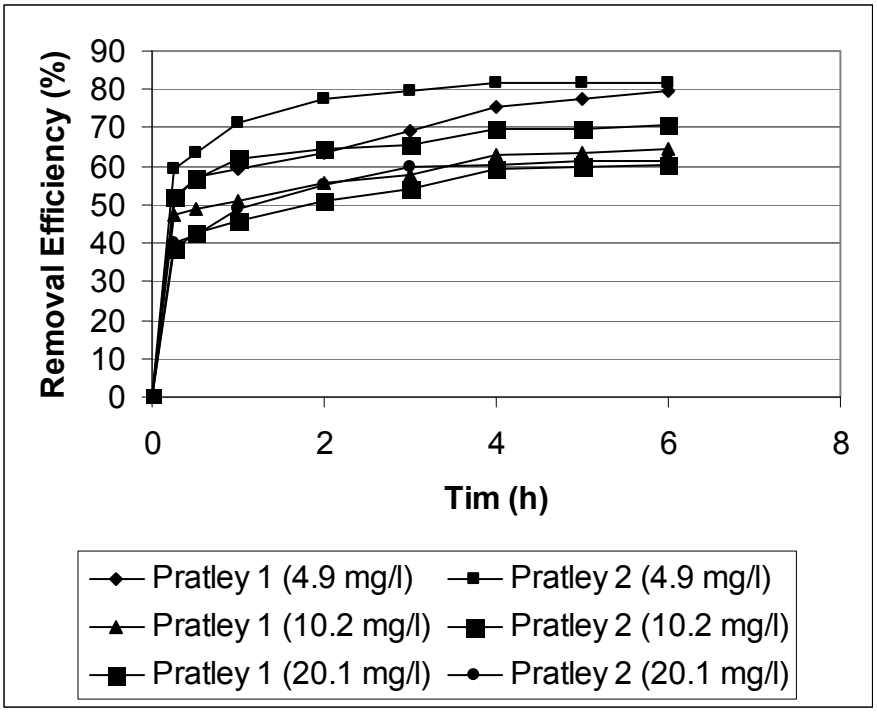


Figure 4a: Removal efficiency as a function of contact time for the unconditioned clinoptilolite (0,25-0,7 mm)

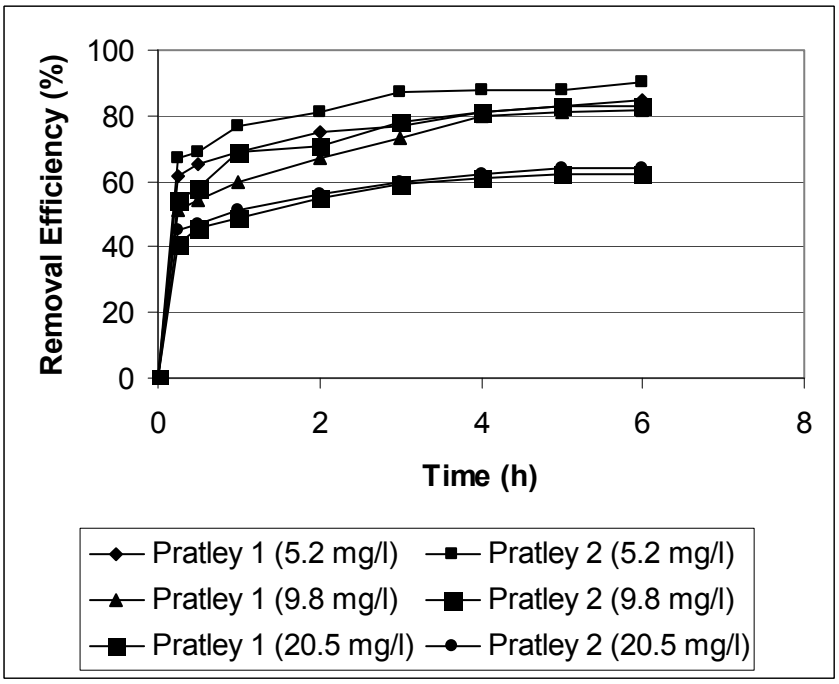


Figure 4b: Removal efficiency as a function of contact time for the conditioned clinoptilolite (0,25-0,7 mm)

Adsorption equilibrium has been established after about 3 hours on the unconditioned clinoptilolite (Figure 3a) and after about 4 hours on the conditioned clinoptilolite

(Figure 3b). The ammonia-nitrogen removal rates were slightly higher with the conditioned clinoptilolites. Pratley 2 clinoptilolite also performed a little bit better than Pratley 1 clinoptilolite. It is also interesting to note that approximately 40 percent and more of the ammonia-nitrogen was removed within 15 minutes.

The removal efficiencies of ammonia-nitrogen decreased with increasing feed concentration. The removal efficiencies decreased from about 80 percent (4,9 mg/ℓ feed) to approximately 60 percent (20,1 mg/ℓ feed) for the unconditioned clinoptilolite. The removal efficiencies decreased from approximately 87,5 percent (5,2 mg/ℓ feed) to approximately 63 percent (20,5 mg/ℓ feed) for the conditioned clinoptilolite. Therefore, significant quantities of ammonia-nitrogen can be removed with the unconditioned as well as with the conditioned clinoptilolite.

3.5.2 Langmuir and Freundlich

The Freundlich and Langmuir isotherm plots for different clinoptilolite (Pratley 1) particle sizes are shown in Figures 5 to 10. The detailed results are shown in Appendix E(Table E.1 to E.8).

It appears from the graphs that the Langmuir isotherm fits the experimental data the best for both the 0,5-1,0 mm (Figures 5 and 6) and 0,25-0,7 mm (Figures 7 and 8) diameter particles characterised by larger R^2 values. A very good fit was obtained with the particle size of 0,25-0,7 mm (R^2 = 0,98; Figure 8). However, the fits were not good for the powdered clinoptilolite (Figures 9 and 10). R^2 should be greater than 0,9 for a good fit.

The variables for both the Langmuir and Freunclich models were calculated from the linear graphs. The calculated variables and corresponding equations are shown in Tables 7 and 8. Model calculations are shown in Figures 11 and 12.

The experimental data correlated reasonably well with the model calculations.

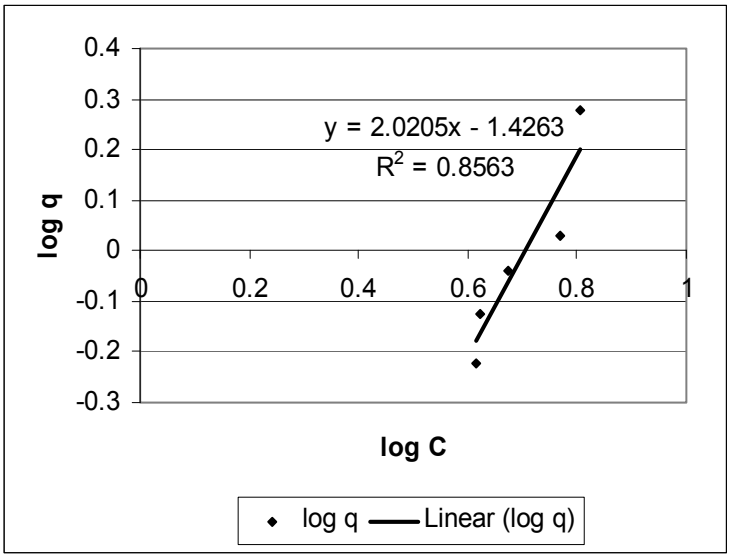


Figure 5: Log q vs log C (3 h, 0,5 to 1,0 mm)

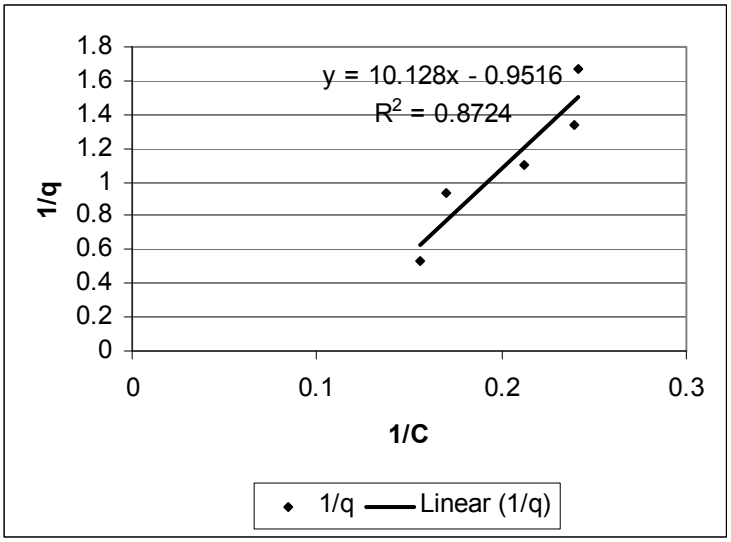


Figure 6: l/q vs l/C (3 h, 0,5 to 1,0 mm)

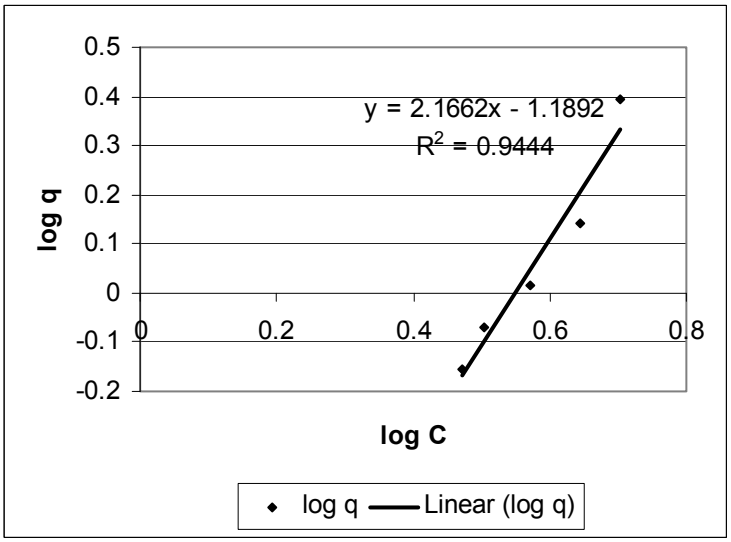


Figure 7: Log q vs log C (3 h, 0,25 to 0,7 mm)

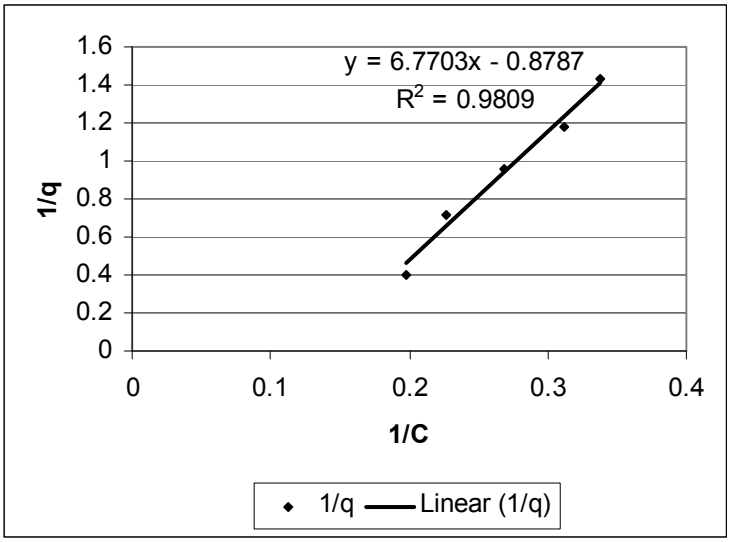


Figure 8: l/q vs l/C (3 h, 0,25 to 0,7 mm)

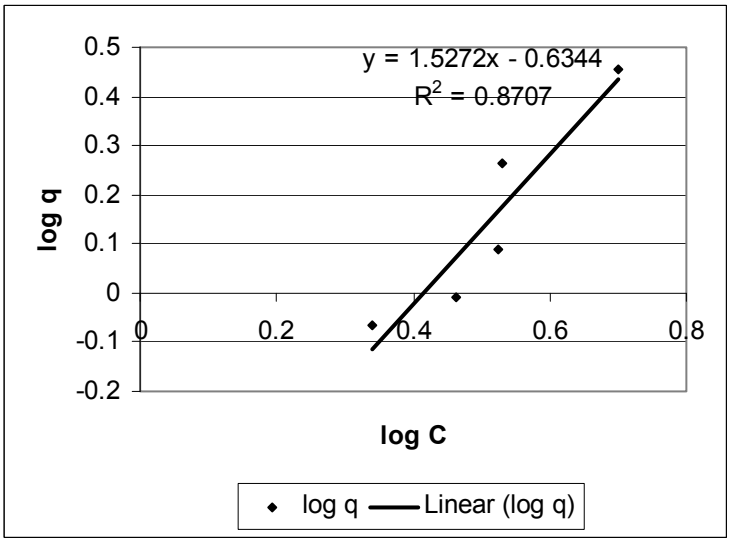


Figure 9: Log q vs Log C (3 h, powdered*)*

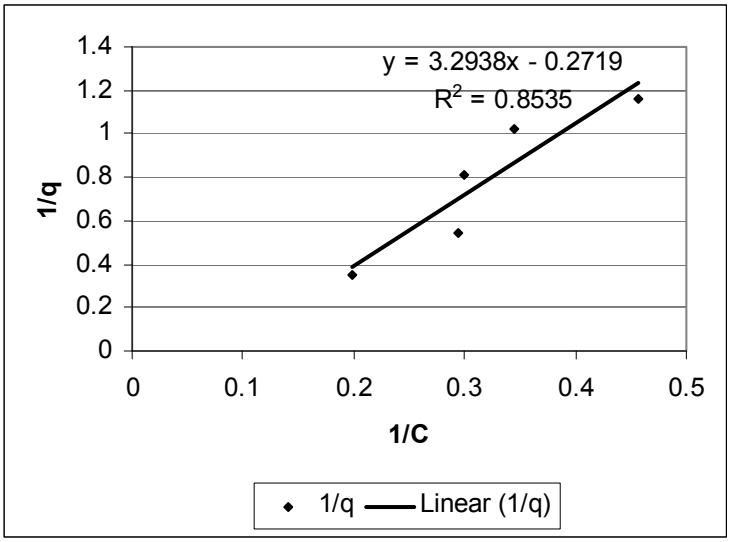


Figure 10: l/q vs l/C (3 h, powdered)

Table 7. Calculated variables for the Freundlich isotherm.

	(0.5-1.0 mm)	(0.25-0.7 mm)	(Powder)
K_F	0.0375	0.0674	0.2321
N	0.4938	0.4616	0.6548
Freundlich isotherm equation	$q = 0{,}0375C^{2{,}0251}$	$q = 0{,}0647C^{2{,}1662}$	$q = 0{,}2321C^{1{,}5272}$

Table 8. Calculated variables for the Langmuir isotherm

	(0.5-1.0 mm)	(0.25-0.7 mm)	(Powder)
q_m	-1.0509	-1.1380	-3.6778
K_{ads}	-0.0932	-0.1298	-0.0825
Langmuir isotherm equation	$q = \frac{0.0979C}{1-0.0932C}$	$q = \frac{0.1477C}{1-0.1298C}$	$q = \frac{0.3034C}{1-0.0825C}$

The model calculations are shown in Figures 11 and 12.

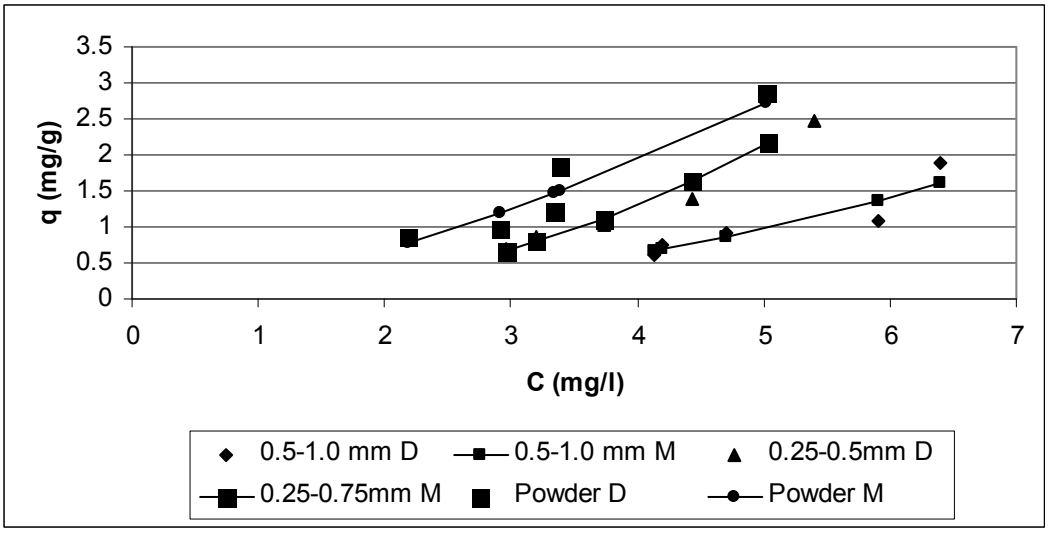


Figure 11: Fitting of experimental data to calculated Freundlich models

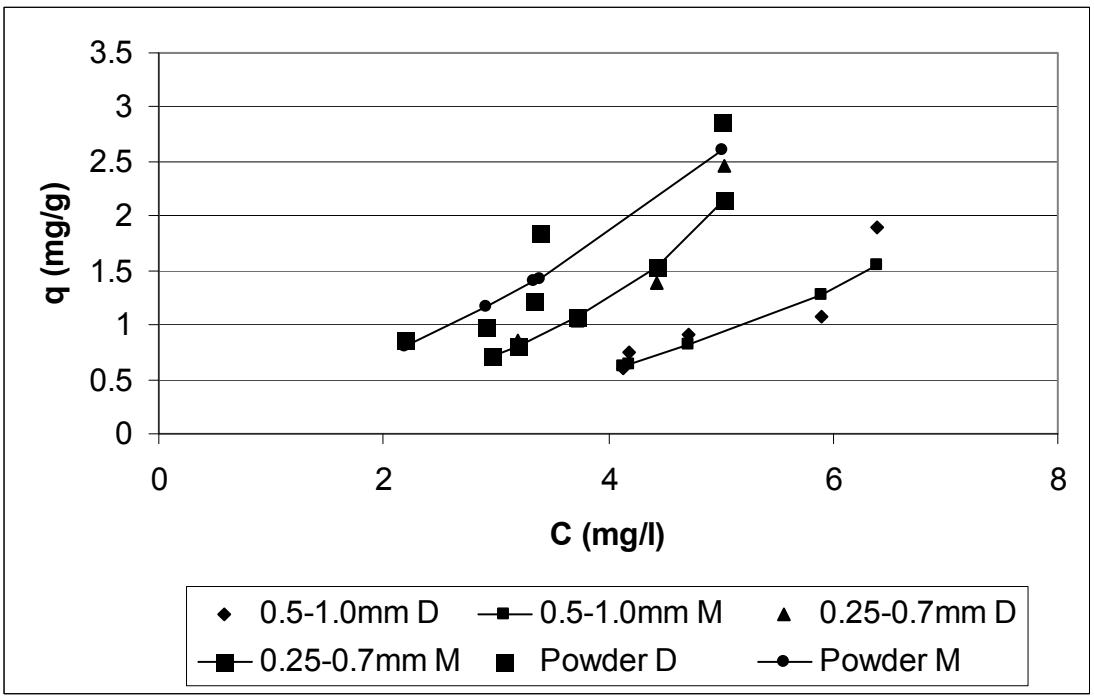


Figure12: Fitting of experimental data to calculated Langmuir models

3.6 Ammonia-nitrogen removal with powdered clinoptilolite

A number of experiments were conducted to determine the efficiency of unconditioned and conditioned clinoptilolite for ammonia-nitrogen removal from tap water spiked with ammonia-nitrogen and from secondary sewage.

3.6.1 Efficiency of unconditioned and conditioned powdered clinoptilolite (Pratley 1) for ammonia-nitrogen removal from tap water spiked with approximately 10 and 20 mg/ℓ ammonia-nitrogen

The concentration of ammonia-nitrogen remaining in the water as a function of the applied dosage of clinoptilolite is shown in Figure 13. The detailed results are shown in Appendix F, Table F.1).

The conditioned clinoptilolite performed much better than the unconditioned clinoptilolite for ammonia-nitrogen removal from tap water. Ammonia-nitrogen could be reduced from 19,1 mg/ℓ to 5,8 mg/ℓ (69,6% removal) with the 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 from 20 mg/ℓ to 6 mg/ℓ (70% removal) in the case of the conditioned clinoptilolite. Ammonia-nitrogen could be reduced from 9,5 mg/ℓ to 5,3 mg/ℓ (44,2% removal) with a dosage of 8 g/ℓ in the case of the unconditioned clinoptilolite whereas a concentration of 1,8 mg/ℓ (80,9% removal) was achieved in the case of the conditioned clinoptilolite. Therefore, it appears that it should be better to pre-treat (regenerate) the clinoptilolite prior to use. However, it appears that high dosages of clinoptilolite would be required to remove significant concentrations of ammonia-nitrogen from water.

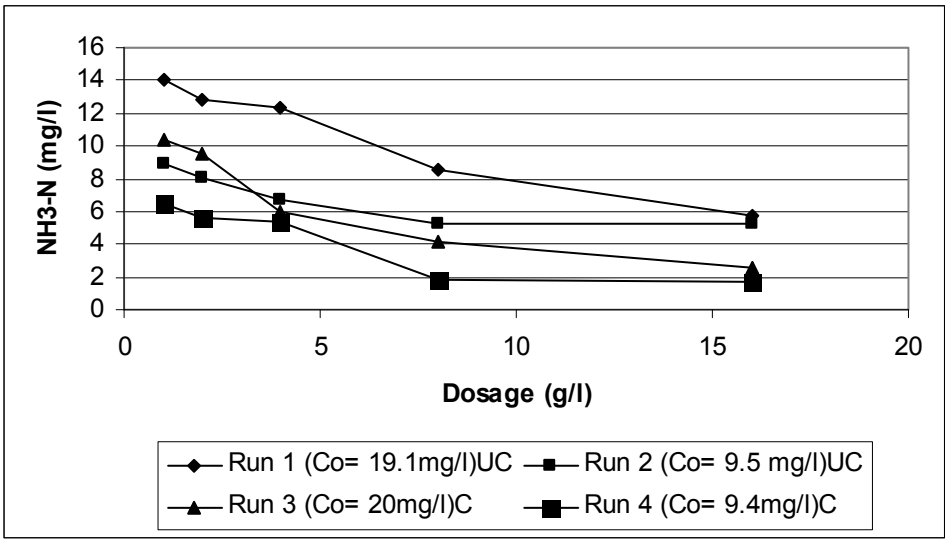


Figure 13: The efficiency of unconditioned and conditioned powdered clinoptilolite (Pratley 1) for the removal of ammonia-nitrogen from tap water spiked with approximately 10 and 20 mg/ℓ ammonia-nitrogen

3.6.2 Efficiency of different (Pratley 1, Pratley 2 and Heidelberg) unconditioned and conditioned clinoptilolites for ammonia-nitrogen removal from secondary effluent

3.6.2.1 Pratley 1

The ammonia-nitrogen concentration remaining in the water as a function of the dosage of clinoptilolite for the unconditioned and conditioned clinoptilolite is shown in Figures 14 and 15, respectively. Detailed results are shown in Appendix F, Table F2.

No significant further reduction in the ammonia-nitrogen concentration was observed after a 30 minutes contact time (Figures 14 and 15). Therefore, a 30 minutes contact time of the clinoptilolite with the effluent should be suitable for ammonia-nitrogen removal. Ammonia-nitrogen could be reduced from approximately 13 mg/ℓ in the feed to approximately 6 mg/ℓ with dosages of 10 g/ℓ (unconditioned) and 6 g/ℓ (conditioned) clinoptilolite (30 minutes contact time).

3.6.2.2 Pratley 2

The ammonia-nitrogen concentration remaining in the water as a function of the dosage of clinoptilolite for the unconditioned and conditioned clinoptilolite is shown in Figures 16 and 17, respectively. The detailed results are shown in Appendix F, Table F2. Ammonia-nitrogen could be reduced from 12 mg/ℓ in the feed to approximately 4 mg/ℓ in the treated effluent (unconditioned clinoptilolite; 30 minutes contact) with a dosage of 4 g/ℓ clinoptilolite. Increasing the dosage to 8 g/ℓ reduced the ammonia-nitrogen concentration to approximately 2 mg/ℓ in the treated effluent.

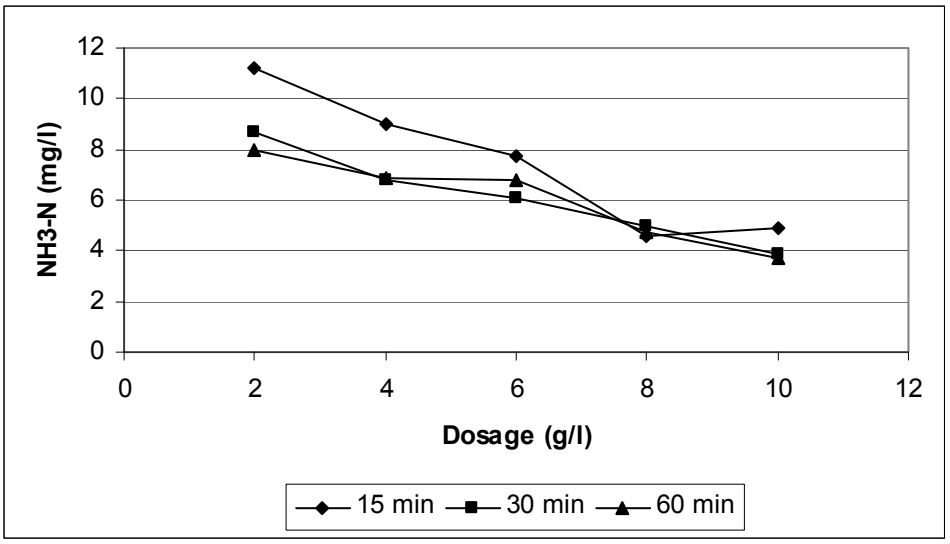


Figure 14: The efficiency of unconditioned Pratley 1 clinoptilolite for the removal of ammonia-nitrogen from secondary effluent.

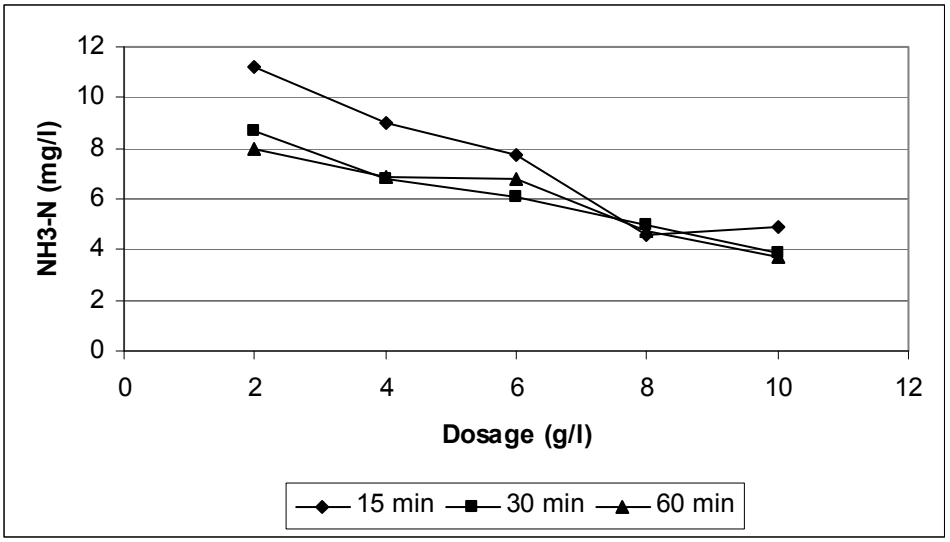


Figure 15: The efficiency of conditioned Pratley 1 clinoptilolite for the removal of ammonia-nitrogen from secondary effluent.

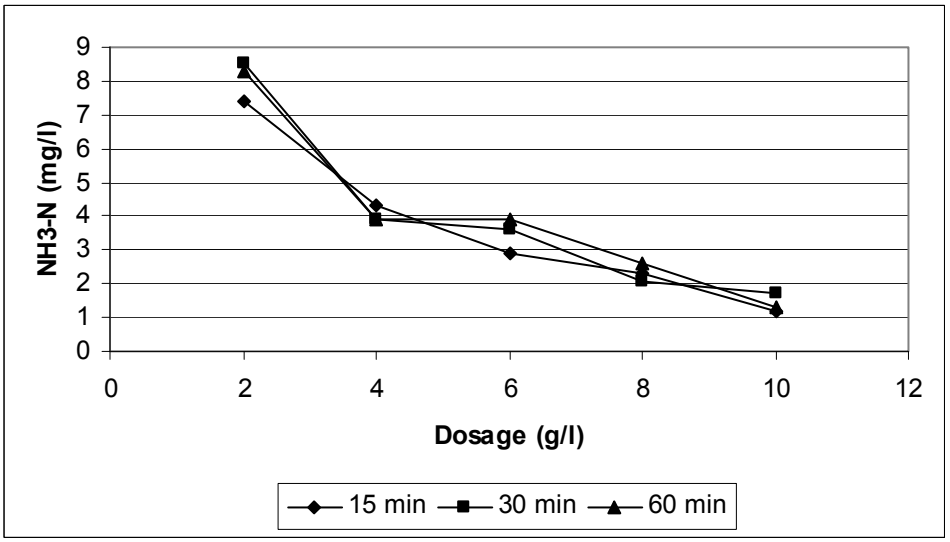


Figure 16: The efficiency of unconditioned Pratley 2 clinoptilolite for the removal of ammonia-nitrogen from secondary effluent

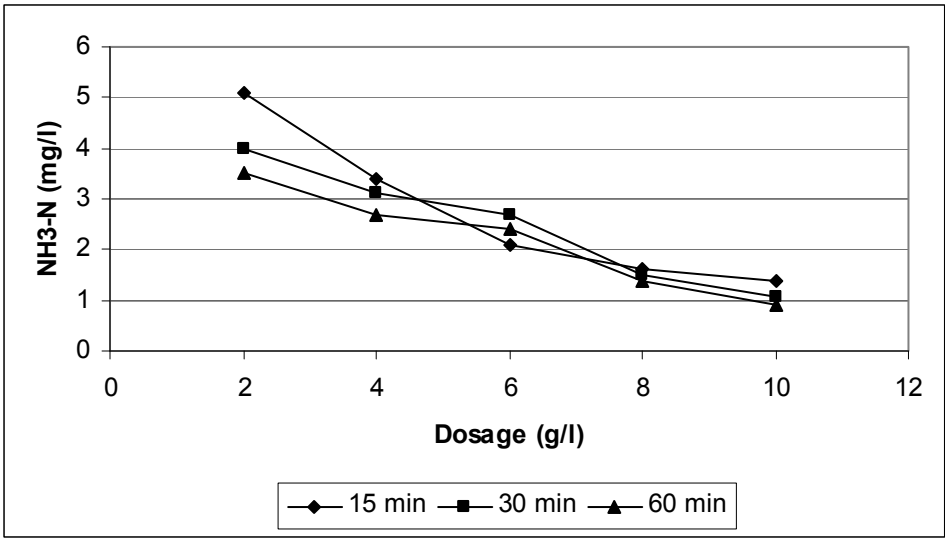


Figure 17: The efficiency of conditioned Pratley 2 clinoptilolite for the removal of ammonia-nitrogen from secondary effluent.

A dosage of less than 2 g/ℓ clinoptilolite would be required to reduce the ammonia-nitrogen concentration of approximately 9 mg/ℓ in the feed to less than 6,0 mg/ℓ in the treated feed (conditioned clinoptilolite; 30 minutes contact). A dosage of 10 g/ℓ clinoptilolite would be required to reduce the ammonia-nitrogen to approximately 1 mg/ℓ.

3.6.2.3 Heidelberg

The ammonia-nitrogen concentration remaining in the water as a function of the dosage of clinoptilolite for the unconditioned and conditioned clinoptilolite is shown in Figures 18 and 19, respectively. The detailed results are shown in Appendix F, Table F2. Ammonia-nitrogen could be reduced from approximately 10 mg/ℓ in the feed to 6,0 mg/ℓ in the treated feed at a dosage of 2 g/ℓ (unconditioned clinoptilolite; 30 minutes contact). The same result was obtained with the conditioned clinoptilolite. It further appears that it should be possible to reduce the ammonia-nitrogen to approximately 1 mg/ℓ with a dosage of 10 g/ℓ (unconditioned and conditioned clinoptilolite).

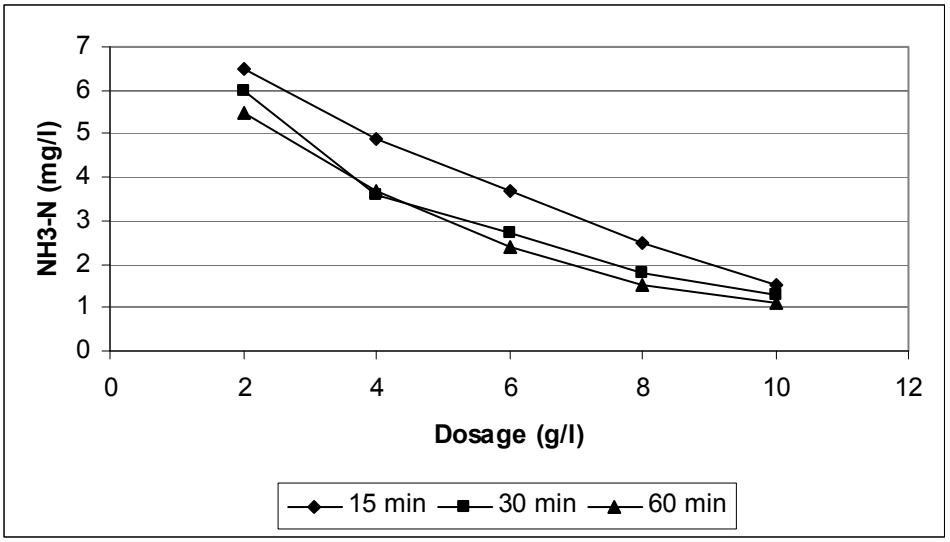


Figure 18: The efficiency of unconditioned Heidelberg clinoptilolite for the removal of ammonia-nitrogen from secondary effluent

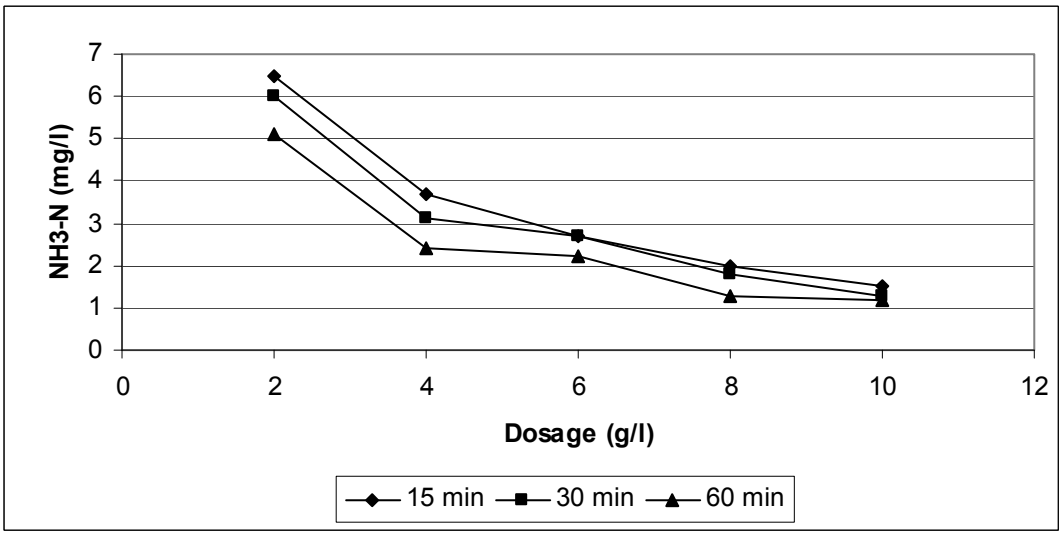


Figure 19: The efficiency of conditioned Heidelberg clinoptilolite for the removal of ammonia-nitrogen from secondary effluent.

3.7 Effect of loading flow rate, particle size, feed concentration and pH on the performance of clinoptilolite for ammonia-nitrogen removal

3.7.1 Effect of loading flow rate and particle size

Pre-washed and dried Pratley 1 clinoptilolite (150 mℓ) was regenerated with 30 BV 0.1 M NaCl at a flow rate of 5 BV/h. A run was then conducted at a loading flow rate of 5 BV/h with approximately 20 mg/ℓ ammonia-nitrogen in the feed. A second run was conducted after regeneration of the clinoptilolite to determine the effect of loading/regeneration on the run length. The breakthrough curves for the runs with

different clinoptilolite particle sizes are shown in Figures 20 and 21. The detailed results are shown in Appendix G, Table G.1 and G.2.

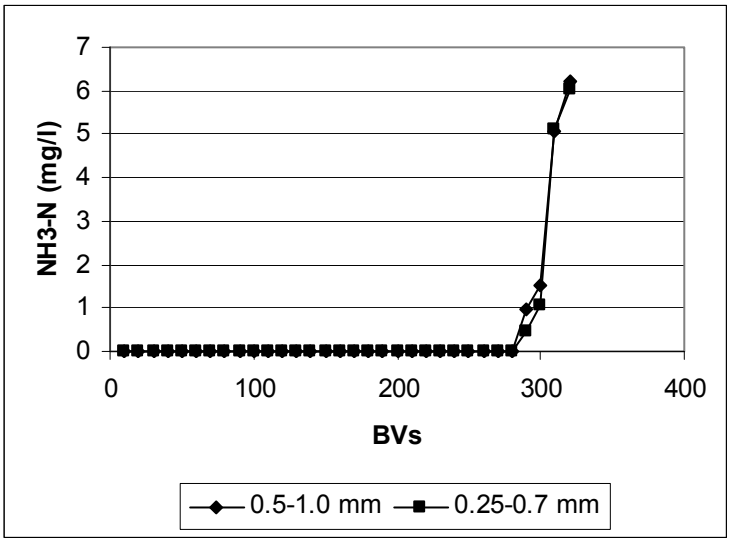


Figure 20: Effect of particle size on process performance. Loading and regeneration flow rate 5 BV/h

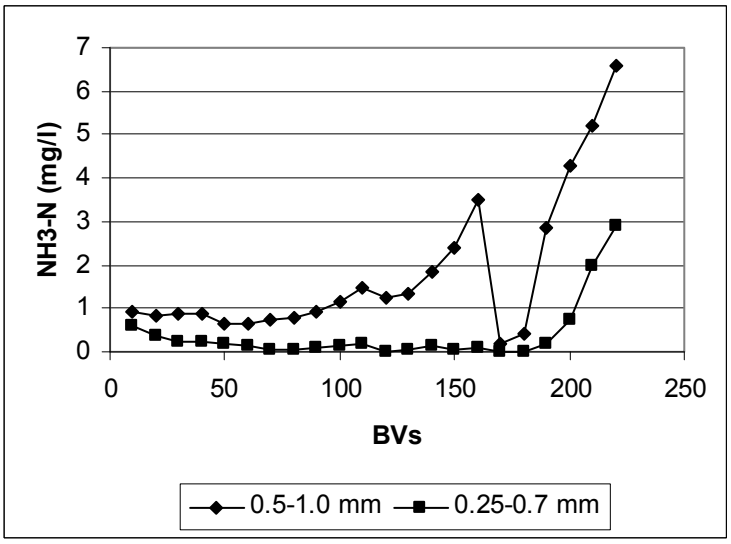


Figure 21: Effect of particle size on process performance. Loading and regeneration flow rate 5 BV/h

The ammonia-nitrogen concentration in the feed of approximately 20 mg/ℓ was reduced to approximately 0,1 mg/ℓ during the first run on the fresh surface (Figure 20). Approximately 300 BV of treated water with a concentration of less than 2 mg/ℓ ammonia-nitrogen was produced at a breakthrough of 2 mg/ℓ ammonia-nitrogen (Figure 20). The same number of BV of treated water could be produced with the two different clinoptilolite sizes. However, less BV of treated water with an ammonia-nitrogen concentration of less than 2 mg/ℓ was produced during the second run (Figure 21). This can be ascribed to the incomplete regeneration of the clinoptilolite after the first runs.

More bed volumes of product water were also produced with the smaller clinoptilolite particles (approximately 220 BV) than with the coarser particles (approximately 140 BV). It is also interesting to note that ammonia-nitrogen removal improved significantly after interruption of the run and then decreased quite rapidly when the run was started again (Figure 21). It is also interesting to note that the ammonia-nitrogen leakage from the column was much higher in the case of the coarser particles than in the case of the finer particles.

The effect of higher loading flow rate (10 and 15 BV/h) on the performance of the clinoptilolite for ammonia-nitrogen removal is shown in Figures 22 and 23, respectively. The detailed results are shown in Appendix G, Table G.3 and G.4). Run length to an ammonia-nitrogen breakthrough of 2 mg/ℓ increased with decreasing flow rate. Significant longer run lengths were experienced with the smaller size particles than with the coarser particles. The ammonia-nitrogen leakage was also higher from the coarse particles than from the finer particles.

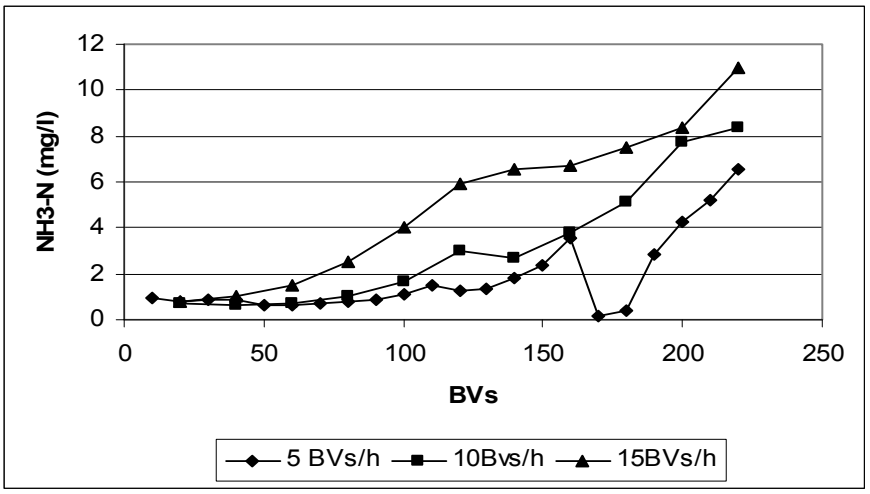


Figure 22: Effect of loading flow rate on clinoptilolite performance (0,5-1,0 mm)

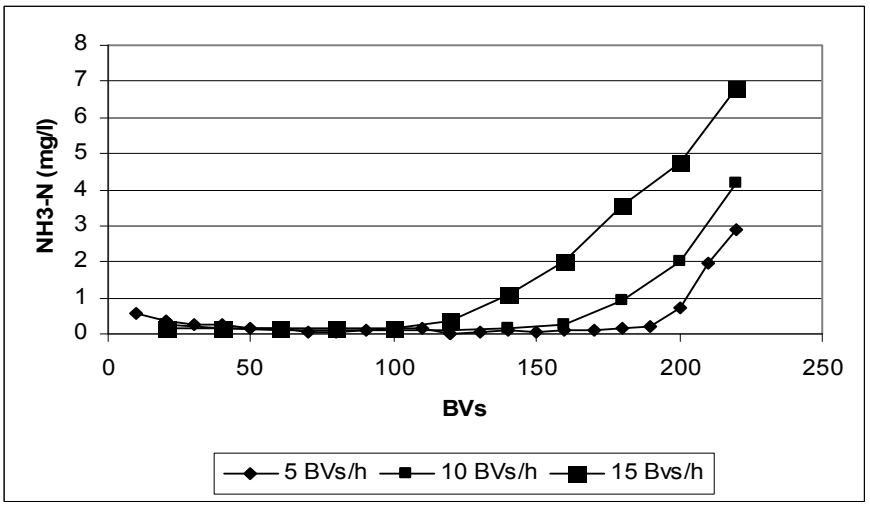


Figure 23: Effect of loading flow rate on clinoptilolite performance (0,25-0,7 mm)

The breakthrough volumes and breakthrough capacities for the runs are shown in Table 9.

Table 9. Breakthrough volumes and NH_4-N removal capacities for the different particle sizes (0,5-1,0 and 0,25-0,7 mm) at different flow rates

Run	Breakthrough volume (BV)		Removal capacity (meq NH_3-N/mℓ clino)	
	A (0,5-1,0 mm)	B (0,25-0,7 mm)	A (0,5-1,0 mm)	B (0,25-0,7 mm)
1 [5 BV/h]	298	301	0,499	0,504
2 [5 BV/h]	145	213	0,197	0,300
3 [10 BV/h]	102	200	0,134	0,268
4 [15 BV/h]	72	158	0,094	0,208

The breakthrough capacities decreased with increasing flow rate and increased with decreasing particle size. This is in correspondence with literature information (Ruhmani et al., 2004). The highest capacities were experienced on the clean clinoptilolite surface (Run 1). This is due to the incomplete regeneration of the clinoptilolite after the first run. It is clear that the breakthrough capacity is much smaller than the total capacity (See Table 4). Koon and Kaufman (1975) reported that the operating capacity is about 60% of the total capacity.

3.7.2 Effect of the initial feed concentration

The effect of different feed ammonia-nitrogen concentrations on the performance of clinoptilolite for ammonia-nitrogen removal is shown in Figures 24 and 25. The detailed results are shown in Appendix G, Table G.5 to G.7).

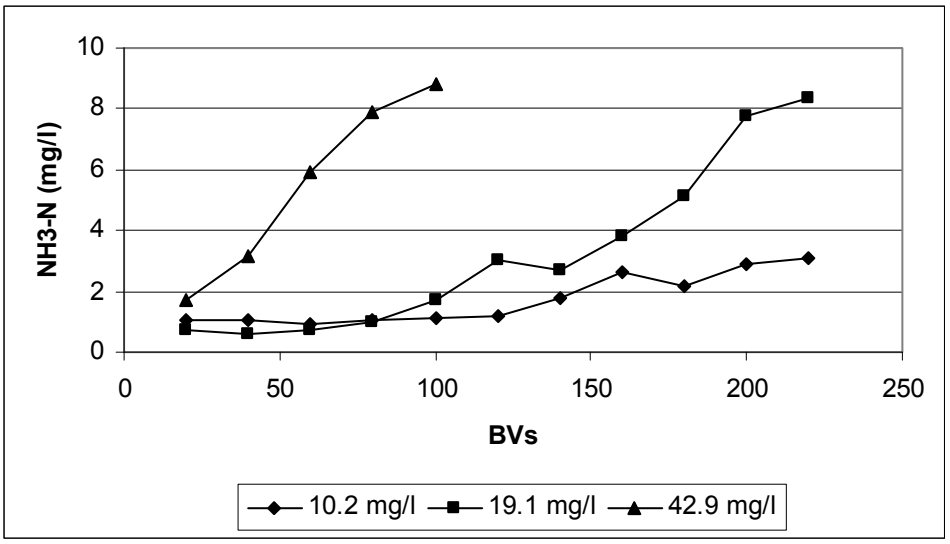


Figure 24: Effect of different NH_4-N feed concentrations on the performance of clinoptilolite for ammonia-nitrogen removal (0,5-1,0 mm; loading and regeneration flow rate 10 BV/h)

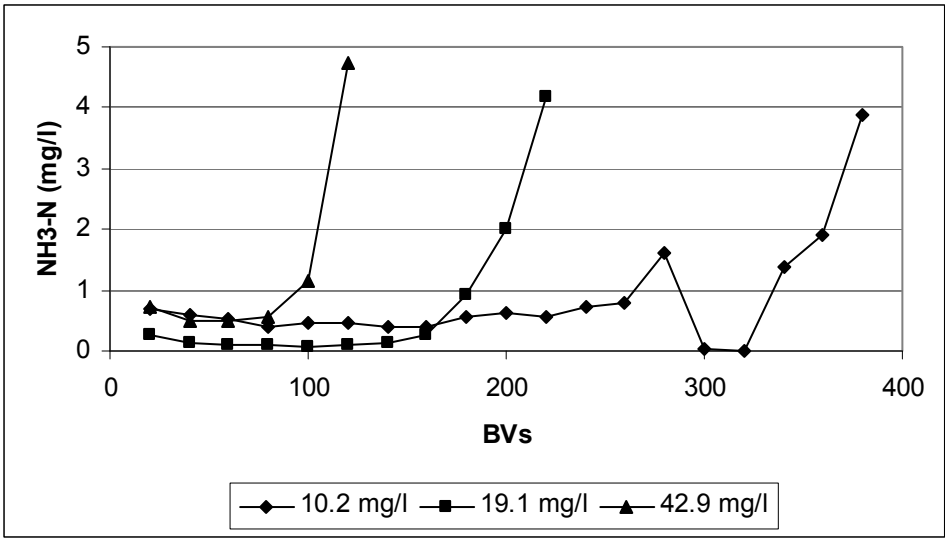


Figure 25: Effect of different NH_4-N feed concentrations on the performance of clinoptilolite for ammonia-nitrogen removal (0,25-0,7 mm; loading and regeneration flow rate 10 BV/h)

The bed volumes produced at breakthrough (2 mg/ℓ NH_3-N) increased with decreasing feed concentration. It is again noted that a significant better performance for ammonia-nitrogen removal is obtained with the finer size particle than with the coarser particles. A very short run length was obtained with the coarser particles at the highest feed concentration (Figure 24). This is due to the slow diffusion of the ammonium ion into the coarser particles.

The breakthrough data (volumes and capacities) are shown in Table 10.

Table 10. Breakthrough volumes and breakthrough capacities for two particle sizes (0,5-1,0 and 0,25-0,7 mm) at different feed concentrations.

Run / Initial Feed Concentration	Breakthrough volume (BV)		Removal capacity (me NH_3-N/mℓ clino)	
	A (0.5-1.0 mm)	B (0.25-0.7 mm)	A (0.5-1.0 mm)	B (0.25-0.7 mm)
1 [10,2 mg/ℓ]	152	362	0,098	0,248
2 [19,1 mg/ℓ]	102	200	0,134	0,268
3 [42,9 mg/ℓ]	24	108	0,072	0,326

The breakthrough capacities (2 mg/ℓ NH_3-N) increased with increasing feed concentration for both the smaller and larger particle sizes. The lower capacity that was observed (0,072) at the highest feed concentration with the coarser particles, could be ascribed to an inaccurate determination of the capacity.

3.7.3 Effect of pH

The effect of different pH values on the performance of clinoptilolite fro ammonia-nitrogen removal is shown in Figure 26. The detailed results are shown in Appendix G, Table G.8).

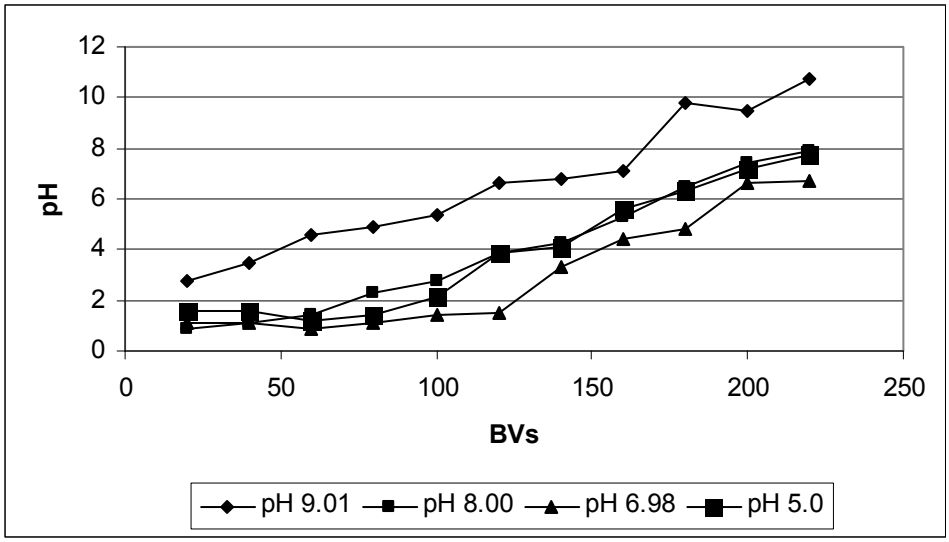


Figure 26: Effect of different feed pH's on the performance of clinoptilolite for ammonia-nitrogen removal (particle size 0,5-1,0 mm, loading and regeneration flow rates 10 BV/h; regenerant 30 BV 0,1 M NaCl).

The highest output of treated water was obtained at a pH of approximately 7 (122 BV). Significantly lower outputs of treated water were experienced at the lower and higher pH values as a result of competing ions. This is in correspondence with literature information (Koon and Kaufman, 1975). Therefore, the feed pH should be maintained at approximately pH 7 for optimum performance for ammonia-nitrogen removal.

3.7.4 Ammonia-nitrogen removal from clinoptilolite

The removal of ammonia-nitrogen during regeneration with 0,1 M NaCl at a pH of 11,3 is shown in Figure 27. The detailed results are shown in Appendix H1, Table H1). The elution curve peaked just over 300 mg/ℓ ammonia-nitrogen for the two regenerations shown and then levelled off. Not significantly more ammonia-nitrogen could be removed from the clinoptilolite with more than 20 BV of regenerant. Approximately 51 me NH_3-N could be eluted with30 BV of regenerant. Approximately 47 me NH_3-N was loaded on the clinoptilolite (Figure 28. Run 4). Therefore, slightly more ammonia-nitrogen was eluted from the clinoptilolite than was put onto the column.

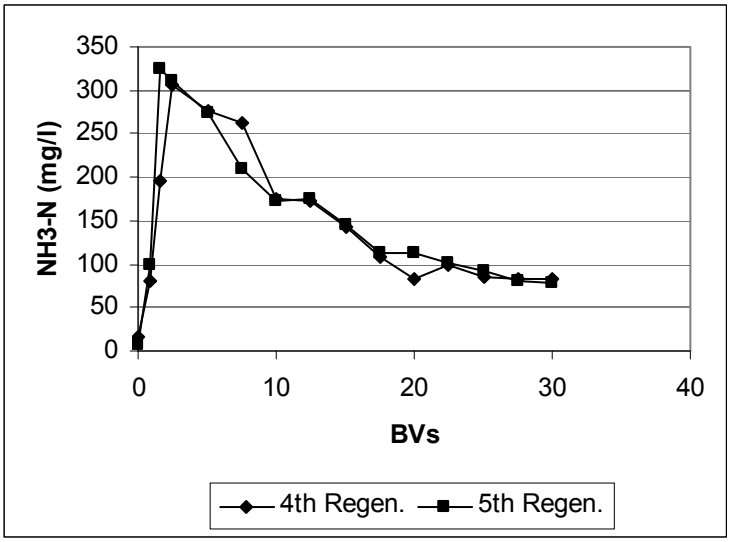


Figure 27: Elution curves during regeneration with 30 BV 0.1 M NaCl

3.8 The effect of a number of runs on the output capacity of clinoptilolite for ammonia-nitrogen removal

A number of runs were conducted using tap water and secondary sewage effluent as feed to determine the output at breakthrough. An elution curve was also established.

3.8.1 Effect of a number of runs on the bed volumes produced at breakthrough using tap water as feed

The breakthrough curves for five runs are shown in Figure 28. The detailed results are shown in Appendix H, Table H.2.

Poor ammonia-nitrogen removal was obtained on the unconditioned clinoptilolite (Run 1). However, a good performance was experienced after regeneration (runs 2 to 5). The approximate number of bed volumes produced after breakthrough for runs 2; 3; 4 and 5 were 160; 118; 130 and 130, respectively. Therefore, it appears that the output capacity for ammonia-nitrogen removal should not be significantly decreased with consecutive loading and regeneration cycles.

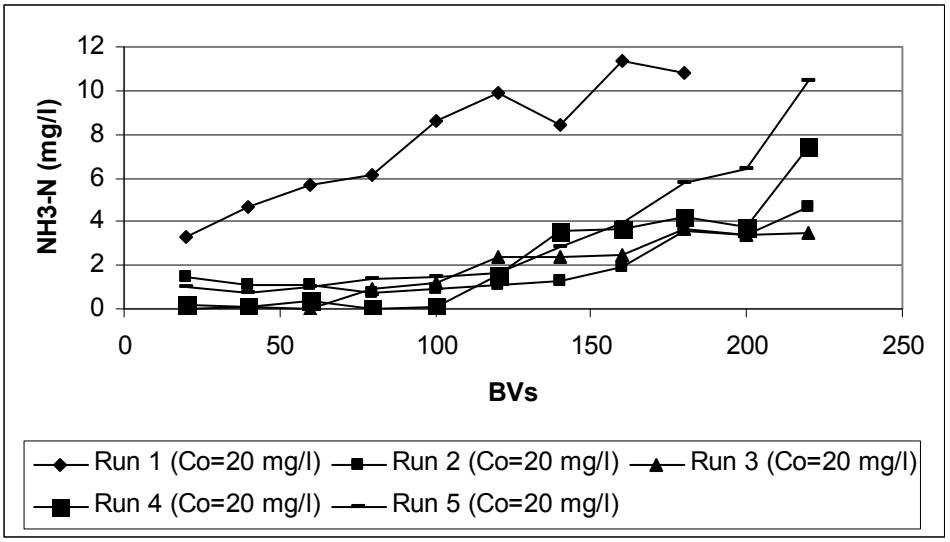


Figure 28: Number of bed volumes produced for five consecutive runs (0,5-1,0 mm particle size; Co = approximately 20 mg/ℓ NH_3-N ; loading and regeneration flow rate 10 BV/h).

3.8.2 Effect of a number of runs on the bed volumes produces at breakthrough using secondary sewage as feed

The breakthrough curves for 4 runs are shown in Figure 29 (runs 6 to 9). The detailed results are shown in Appendix H, Table H.3.

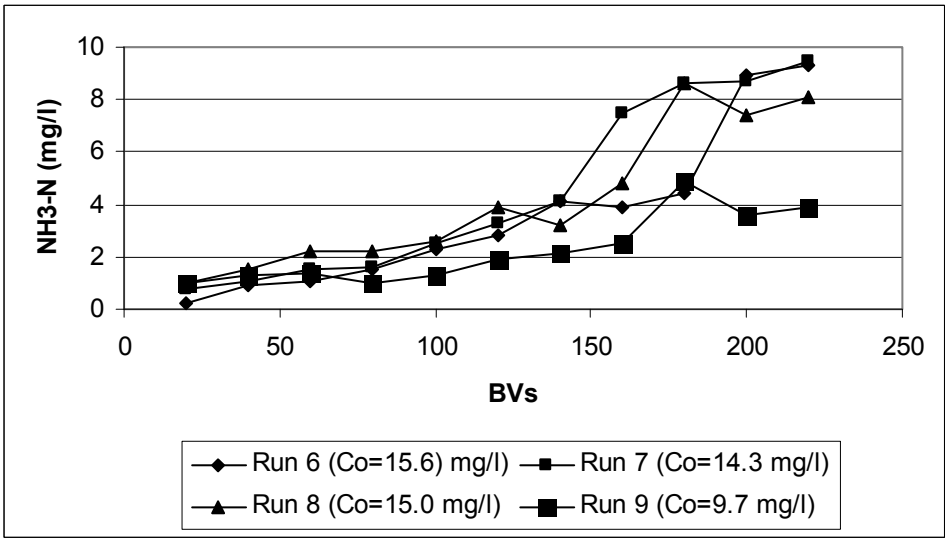


Figure 29: Number of bed volumes produced for four consecutive runs (Co varies from 9,7 to 15,6 mg/ℓ; 0,5-1,0 mm; loading and regeneration flow rate 10 BV/h)

Output capacity for run 6 was about 100 BV and for run 7 and 8 between 100 and 80 BV, respectively. However, the treated water concentration was about 2 mg/ℓ from 100 to 80 BV. Therefore, the reduction in output capacity for ammonia-nitrogen removal

should not be that big. However, a reduction in output capacity was experienced with consecutive runs and the regeneration conditions should be adjusted to compensate for this reduction. Run 9 showed an increase in output (140 BV) due to a lower feed concentration. (Note: The feed concentrations varied as a result of the concentration in the secondary effluent at sample taking).

More runs were conducted and these results are shown in Figure 30 (detailed results in Table H.3, Appendix H).

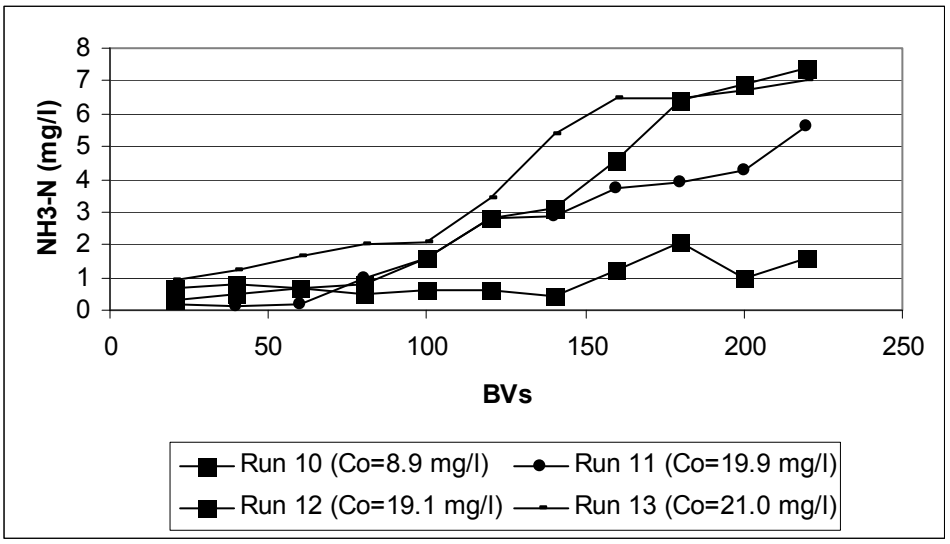


Figure 30: Number of bed volumes produced for four consecutive runs (Co varies from 8,9 to 21,0 mg/ℓ; 0,5-1,0 mm; loading and regeneration flow rate 10 BV/h)

Approximately 110 BV were produced at breakthrough for runs 11 to 12 and 100 BVs for run 13. Therefore, it appears that about the same number of bed volumes could be produced for these runs. However, the leakage was higher for run 13 than for the other two runs. Therefore, a reduction in output capacity could be expected. A much longer run, however, was obtained during run 10. However, the feed concentration was significantly lower.

3.8.3 Effect of regenerant reuse on the output capacity

The effect of regenerant reuse on the output capacity is shown in Figure 31. The detailed results are shown in Appendix H, Table H.4.

The output capacities for the first two runs after regenerant reuse were about 100 BV and decreased to about 90 to 80 BV for the next two runs. The regenerant was air stripped prior to reuse to remove the ammonia-nitrogen and the volume of the regenerant was reduced to approximately 4,0 litres. The spent regenerant was made up to 4,5 litres with 0,1 M NaCl prior to regeneration (160 mℓ 1N NaOH to raise the pH to approximately 12). Approximately 80 mℓ 1N NaOH was required to raise the pH to approximately 12 when the regenerant was not reused.

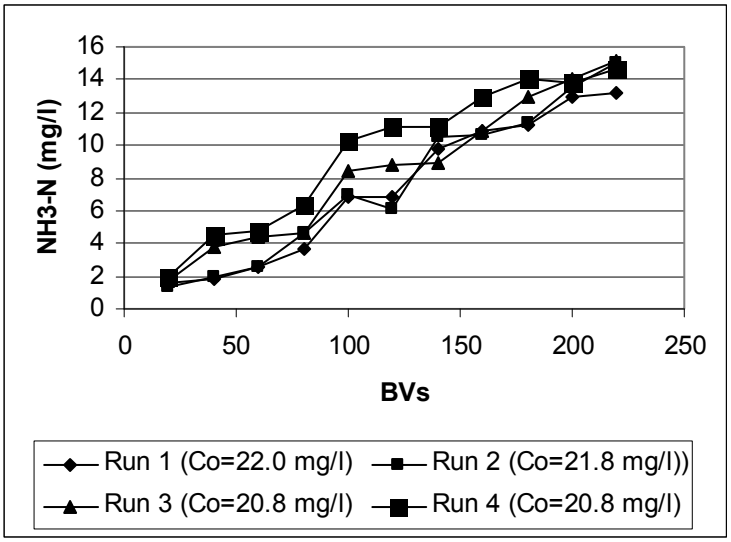


Figure 31: Effect of regenerant reuse on output capacity, (particle size 0,5-1,0 mm, loading and regeneration flow rates 10 BV/h)

An attempt was made to restore the capacity of the clinoptilolite by regenerating the clinoptilolite with a stronger regenerant solution (1,0 M NaCl) (Figure 32) (Appendix H, Table H5). The BV produced at breakthrough increased to 220 BV with the stronger regenerant solution. However, the BV decreased to 120 BV with subsequent regeneration with 0,1 M NaCl solution. One regenerant reuse had the effect to increase the BV produced at breakthrough to approximately 160 BV. However, a second regenerant reuse reduced the number of BV produced to approximately 100.

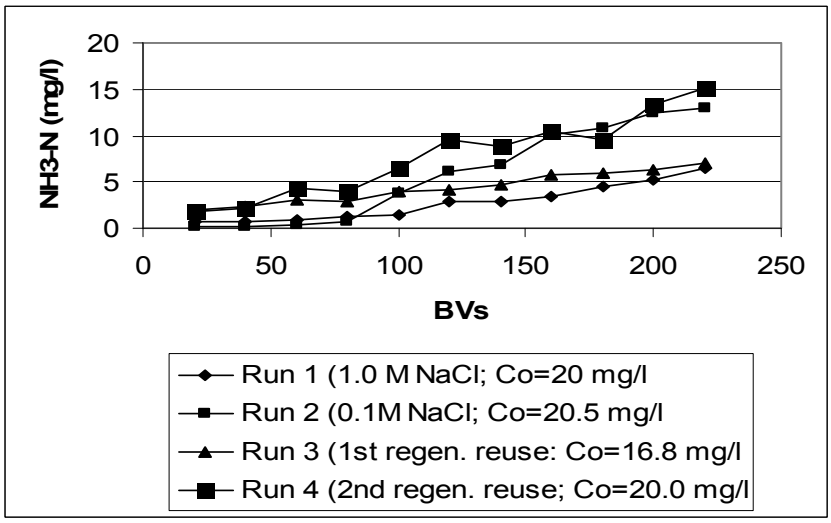


Figure 32: Effect of regenerant reuse on output capacity, (particle size 0,5-1,0 mm, loading and regeneration flow rates 10 BV/h)

3.8.4 Ammonia-nitrogen removal from spent regenerant with air stripping

Ammonia-nitrogen removal with air stripping using Raschig rings and simple air stripping in an open beaker using a small porous diffuser is shown in Figure 33 and 34. Detailed results are shown in Appendix H, Table H.6 and H.7.

Ammonia-nitrogen could be reduced from approximately 65 mg/ℓ in the spent regenerant to approximately 1,0 mg/ℓ (Raschig rings) and 9,0 mg/ℓ (porous diffuser) in about 24 hours. The initial removal rate of ammonia was high but slowed down after about 7 hours. Ammonia-nitrogen removal from the spent regenerant was not optimised and further work would be required in this regard. The ammonia-nitrogen should be dissolved in acid to produce fertilizer.

In another case the ammonia-nitrogen was removed from about 120 mg/ℓ to 10 mg/ℓ after 24 hours (Figure 34) (Appendix H, Table H.7). This again shows that it will take time to remove the ammonia-nitrogen from the spent regenerant.

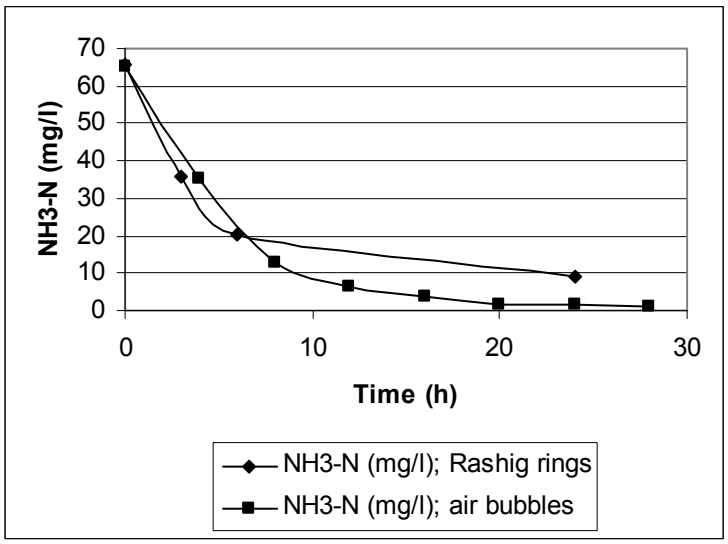


Figure 33: Ammonia-nitrogen removal from spent regenerant with air stripping.

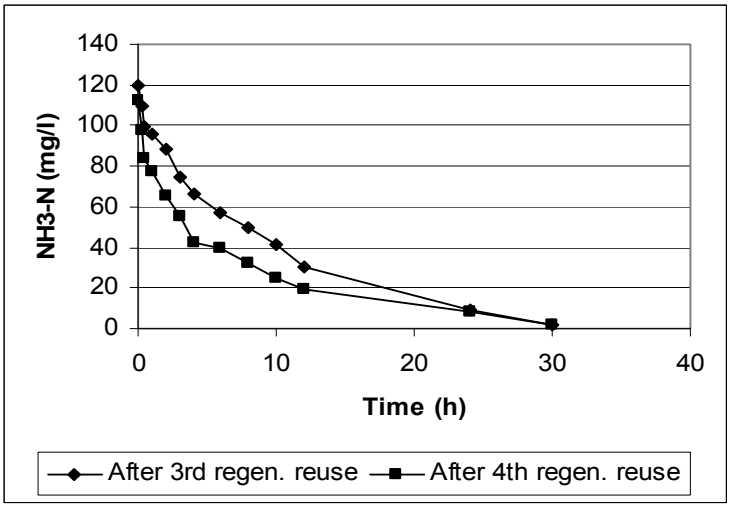


Figure 34: Ammonia-nitrogen removal from spent regenerant with air stripping.

3.8.5 Effect of regenerant reuse on run length using particle size of 0.25-0.7 mm (Pratley 1) (Secondary effluent)

The breakthrough curves are shown in Figures 35 and 36. Detailed results are shown in Appendix H, Tables H.8 and H.9.

Approximately 220 BV were produced after the first regenerant reuse. It should be noted that the feed concentration was lower (16,8 mg/ℓ) in this case. Approximately 160 and 180 BV were produced after the second and third regenerant reuses, respectively. The bedvolumes produced at breakthrough then stabilises at approximately 140 BV for runs 4 to 8. It therefore appears that regenerant reuse should be practiced without a serious reduction in output capacity.

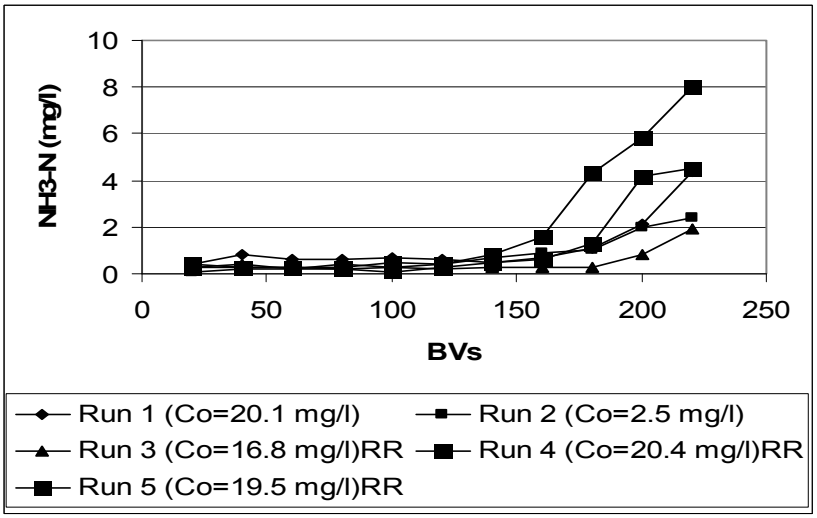


Figure 35: Effect of regenerant reuse on output capacity, (particle size 0,25-0,7 mm; loading and regeneration flow rates 10 BV/h)

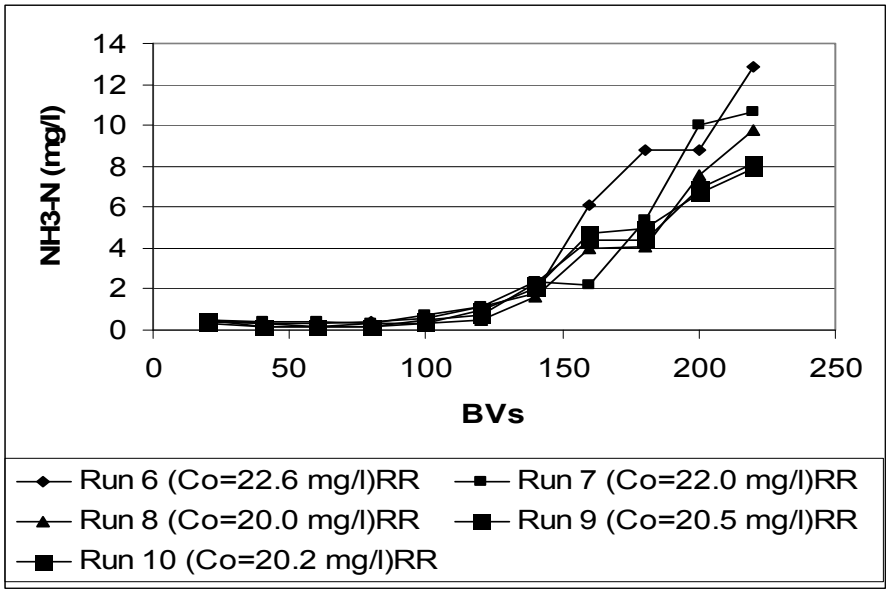


Figure 36: Effect of regenerant reuse on output capacity, (particle size 0,25-0,7 mm; loading and regeneration flow rates 10 BV/h)

3.8.6 Effect of regenerant reuse on run length using particle size of 0,25-0,77 mm (Pratley 2) (Secondary effluent)

The breakthrough curves shown in Figures 37 and 38 represent the results obtained during regenerant reuse. The clinoptilolite was regenerated with 30 BV of 0.1 M NaCl (detailed results in Appendix H, Table H.10 and Table H.11).

Approximately 120 BV were produced at breakthrough during the first run. Thereafter the BV at breakthrough increased to 160 (run 2), and remained at more or less 140 BV during regenerant reuse up to 8 regenerant reuse cycles. More or less the same results were obtained with Pratley 1 and Pratley 2 clinoptilolites.

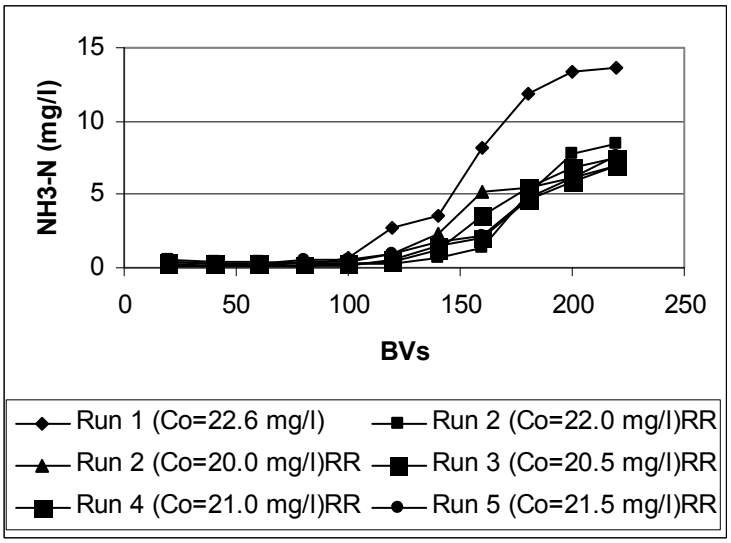


Figure 37: Effect of regenerant reuse on output capacity, (particle size 0,25-0,7 mm; loading and regeneration flow rates 10 BV/h)

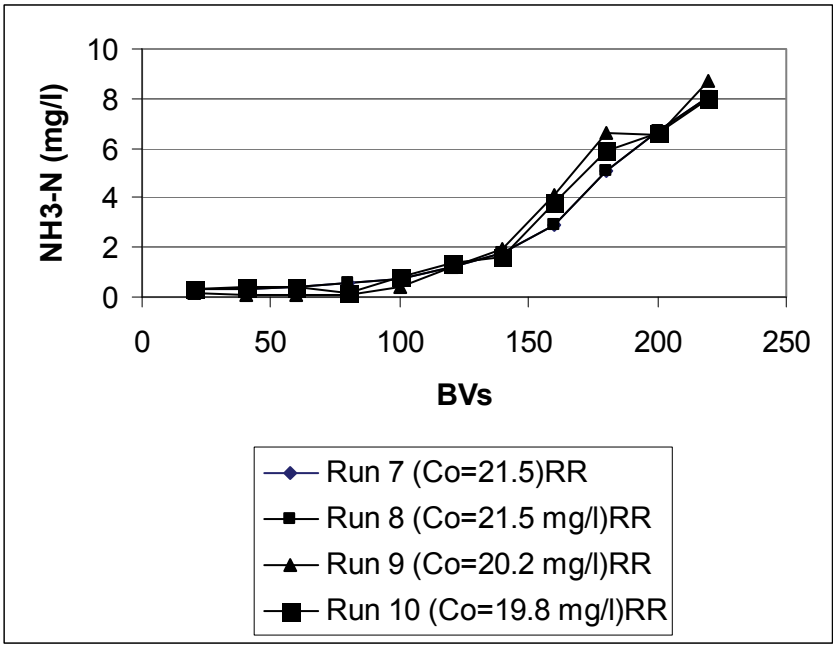


Figure 38: Effect of regenerant reuse on output capacity, (particle size 0,25-0,7 mm; loading and regeneration flow rates 10 BV/h)

3.8.7 Effect of regenerant reuse on run length using less regenerant (15 BV) (Pratley 2) (Secondary effluent)

The breakthrough curve shown in Figure 39 represents the results obtained during regenerant reuse. The clinoptilolite was regenerated with 15 BV of 0.1 M NaCl; amount of 1 M NaOH = 40 mℓ; pH = 12.01 (detailed results in Appendix H, Table H.12).

Approximately 120 BV of product water was produced after the first regenerant reuse when 15 BV of regenerant was used instead of 30 BV. Only 80 BV of product water could be produced after the third regenerant reuse and the number of BV decreased to only 40 BV after the fourth and fifth regeneration reuses. Therefore, it appears that 15 BV of regenerant should not be good for the successful regeneration of the clinoptilolite.

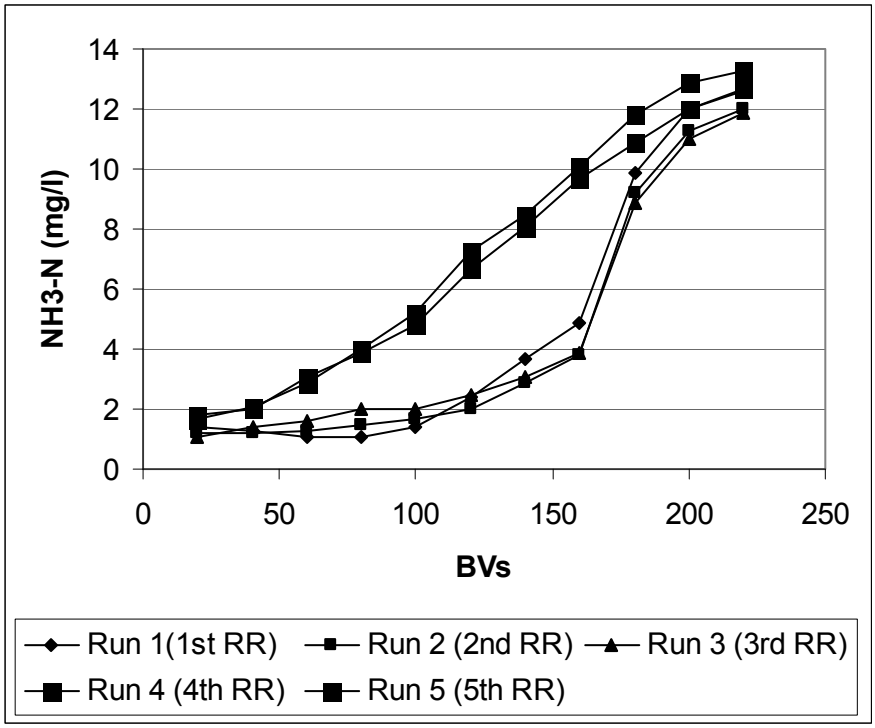


Figure 39: Effect of regenerant reuse on output capacity, (particle size 0,25-0,7 mm; loading and regeneration flow rates 10 BV/h)

The breakthrough capacities are summarised in Table 11 below.

Table 11. Summary of loading and regeneration conditions, breakthrough results and capacities obtained with the Pratley 1 and 2 clinoptilolites (0.25-0.7 mm).

Run No	Type of clinoptilolite	Inf NH_3N mg/ℓ	BV produced at breakthrough (2 mg/ℓ)	Capacities at breakthrough (me/mℓ)	NaCl conc	pH of regenerant	BV used	Amount of NaOH added to raise pH
Loading after 1st Regenerant reuse	Old Pratley New Pratley New Pratley	16.8 22.0 19,6	220 150 110	0.257 0.229 0.145	0.1 M NaCl	12.01 12.0 12.01	30 30 15	80 mℓ 83 mℓ 40 mℓ
Loading after 2nd Regenerant reuse	Old Pratley New Pratley New Pratley	20.4 20.0 20.1	170 125 120	0.240 0.174 0.162	0.1 M NaCl	12.00 12.03 12.02	30 30 15	85 mℓ 85 mℓ 40 mℓ
Loading after 3rd Regenerant reuse	Old Pratley New Pratley New Pratley	19.5 20.5 19.8	190 150 80	0.258 0.215 0.111	0.1 M NaCl	12.1 12.0 12.04	30 30 15	150 mℓ 130 mℓ 50 mℓ
Loading after 4th Regenerant reuse	Old Pratley New Pratley New Pratley	22.6 21.0 20.0	145 155 40	0.226 0.223 0.054	0.1 M NaCl	12.04 12.01 12.05	30 30 15	220 mℓ 150 mℓ 50 mℓ
Loading after 5th Regenerant reuse	Old Pratley New Pratley New Pratley	22.0 21.5 20.2	130 150 40	0.204 0.222 0.055	0.1 M NaCl	12.00 12.00 12.03	30 30 15	300 mℓ 250 mℓ 50 mℓ
Loading after 6th Regenerant reuse	Old Pratley New Pratley	20.0 21.5	150 150	0.208 0.224	0.1 M NaCl	12.04 12.20	30 30	300 mℓ 260 mℓ

The breakthrough capacity for Pratley 2 remained at approximately 0,22 me/mℓ when six regenerant reuses were applied and when 30 BV of regenerant were used. It appears that the breakthrough capacity for Pratley 2 was slightly lower (0,21 me/mℓ) after six regenerant reuses. This difference, however, is insignificant.

It is further worth noting that the amount of caustic soda required to raise the pH increased significantly with increasing regenerant reuse cycles. It is also clear that 15 BV of regenerant are not sufficient for the proper regeneration of the clinoptilolite.

3.9 Operational Costs

3.9.1 Powdered Clinoptilolite

The chemical costs to reduce ammonia-nitrogen from 13 to 6 mg/ℓ in secondary effluent at a dosage of 10 g/ℓ was determined at R17,16/m^3 (unconditioned). The chemical cost to reduce ammonia-nitrogen from 13 to 6 mg/ℓ in secondary effluent at a dosage of 6 g/ℓ was determined at R10,57/m^3 (conditioned). These costs are very high and it appears that the use of powdered clinoptilolite should not be an option to reduce ammonia-nitrogen in secondary effluent.

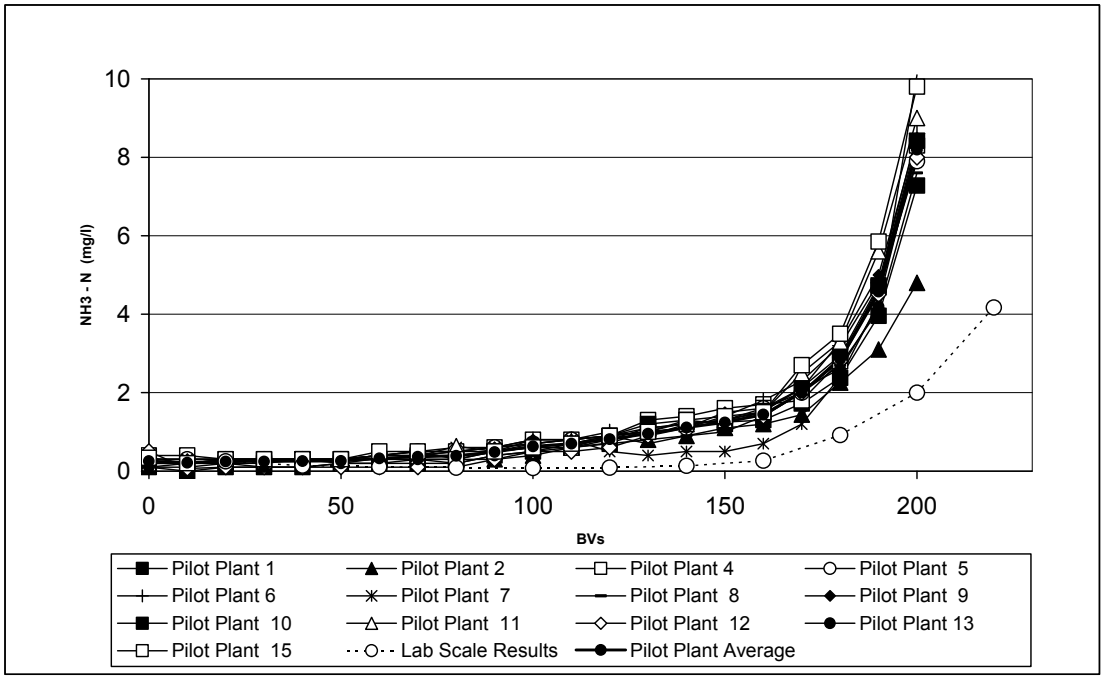


Figure 40: Breakthrough curves.

3.9.2 Column studies

The chemical cost to reduce ammonia-nitrogen from approximately 20 mg/ℓ to less than 2 mg/ℓ in secondary effluent was determined at R0.76/m^3. Reuse of the regenerant should reduce this cost if the caustic soda requirements of the spent regenerant is not too excessive. Costs should be further reduced with the recovery of ammonia from the spent regenerant to produce fertiliser.

Note: Cost of NaCl and NaOH (100%) is R350/ton and R 4,25/kg, respectively.

4. RESULTS AND DISCUSSION (PILOT STUDIES)

4.1 Breakthrough curves after chemical regeneration

The breakthrough curves for 15 consecutive runs are shown in Figure 40. The detailed results are shown in Appendix I. The bed volumes produced at breakthrough (2 mg/ℓ NH_3-N) vary between approximately 165 and 175. No significant reduction in output was experienced. Therefore, it appears that the clinoptilolite surface should not be fouled by the effluent. It is further interesting to note that a somewhat better performance was obtained with the laboratory column. Approximately 200 BV of product water could be produced at breakthrough (2 mg/ℓ NH_3-N).

4.2 Breakthrough curves after different loading flow rates

The effect of different loading flow rates on the breakthrough capacity is shown in Figure 41. The detailed results are shown in Appendix J. The breakthrough capacity increased with decreasing loading flow rate from 15 to 5 BV/h. Similar results were obtained during the laboratory investigation. A loading flow rate of 10 BV/h correspond more or less to the contact time required (approximately 6 minutes) for ion-exchange applications.

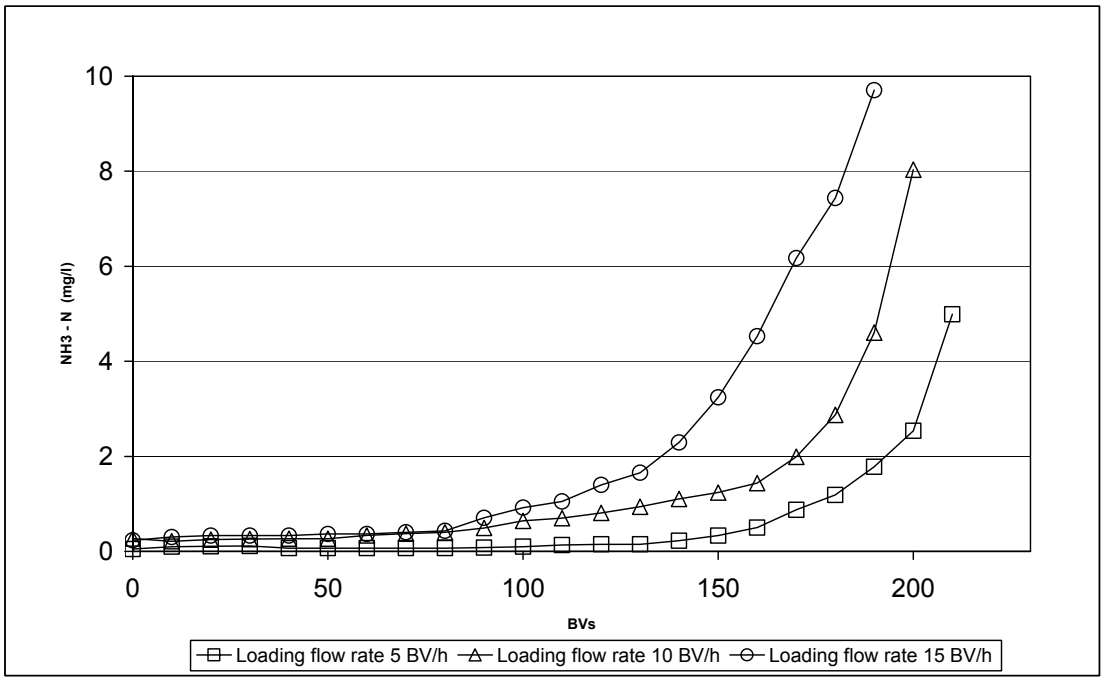


Figure 41: Effect of loading flow rate on the breakthrough capacity.

4.3 Elution curves

4.3.1 Elution curves after loading cycles 10 to 13

The elution curves after loading cycles 10, 11, 12 and 13 are shown in Figure 42. The detailed results are shown in Appendix K. The ammonia-nitrogen peaks varied from approximately 300 to 500 mg/ℓ after approximately 1,5 bedvolumes of regenerant had been passed through the column. The ammonia-nitrogen concentration levels then decreased and almost all the ammonia-nitrogen was removed from the column after 15 bedvolumes of regenerant was passed through the column.

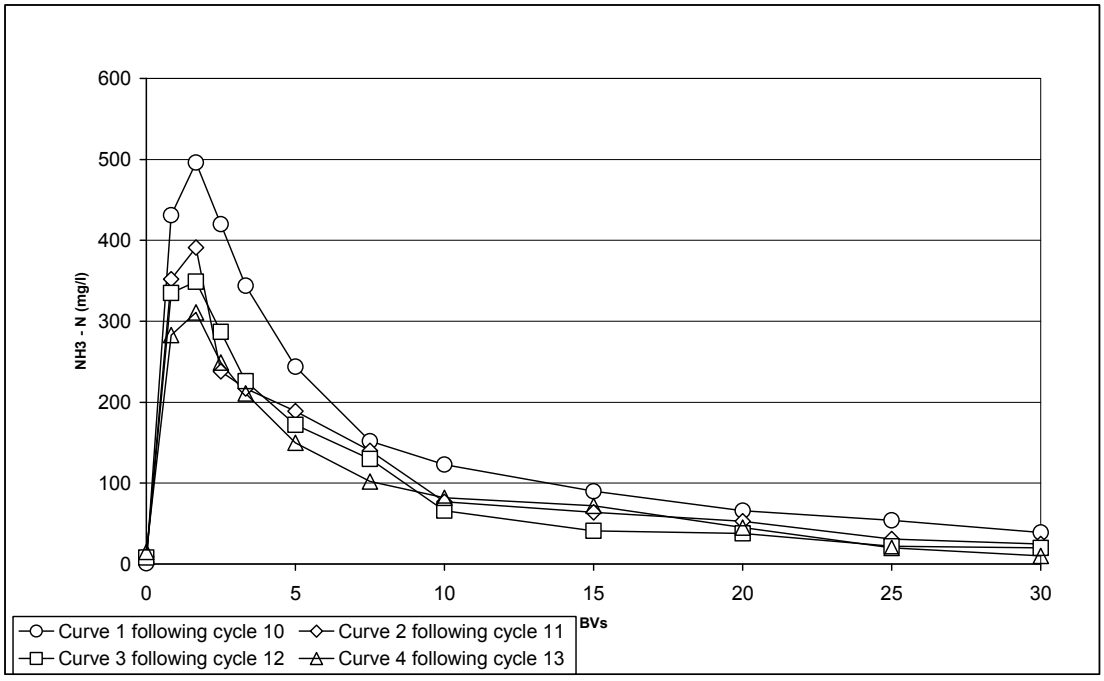


Figure 42: Elution curves after loading cycles 10, 11, 12 and 13.

4.3.2 Elution curves after laboratory, pilot and literature data

Elution curves after laboratory loading cycles (4 and 5), after pilot studies and after literature data (Cooney et al., 1999) are shown in Figure 43. The detailed results are shown in Appendix L. The literature data and the pilot data showed sharper peaks than the laboratory data. A sharper decrease in the ammonia-nitrogen concentration was also observed during the pilot and literature data. This showed that the ammonia-nitrogen moves down in the column as a sharp band. Also, about 15 to 20 bedvolumes of regenerant should be efficient for regeneration of the clinoptilolite.

4.3.3 Elution curves for sodium, potassium, calcium and magnesium

The elution curves for sodium, potassium, calcium and magnesium are shown in Figures 44, 45, 46 and 47, respectively. The detailed results are shown in Appendix M.

The sodium concentration in the spent regenerant is initially high when most of the ion-exchange sites are occupied by ammonium ions but decreases as more ammonium ions are eluted from the clinoptilolite (Figure 44). Sharp decreases were observed in the concentrations of potassium (Figure 45), calcium (Figure 46) and magnesium (Figure 47). This shows that these ions can be effectively eluted from the clinoptilolite.

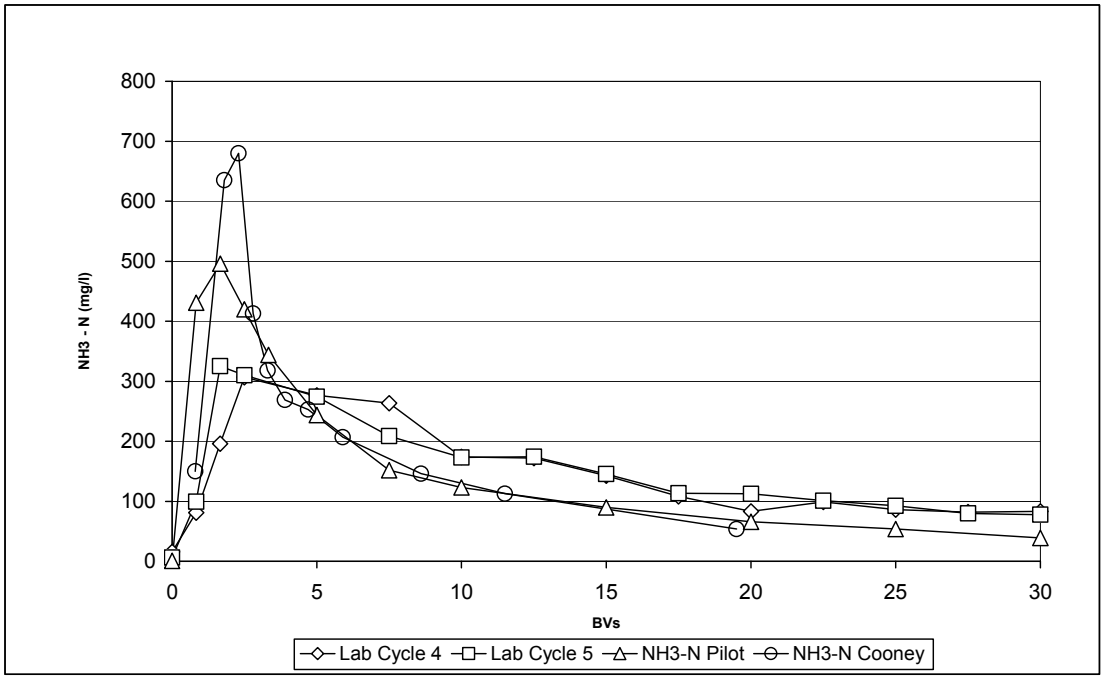


Figure 43: Elution curves after laboratory, pilot and literature information.

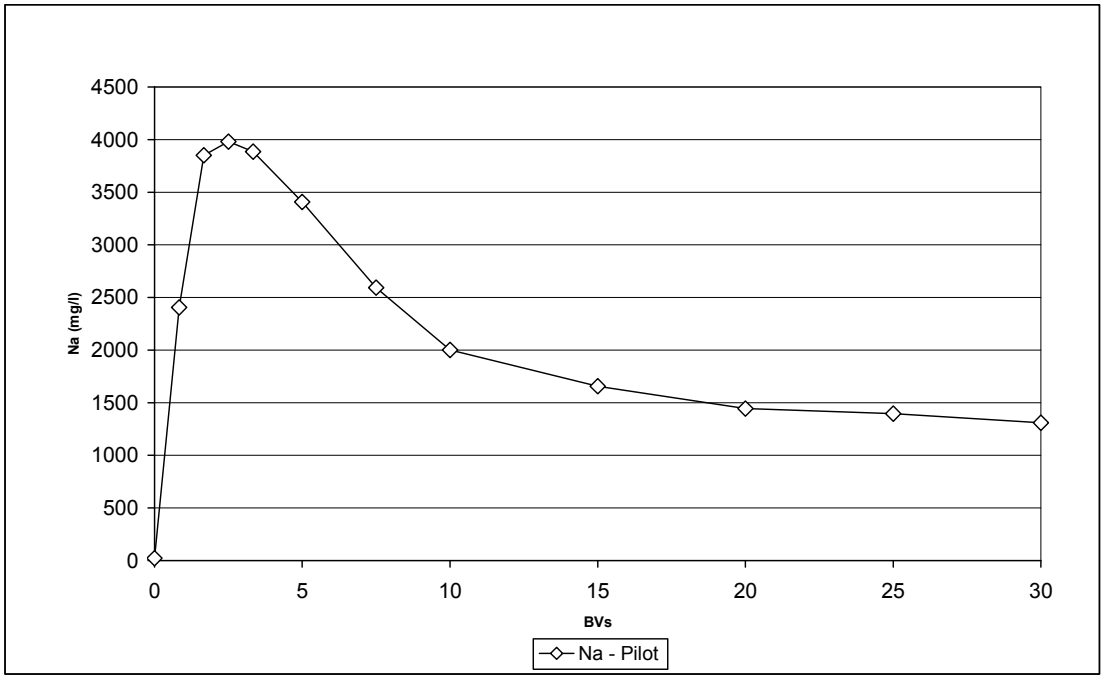


Figure 44: Sodium elution curve.

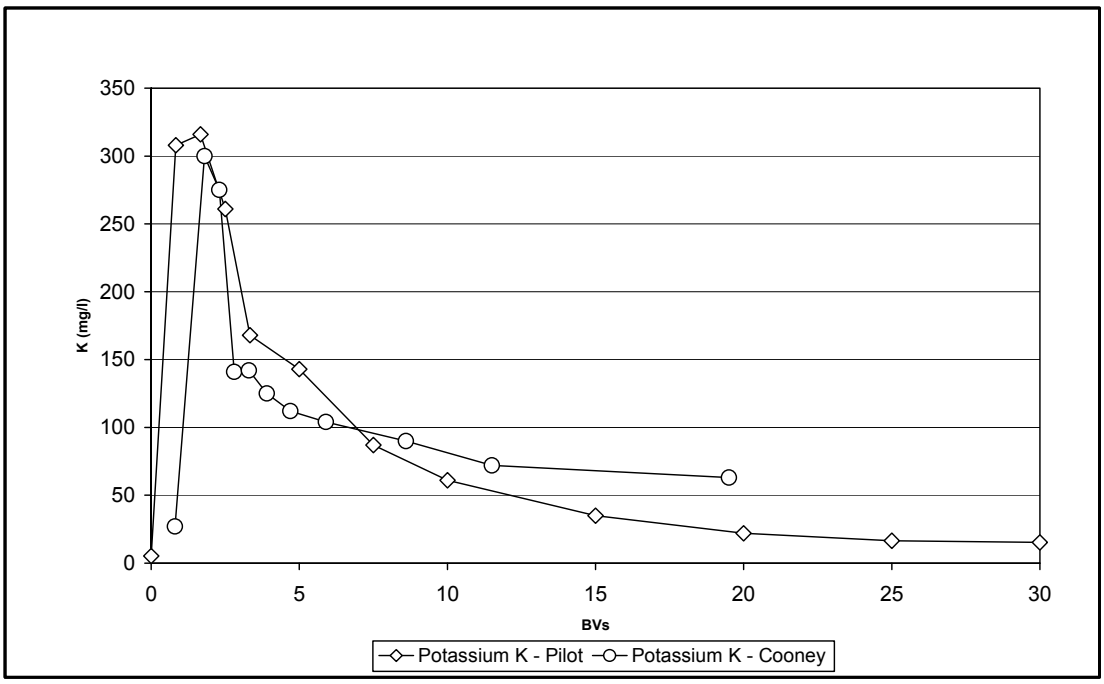


Figure 45: Potassium elution curve.

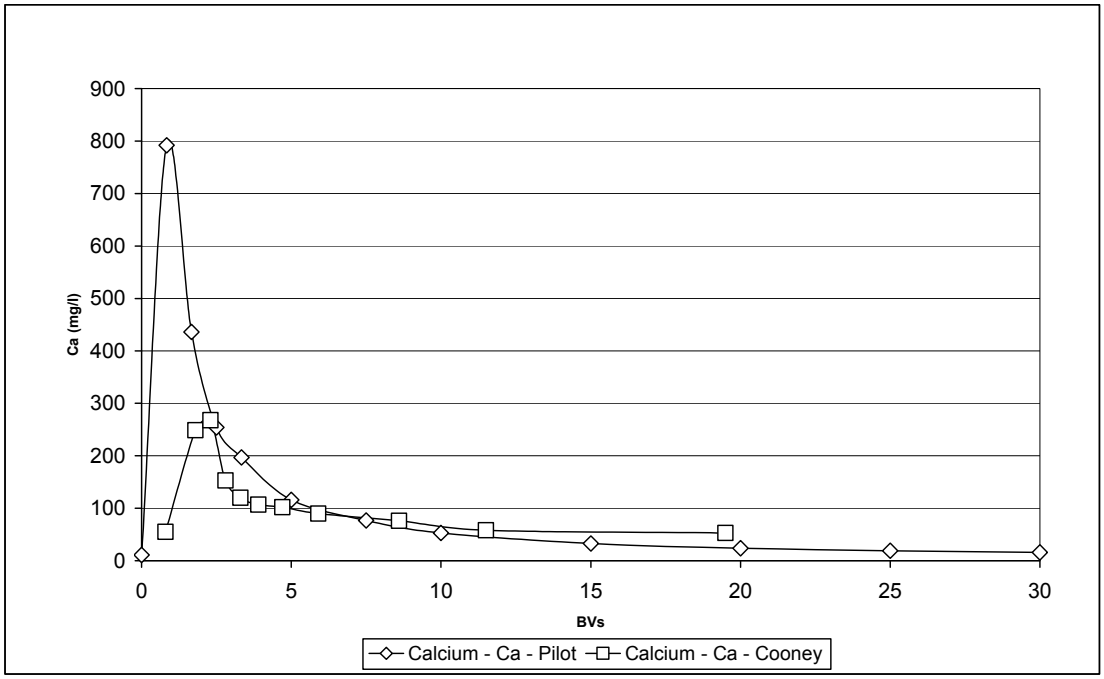


Figure 46: Calcium elution curve.

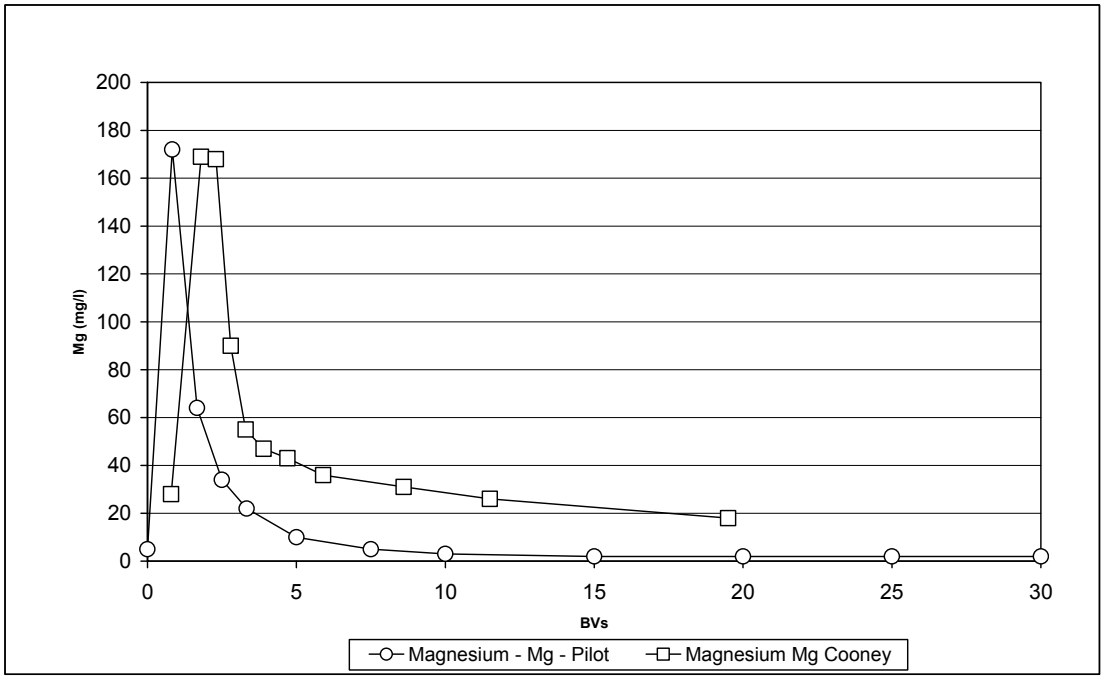


Figure 47: Magnesium elution curve.

4.4 Backwash flow rate and bed expansion

The percentage bed expansion as a function of the backwash flow rate is shown in Figure 48. The detailed results are shown in Appendix N.

A flow rate of approximately 700 ℓ/h is required for a 50 percent bed expansion that is required for bed expansion for efficient backwash.

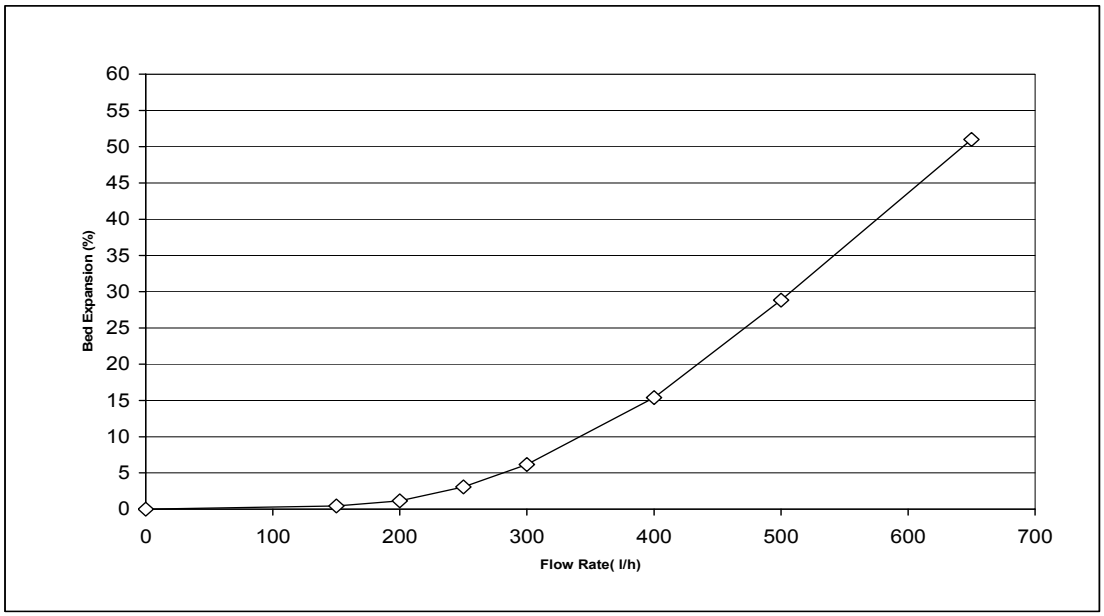


Figure 48: Percentage bed expansion as a function of flow rate.

4.5 Ammonia speciation

Ammonia/ammonium speciation as a function of pH is shown in Figure 49. The ammonium ion concentration starts to decrease above a pH of 7. Therefore, the clinoptilolite column should be operated at a pH of 7 and less for optimum ammonium ion removal. However, a good performance for ammonia-nitrogen removal should still be obtained at a pH of 7,5.

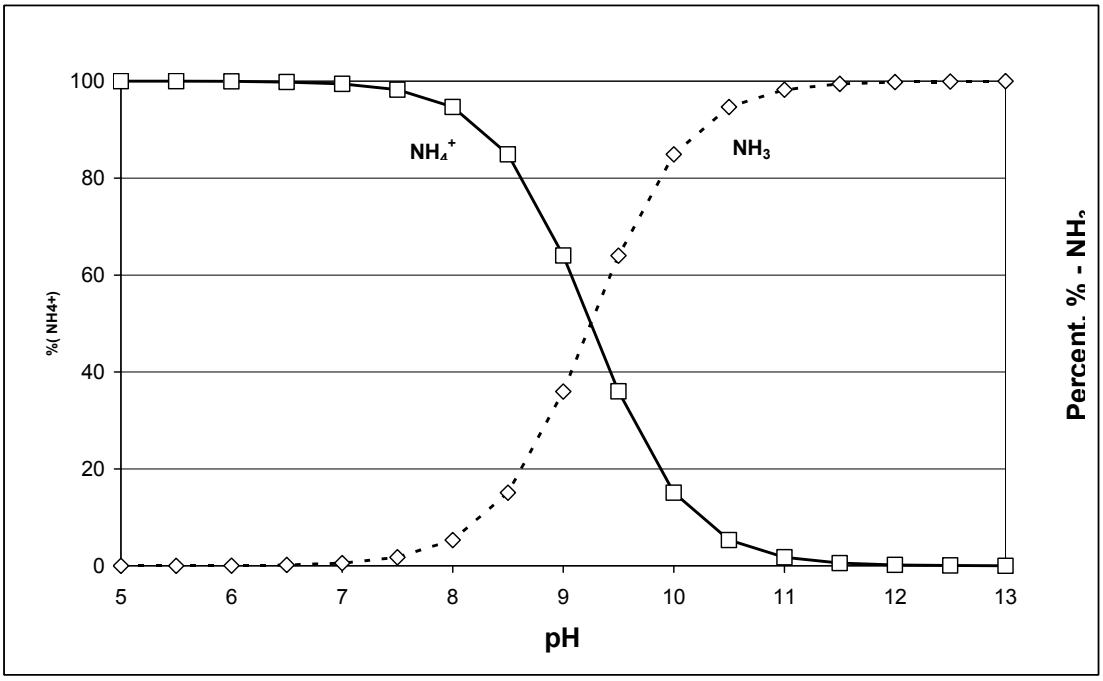


Figure 49: Percentage ammonia/ammonium speciation as a function of pH.

4.6 Breakthrough curves after biological regeneration

The breakthrough curves for 3 consecutive runs are shown in Figure 50. The detailed results are shown in Appendix O.

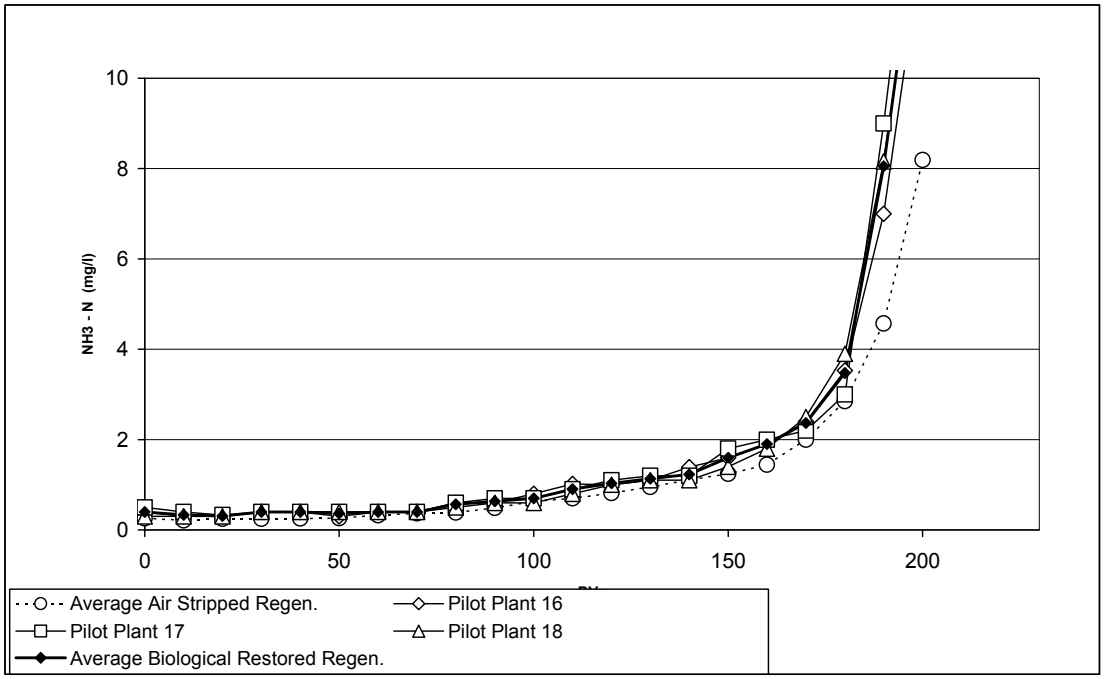


Figure 50: Breakthrough curves.

Approximately 160 BV of product water could be produced and there was no reduction in output. This shows that the clinoptilolite surface is not adversely affected during biological regeneration. It also appears that a slightly better performance was obtained during conventional regeneration (average air stripped regenerant).

4.7 Process design criteria

Process design criteria for a full-scale plant derived from the pilot plant study are shown in Table 12. A loading flow rate of 10 BV/h was selected for a full-scale plant because the retention time in the column is more or less in line with ion-exchange applications. The nitrogen removal at a breakthrough of 2 mg/ℓ NH_3-N was determined at 3,1 g NH_3-N/ℓ clinoptilolite. Between 120 and 170 BV of product water could be produced. Thirty BV regenerant were used.

Table 12: Process design criteria.

Design Criteria for Pilot Plant				
Criterion	**Value / Comment**			
	Air stripping of ammonia from regenerant			**Biologically restored regenerant**
Mode:	Downflow	Downflow	Downflow	Downflow
Loading flow rate:	5 BV/h	10 BV/h	15 BV/h	10 BV/h
EBCT	12 min	6 min	4 min	6 min
Particle size:	0.25 mm-0.7 mm	0.25 mm-0.7 mm	0.25 mm-0.7 mm	0.25 mm-0.7 mm
NH_3-N exchange capacity:	0.22 me/mℓ 3.1 gNH3-N/L Clino	0.187 me/mℓ 2.6 gNH3-N/L Clino	0.154 me/mℓ 2.2 gNH3-N/L Clino	0.190 me/mℓ 2.7 gNH3-N/L Clino
Bed Volume (BV):	Determined see note (1)	Determined see note (1)	Determined see note (1)	Determined see note (1)
Loading time:	Until breakthrough see note (2)	Until breakthrough see note (2)	Until breakthrough see note (2)	Until breakthrough see note (2)
Product water volume:	120 BV-170 BV see note (3)	120 BV-170 BV see note (3)	120 BV-170 BV see note (3)	120 BV-170 BV see note (3)
Regenerant:	0.1 M NaCl pH 11.4	0.1 M NaCl pH 11.4	0.1 M NaCl pH 11.4	0.4 M NaCl pH 8
Regeneration flow rate:	10 BV/h Downflow	10 BV/h Downflow	10 BV/h Downflow	10 BV/h Downflow
Regeneration time:	3 h	3 h	3 h	3 h
Regenerant usage:	30 BV	30 BV	30 BV	30 BV
Regenerant reuses:	4 (min)	4 (min)	4 (min)	Undetermined
45% NaOH added for pH correction	0.797 mℓ/ℓ regen 550 mℓ / 30 BV regen	0.586 mℓ/ℓ regen 405 mℓ / 30 BV regen	0.521 mℓ/ℓ regen 360 mℓ / 30 BV Regen	NA
Backwash water:	Potable water	Potable water	Potable water	Potable water
Backwash flow rate:	30 BV/h-40 BV/h see note (3)	30 BV/h-40 BV/h see note (3)	30 BV/h-40 BV/h see note (3)	30 BV/h-40 BV/h see note (3)
Backwash time:	10 min	10 min	10 min	10 min
Backwash water usage:	5 BV-7 BV	5 BV-7 BV	5 BV-7 BV	5 BV-7 BV
Rinse	Potable water	Potable water	Potable water	Potable water
Rinse flow rate:	10 BV/h	10 BV/h	10 BV/h	10 BV/h
Rinse time:	10 min	10 min	10 min	10 min
Rinse water usage:	1.7 BV	1.7 BV	1.7 BV	1.7 BV
Total cycle time:	To be determined from Loading Time (approximately 22 hrs)			

Note:
(1) To be determined from feed ammonia concentration, loading time and exchange capacity.
(2) Until breakthrough. To be determined from feed ammonia concentration, clinoptilolite volume and exchange capacity (typical 17 hrs).
(3) To be determined from Loading flow rate and loading time until breakthrough.(typical 120 BV-170 BV).
(4) 30-40 BV/h in upflow direction for 50% bed expansion; temperature dependant.

550 mℓ 45% NaOH was added to 30 BV (i.e. 3 x 23 = 690 ℓ) regenerant after regeneration to correct the pH of the regenerant:

$$\therefore \frac{550}{690} = \frac{0{,}7897 \text{ mℓ } 45\% \text{ NaOH}}{\text{ℓ regenerant}}$$

4.8 Proposed designs options

Design options for a clinoptilolite ammonia-nitrogen removal plant are shown in Figures 51, 52 and 53.

Figure 51. Feed water source.

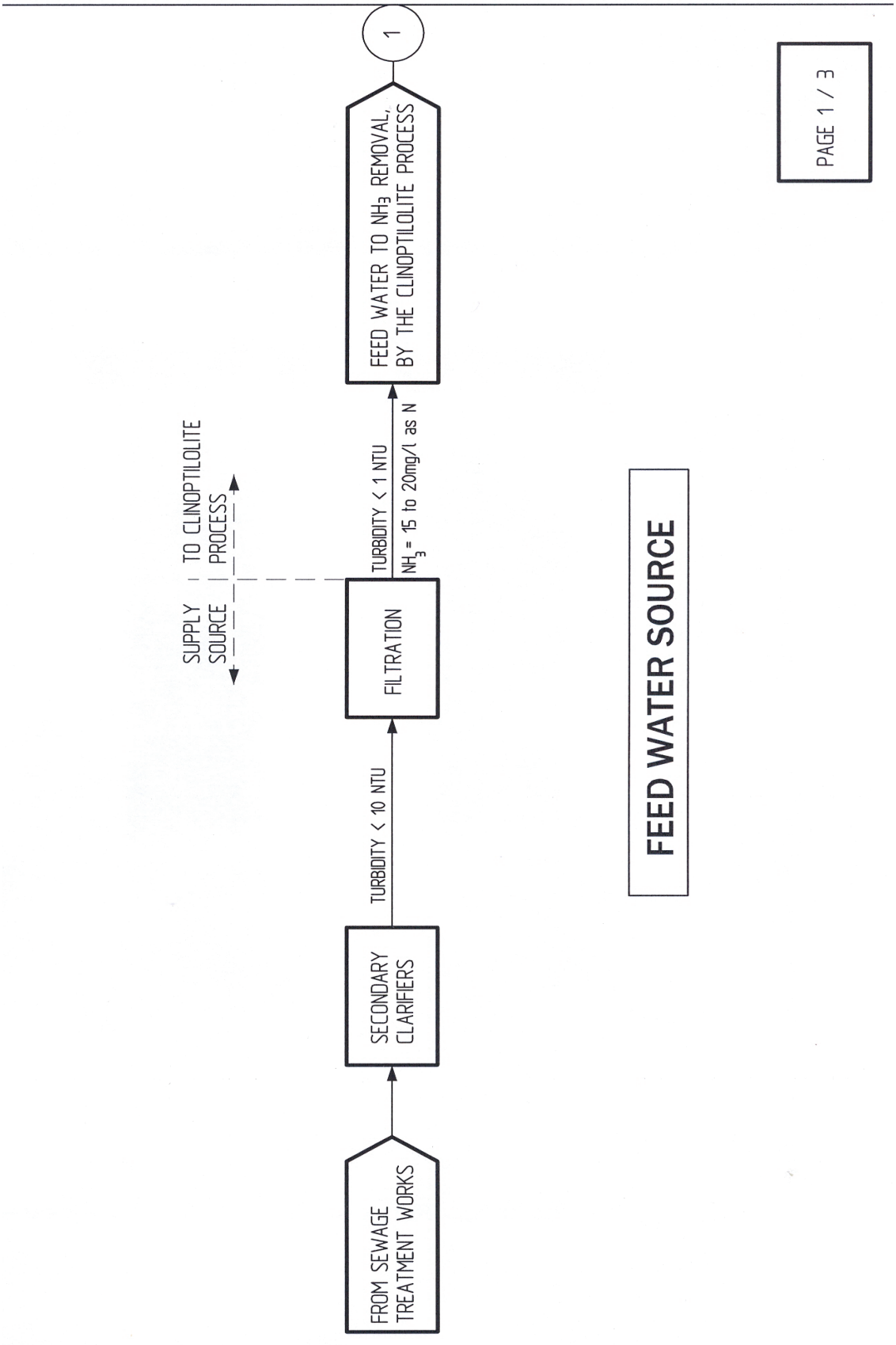


Figure 52. Clinoptilolite reactor.

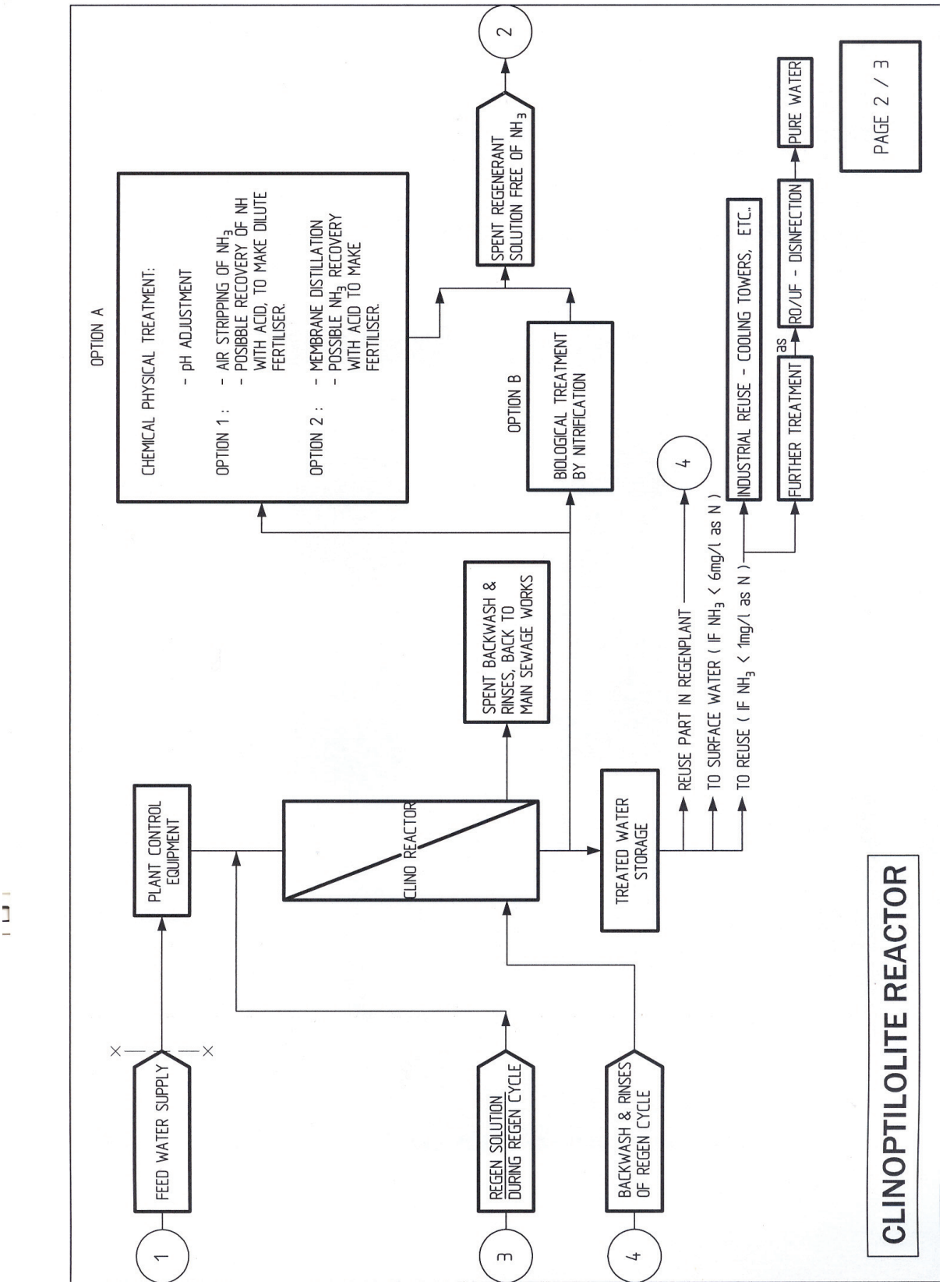
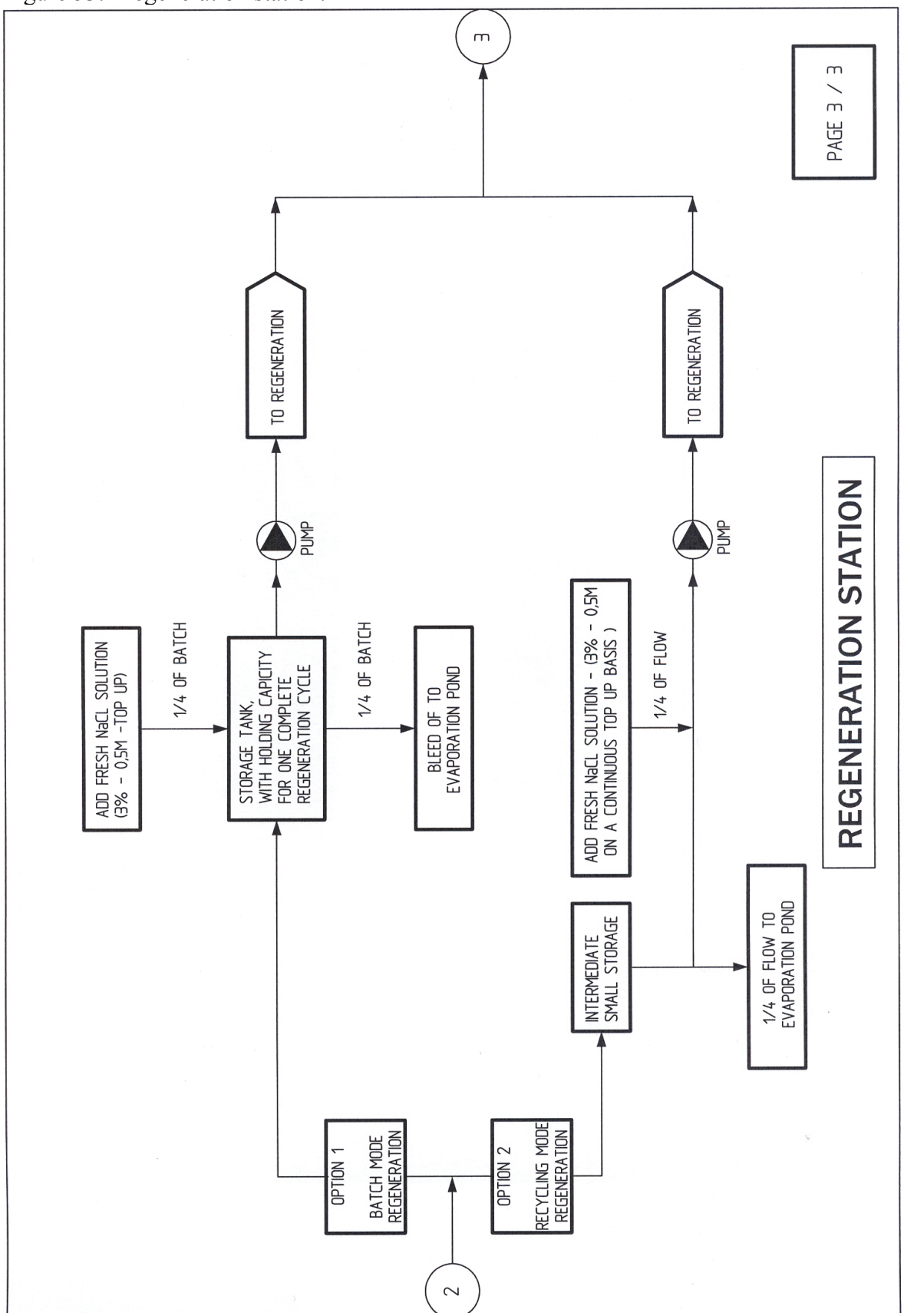


Figure 53: Regeneration station.



Effluent from the secondary clarifiers with a turbidity of less than 10 NTU will be filtered through a sand filter to reduce the turbidity to less than 1 NTU to protect the clinoptilolite bed from plugging (Figure 51). Filtered feed water with an ammonia-nitrogen concentration of between 15 and 20 mg/ℓ NH_3-N will be the feed to the clinoptilolite column.

Backwash and rinse waters will be directed back to the main sewage works (Figure 52).

The treated effluent will be stored in a treated water storage tank. Part of this water can be used for regenerant make-up. The remaining water can be discharged back into the water environment with an ammonia-nitrogen concentration of less than 6 mg/ℓ. Alternatively, this water can be used as cooling water if the ammonia-nitrogen concentration is less than 1 mg/ℓ. Another possibility could be to produce pure water with UF/RO for industrial use.

The spent regenerant can either be biologically or chemical/physical treated for ammonia removal to recover the regenerant for reuse (Figure 52). Biological treatment will comprise the conversion of ammonia-nitrogen biologically to nitrate-nitrogen. The treated effluent can then be reused. Physical/chemical treatment will consist of air stripping or membrane distillation to remove ammonia-nitrogen from the spent regenerant prior to reuse.

Regeneration can be conducted in the batch or recycling modes (Figure 53). In both cases it will be necessary to add sodium chloride to top-up the recovered regenerant. A quarter of the batch or flow can be bleed of to an evaporation pond. The remaining part of the regenerant can be used for regeneration.

4.9 Costs

The estimated capital and operational costs for 50 and 100 m^3/d plants are shown in Table 13. The detailed results are shown in Appendix P.

Table 13: Estimated capital and operational costs for 50 and 100 m^3/d plants with and without ammonia-nitrogen recovery.

Item	**50 m^3/d Plant**	**100 m^3/d Plant**
Capital cost without NH_3-N recovery	R250 000	R350 000
Operational costs/d	R57,55	R85,1
Capital cost with NH_3-N recovery	R290 000	R390 000
Operational costs/d	R61,75	R93,5

Note: Value of ammonia sulphate as fertilizer for 50 and 100 m^3/d plants are R19,50 and R39/d, respectively.

5. SUMMARY AND CONCLUSIONS

- 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 oversees 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 are low (13 to 17 m^2/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.

- The removal efficiencies of ammonia-nitrogen with clinoptilolite (0,25 to 0,7 mm) 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 clinoptilolite.

- 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.

- 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 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 ammonia-nitrogen 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 affect output adversely as a result of competing ions. Almost all the ammonoia-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 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. It was also 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 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 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.

- A deteriorating performance for ammonia-nitrogen removal was observed when 15 bedvolumes 0,1 M NaCl was used for regenerant reuse.

- 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. 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^3. However, this cost should be significantly reduced with regenerant reuse and ammonia recovery. Chemical cost with powdered clinoptilolite is very high and is not an option for the removal of ammonia-nitrogen from secondary effluent.

- 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 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 should be conducted to prove this point.

- Process design criteria for a full-scale plant has been successfully derived from pilot studies. A loading flow rate (15 to 20 mg/ℓ NH_3-N) of 10 bedvolumes per hour is suggested because the retention time in the column is in the same order as that of ion-exchange applications. The ammonia-nitrogen capacity at a breakthrough of 2 mg/ℓ NH_3-N is 3,1 g NH_3/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) should be filtered through a sandfilter (< 1 NTU) to protect the clinoptilolite bed from plugging. Feed water containing 15

to 20 mg/ℓ ammonia-nitrogen should 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. 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^3/d plants are as follows:

50 m^3/d plant	R250 000 without NH_3-N recovery R290 000 with NH_3-N recovery
100 m^3/d plant	R350 000 without NH_3-N recovery R390 000 with NH_3-N recovery

- The estimated operational costs for 50 and 100 m^3/d plants are as follows:

50 m^3/d plant	R57,55/d without NH_3-N recovery R61,75/d with NH_3-N recovery
100 m^3/d plant	R85,1/d without NH_3-N recovery R39,5/d with NH_3-N recover

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APPENDIX A

Phenate method

(Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 1995)

1. General Discussion

a. Principle: An intensely blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside.
b. Interferences: Complexing magnesium and calcium with citrate eliminates interference produced by precipitation of these ions at high pH. There is no interference from other trivalent forms of nitrogen. Remove interfering turbidity by distillation or filtration. If hydrogen sulphide is present, remove by acidifying samples to pH 3 with dilute HCl and aeration vigorously until sulphide odour no longer can be detected.

2. Apparatus Used

Spectrophotometer for use at 640 nm with a light path of 1 cm or greater.

3. Reagents

a. Phenol solution: Mix 11.1 m liquefied phenol (≥89%) with 95% v/v ethyl alcohol to a final volume of 100 mL. Prepare weekly. Caution: Wear gloves an eye protection when handling phenol: use good ventilation to minimise all personnel exposure to this toxic volatile substance.
b. Sodium nitroprusside, 0.5% w/v: Dissolve 0.5 g sodium nitroprusside in 100 mL deionised water. Store in amber bottle for up to 1 month.
c. Alkaline citrate: Dissolve 200 g trisodium citrate and 10 g sodium hydroxide in deionised water. Dilute to 1000 mL.
d. Sodium hypochlorite, commercial solution, about 5%. This solution slowly decomposes once the seal on the bottle cap is broken. Replace about every 2 months.
e. Oxidising solution: Mix 100 mL alkaline citrate solution with 25 mℓ sodium hypochlorite. Prepare fresh daily.
f. Stock ammonium solution: Dissolve 3.819 g anhydrous NH_4Cl (dried at 100°C) in water, and dilute to 1 000 mℓ; 1.00 mL = 1.00 mg N = 1.22 mg NH_3.
g. Standard ammonium solution: Use stock ammonium solution and water to prepare a calibration curve in a range appropriate for the concentration of the samples.

4. Procedure

To a 25 mL sample in a 50 mL Erlenmeyer flask, add, with thorough mixing after each addition, 1 mL phenol solution, 1 mL sodium nitroprusside solution and 2.5 mL oxidising solution. Cover samples with plastic wrap or paraffin wrapper film. Let colour develop at room temperature (22 to 27°C) in subdued light for at least 1 h. Colour is stable for 24 h. Measure absorbance at 640 nm. Prepare a blank and at least two other standards by diluting stock ammonia solution into the sample concentration range. Treat standards the same as samples.

5. Calculations

Prepare a standard curve by plotting absorbance readings of standards against ammonia concentrations of standards. Compute sample concentration by comparing sample absorbance with the standard curve.

Table B.1. Calibration curve data for 2006-12-07

Sample NH_3-N concentration (mg/ℓ)	Absorbance at 640 nm
0.0 (Blank)	0.000
0.1	0.097
0.2	0.191
0.3	0.269
0.4	0.384

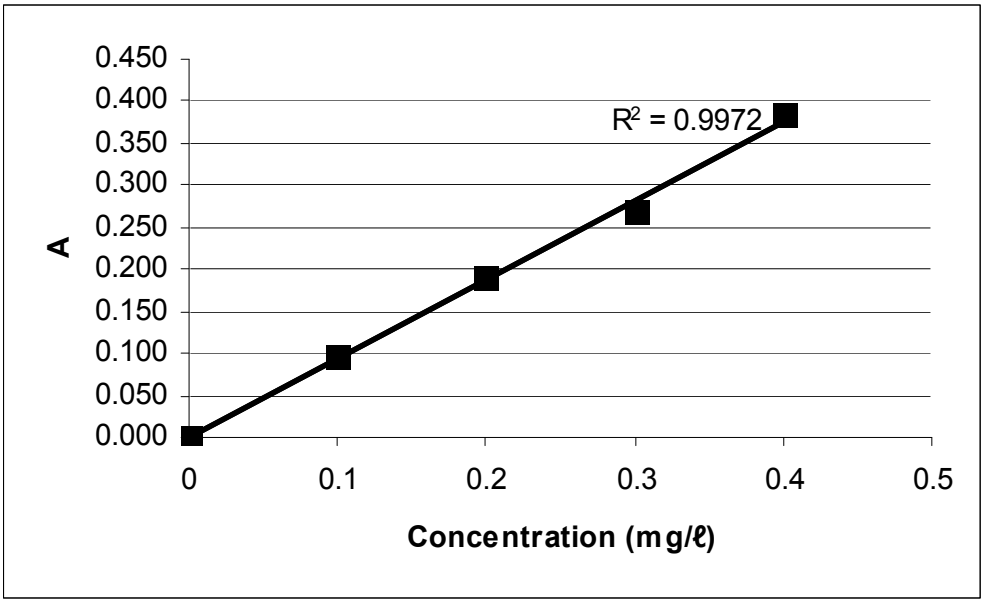

Figure B.1. Calibration curve for 2006-12-07

APPENDIX B

UNIVERSITY OF PRETORIA

DEPARTMENT OF CHEMICAL ENGINEERING

WATER UTILISATION DIVISION

EVALUATION OF A SOUTH AFRICAN CLINOPTILOLITE FOR THE REMOVAL OF AMMONIA-NITROGEN FROM SECONDARY EFFLUENT FOR POLLUTION CONTROL

(Progress report: Design criteria and design of a pilot plant)

by

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Pretoria: July 2007

1. DESIGN OF AN APPROXIMATELY 1 m^3/d PILOT PLANT FOR THE REMOVAL OF NH_4-N FROM SECONDARY EFFLUENT

1.1 Design criteria

The suggested process design criteria for an approximately 1 m^3/d NH_4-N removal pilot plant derived from laboratory studies is shown in Table 1.

Table 1. Process design criteria.

Clinoptilolite particle size:	0,25-0,7 mm
NH_4-N exchange capacity:	0,22 me/mℓ or 3,08 mg/mℓ
Loading flow rate:	10 BV/h
Loading time:	15 h
Product water produced:	150 BV
Regeneration flow rate:	10 BV/h
Regenerant usage:	30 BV 0,1 M NaCl adjusted to pH 12 with 0,08 mℓ NaOH/ℓ regenerant solution. For regenerant reuse, approximately 80 mℓ NaOH/ℓ must be added for pH adjustment to 12 after air stripping
Regeneration time:	3 h
Rinsing time:	10 min.
NH_4-N reduction:	Approximately 20 mg/ℓ
Total cycle time:	20
Cycles per day:	1
Attrition losses:	2% / annum
Water recovery:	98%
Waste regenerant produced:	3,3% (depending on reuse)

The process design has been based on a service cycle of 15 hours (150 BV/10 BV/h) followed by backwashing, regeneration, rinsing (approximately 5 hours) and loading. Regeneration will take approximately 3 hours (10 BV/h and 30 BV regenerant).

1.2 Volume of Clinoptilolite required

Water required per day:	1 m^3/d
Water required per week:	7 m^3/week

Assume that 2 runs will be conducted per week and that each loading cycle will last approximately 15 hours. Therefore, 3,5 m^3 water must be produced over 15 hours.

Feed water flow rate:

$\frac{3,5\ m^3}{15\ h}$ = 0,233 m^3/h

= 1,864 m^3/d (8 hours)

NH_4-N removed per day:

$\frac{1,864\ m3}{d}$ x $\frac{20\ g}{m^3}$

= 37,28 g/d (8 h)

= 4,66 g/h

NH_4-N removed per run:

15 h x 4,66 g/h

= 69,9 g NH_4-N

Therefore, volume of Clinoptilolite required:

$\frac{69,9\ g\ NH_4\text{-}N}{3,08\ g/\ell}$

= 22,69 litre (1 BV)

Say 23 *l*.

1.3 Size of contactor vessel

Diameter: 0,15 m
Height: 1,27 m

Cross sectional area:

πr^2 = $\frac{22}{7}$ x $(0,075\ m)^2$

= 0,018 m^2

Height of vessel:

πr^2 x h = Volume

h = $\frac{Volume}{\pi r^2}$

= $\frac{23\ litre}{0,018\ m^2}$

$$= \frac{0{,}023\ m^3}{0{,}018\ m^2}$$

$$= 1{,}27\ m$$

1.4 Flow rates and periods

1.4.1 Feed water flow rate

Instantaneous feed water flow rate:

$$\frac{3{,}5\ m^3}{15\ h \times 60\ min}$$

$$= 0{,}00389\ m^3/min$$

$$= 3{,}89\ l/min$$

With a clinoptilolite charge of 23 *l*, the retention time will be:

$$\frac{23\ l}{3{,}89\ l/min} = 5{,}91\ min.$$

1.4.2 Backwash flow rate and period

Backwash flow rate (50% expansion):

116 mℓ/min = 0,77 BV/min (1 BV = 150 mℓ)

= 46,4 BV/h

Using a charge of 23 *l*:

$$46{,}4\ \frac{BV}{H} \times \frac{23\ l}{1\ BV} = 1\,067{,}2\ \frac{l}{h}$$

$$= 1{,}07\ m^3/h$$
$$= 0{,}0178\ m^3/min$$

Cross sectional area is 0,018 m^2.

Therefore, backwash loading flow rate:

$$\frac{1{,}07\ m^3}{0{,}018\ h.m^2}$$

$$= 59{,}444\ \frac{m^3}{h.m^2}$$

$$= \quad 0{,}991 \quad \frac{m^3}{min.m^2}$$

Backwash time (10 min):

Therefore, backwash volume:

$$0{,}0178 \frac{m^3}{min} \times 10 \text{ min} = 0{,}178 \text{ m}^3$$

$$= 178 \textit{ l}$$

1.4.3 Regeneration flow rate and period

Regeneration flow rate:

$$10 \frac{BV}{H} \times \frac{23 \textit{ l}}{180} \times \frac{1 \text{ h}}{60 \text{ min}} = 2{,}833 \frac{\textit{l}}{min}$$

or $\frac{212{,}9 \textit{ l}}{m^2.min}$ (area 0,018 m^2)

Regeneration time:

$$\frac{690 \textit{ l} \quad (30 \text{ BV})}{3{,}833 \text{ l/min}} \quad (1 \text{ BV} = 23 \textit{ l})$$

$$= \quad 180 \text{ min}$$
$$= \quad 3 \text{ h}$$

1.4.4 Rinsing flow rate and period

Rinsing flow rate:

$$10 \frac{BV}{h} \times \frac{23 \textit{ l}}{1 \text{ BV}} \times \frac{1 \text{ h}}{60 \text{ min}} = 3{,}833 \frac{\textit{l}}{min}$$

or $\frac{212{,}944 \textit{ l}}{min.m^2}$ (area 0,018 m^2)

Rinse time 30 min, therefore rinse volume:

$$3{,}833 \frac{\textit{l}}{Min} \times 30 \text{ min}$$

$$= \quad 114{,}99 \textit{ l}$$

1.4.5 Loading flow rate and period

Loading flow rate 10 BV/h:

$$10\ \frac{BV}{H} \times \frac{23\ l}{BV} \times \frac{1\ h}{60\ min} = 3{,}833\ \frac{l}{min}$$

or $\frac{212{,}9\ l}{min.m^2}$ (0,018 m^2 area)

Loading time:

$$\frac{150\ BV}{10\ B/h}$$

= 15 h

1.4.6 Down time

Backwash time:	10 min
Regeneration time:	3 hours
Rinsing time:	0,5 hours
Total:	3,67 hours (Say 5 hours)

1.5 Chemical quantities and costs

1.5.1 Sodium chloride required for regeneration

30 BV 0,1 M NaCl is required for regeneration.

1 BV = 23 l
and 30 BV = 690 l

Therefore, NaCl required for regeneration:

$$690\ l \times \frac{5{,}85\ g}{l}$$ (0,1 M NaCl)

= 4 036,5 g
= 4,037 kg

Cost of NaCl:

$$\frac{R350}{ton} = \frac{R350}{1000\ kg} = \frac{R0{,}35}{kg}$$

Therefore:

$$\frac{R0,35}{kg} \times \frac{4,037\ kg}{Regen} \times \frac{R1,413}{Regen}$$

Therefore, regeneration cost per run:

$$150\ BV \times \frac{23\ l}{1\ BV} = 3\ 450\ l$$

That is:

$$\frac{R1,413}{3\ 450\ l} \qquad \frac{1\ 000\ l}{m^3} \qquad = \qquad \frac{R0,41}{m^3}$$

1.5.2 Caustic soda required for pH adjustment of spent regenerant

Eighty mℓ 1 N NaOH required to raise pH of spent regeneration to approximately 12.

40 g NaOH in 1 litre is 1 N.
1 000 mL NaOH solution contains 40 g NaOH and 80 mℓ NaOH solution contains: $\frac{80}{1\ 000} \times 40\ g$

$$= 3,2\ g\ NaOH$$

Caustic costs:

$$\frac{3,2\ g}{4,5\ l} = 0,711\ g \quad (1\ BV = 150\ m\ell)$$

That is: $\frac{0,711\ g}{l} \times 690\ l$ (30 BV)

$$= 490,59\ g\ NaOH$$

Costs: $490,59\ g \times \frac{R4,25}{1\ 000\ g}$

$$= R2,09$$

That is: $\frac{R2,09}{3,450\ m^3} = \frac{R0,61}{m^2}$ (1 BV = 23 *l*, 150 BV)

Regeneration costs:

$$\frac{R0,41}{m^3} \quad x \quad \frac{R0,61}{m^3}$$

$$= \quad R1,02/m^3$$

1.5.3 Regeneration costs after first regenerant reuse

Caustic soda required for pH adjustment of spent regenerant:

83 mℓ NaOH solutions contains: $\frac{83}{1\,000} \times 40$ g

$$= \quad 3,32 \text{ g NaOH}$$

Caustic costs:

$$\frac{3,32 \text{ g}}{4,5\ l} = \frac{0,738 \text{ g}}{l} \quad (1 \text{ BV} = 150 \text{ m}\ell)$$

That is: $\frac{0,738 \text{ g}}{l} \times 690 \text{ l} \quad (30 \text{ BV})$

$$= \quad 509,22 \text{ g NaOH}$$

Costs: $509,22 \text{ g} \times \frac{R4,25}{1\,000 \text{ g}}$

$$= \quad R2,16$$

That is: $\frac{R2,16}{3,450\ m^3} = \frac{R0,63}{m^3} \quad (1 \text{ BV} = 23\ l;\ 150 \text{ BV})$

Regeneration costs: $\frac{R0,63}{m^3}$

1.5.4 Regeneration costs after second regenerant reuse

Caustic soda required for pH adjustment of spent regenerant.

85 mℓ NaOH solutions contains: $\frac{85}{1\,000} \times 40$ g

$$= \quad 3,4 \text{ g NaOH}$$

Caustic costs:

$\frac{3{,}4\ g}{4{,}5\ l} = \frac{0{,}756\ g}{l}$ (1 BV = 150 mℓ)

That is: $\frac{0{,}756\ g}{l} \times 690\ l$ (30 BV)

$= 521{,}64$ g NaOH

Costs: $521{,}64\ g \times \frac{R4{,}25}{1\ 000\ g}$

$= R2{,}22$

That is: $\frac{R2{,}22}{2{,}875\ m^3} = \frac{R0{,}77}{m^3}$ (1 BV = 23 *l*; 125 BV)

Regeneration costs: $\frac{R0{,}77}{m^3}$

1.5.5 Regeneration costs after third regenerant reuse

Caustic soda required for pH adjustment of spent regenerant.

130 mℓ NaOH solutions contains: $\frac{130}{1\ 000} \times 40\ g$

$= 5{,}2$ g NaOH

Caustic costs:

$\frac{5{,}2\ g}{4{,}5\ l} = \frac{1{,}156\ g}{l}$ (1 BV = 150 mℓ)

That is: $\frac{1{,}156\ g}{l} \times 690\ l$ (30 BV)

$= 797{,}64$ g NaOH

Costs: $797{,}64\ g \times \frac{R4{,}25}{1\ 000\ g}$

$= R3{,}39$

That is: $\frac{R3{,}39}{3{,}450\ m^3} = \frac{R0{,}98}{m^3}$ (1 BV = 23 *l*; 150 BV)

Regeneration costs after fourth regenerant reuse

Caustic soda required for pH adjustment of spent regenerant.

150 mℓ NaOH solutions contains: $\frac{150}{1\,000} \times 40$ g

= 6,0 g NaOH

Caustic costs:

$\frac{6,0\text{ g}}{4,5\ l} = \frac{1,333\text{ g}}{l}$ (1 BV = 150 mℓ)

That is: $\frac{1,333\text{ g}}{l} \times 690\ l$ (30 BV)

= 919,77 g NaOH

Costs: 919,77 g x $\frac{R4,25}{1\,000\text{ g}}$

= R3,91

That is: $\frac{R3,91}{3,517\text{ m}^3} = \frac{R1,11}{\text{m}^3}$ (1 BV = 23 *l*; 155 BV)

1.5.6 Regeneration costs after fifth regeneration

Caustic soda required for pH adjustment of spent regenerant.

250 mℓ NaOH solutions contains: $\frac{250}{1\,000} \times 40$ g

= 10,0 g NaOH

Caustic costs:

$\frac{10,0\text{ g}}{4,5\ l} = \frac{2,222\text{ g}}{l}$ (1 BV = 150 mℓ)

That is: $\frac{2,222\text{ g}}{l} \times 690\ l$ (30 BV)

= 1 533,18 g NaOH

Costs: 1 533,18 g x $\frac{R4,25}{1\,000\text{ g}}$

= R6,52

That is: $\frac{R6,52}{3,450\ m^3} = \frac{R1,89}{m^3}$ (1 BV = 23 *l*; 150 BV)

1.5.7 Regeneration costs after sixth regeneration

Caustic soda required for pH adjustment of spent regenerant.

260 mℓ NaOH solutions contains: $\frac{260}{1\ 000} \times 40\ g$

= 10,4 g NaOH

Caustic costs:

$\frac{10,4\ g}{4,5\ l} = \frac{2,311\ g}{l}$ (1 BV = 150 mℓ)

That is: $\frac{2,311\ g}{l} \times 690\ l$ (30 BV)

= 1 594,59 g NaOH

Costs: 1 594,59 g x $\frac{R4,25}{1\ 000\ g}$

= R6,78

That is: $\frac{R6,78}{3,450\ m^3} = \frac{R1,97}{m^3}$ (1 BV = 23 *l*; 150 BV)

1.5.8 Clinoptilolite costs

23 litre clino will be required at a cost of approximately R1 800/ton.

1.5.9 Estimated operational costs

Run	Regeneration costs R/m^3
1	1,02
2 (1st reuse)	0,63
3 (2nd reuse)	0,77
4 (3rd reuse)	0,98
5 (4th reuse)	1,11
6 (5th reuse)	1,89
7 (6th reuse)	1,97
	8,37

The chemical regeneration costs for seven runs were R8,37/m^3. This is R1,20/m^3 on average per run.

Note: The chemical regeneration costs after three runs were R0,80/m^3. Thereafter, the regeneration costs increased as a result of a higher caustic demand to raise the pH to 7. This matter is currently under investigation.

1.6 Size of regeneration tank

30 BV of 0,1 M NaCl will be required for regeneration.

Therefore, volume of NaCl solution required will be:

$$30\ BV \times \frac{23\ l}{1\ BV} = 690\ l$$

Therefore, one 1 000 litre or two 500 litre tanks will be required.

1.7 Regenerant quantities for disposal

Spent NaCl: $\frac{30\ BV}{Run} \times \frac{23\ l}{1\ BV} = 690\ l$

Back wash: = 178 *l*

Rinse: = 115 *l*

Total: = 983 *l*

Product water production per run: 3 450 *l*
Spent regeneration production per run: 690
Backwash: 178 *l*
Rinse: 115 *l*

Therefore, % wastewater: $\frac{690}{3\ 450} \times 100\%$

= 20%

% wastewater after 6 regenerant reuses: $\frac{690 \times 100\%}{6 \times 3\ 450}$

= 3,33%

1.8 Flow diagram of pilot plant

A flow diagram of the pilot plant is shown in Figure 1.

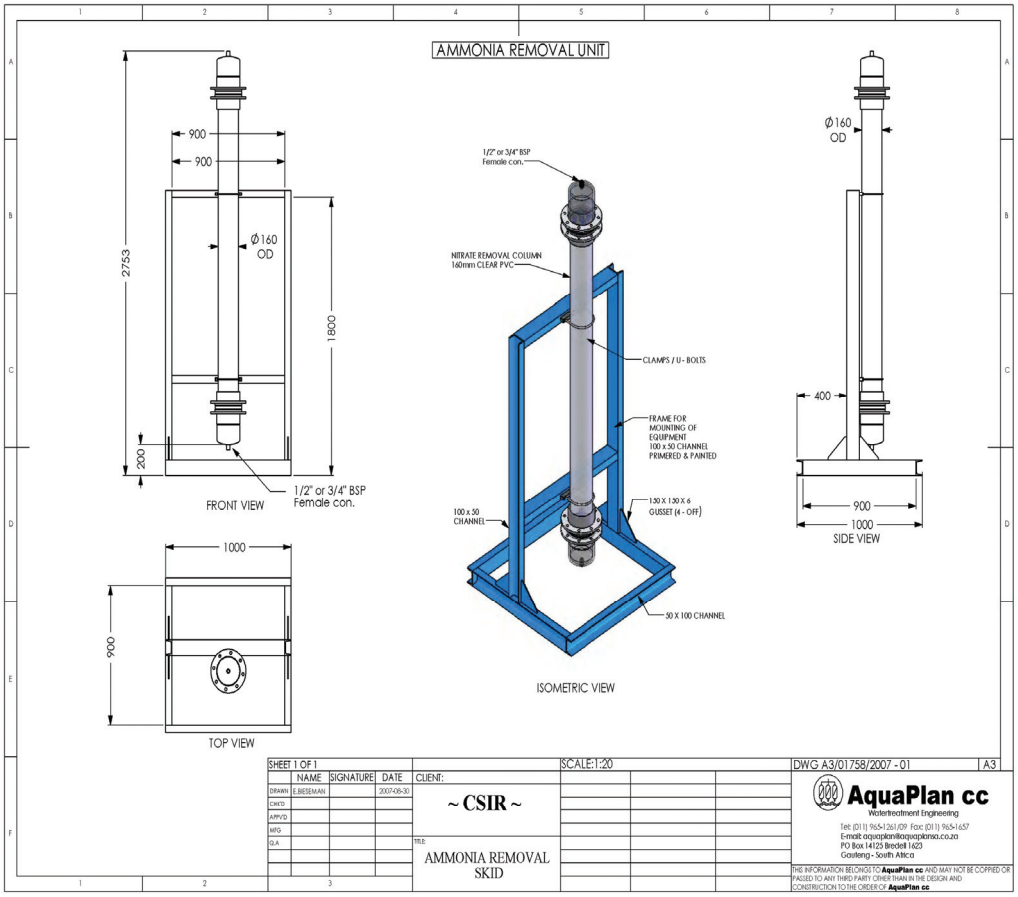

Figure 1: Flow diagram of the pilot plant.

The pilot plant consists of a column and a stand. The necessary pumps and tanks for the feed, regenerant and product will be added on site.

APPENDIX C

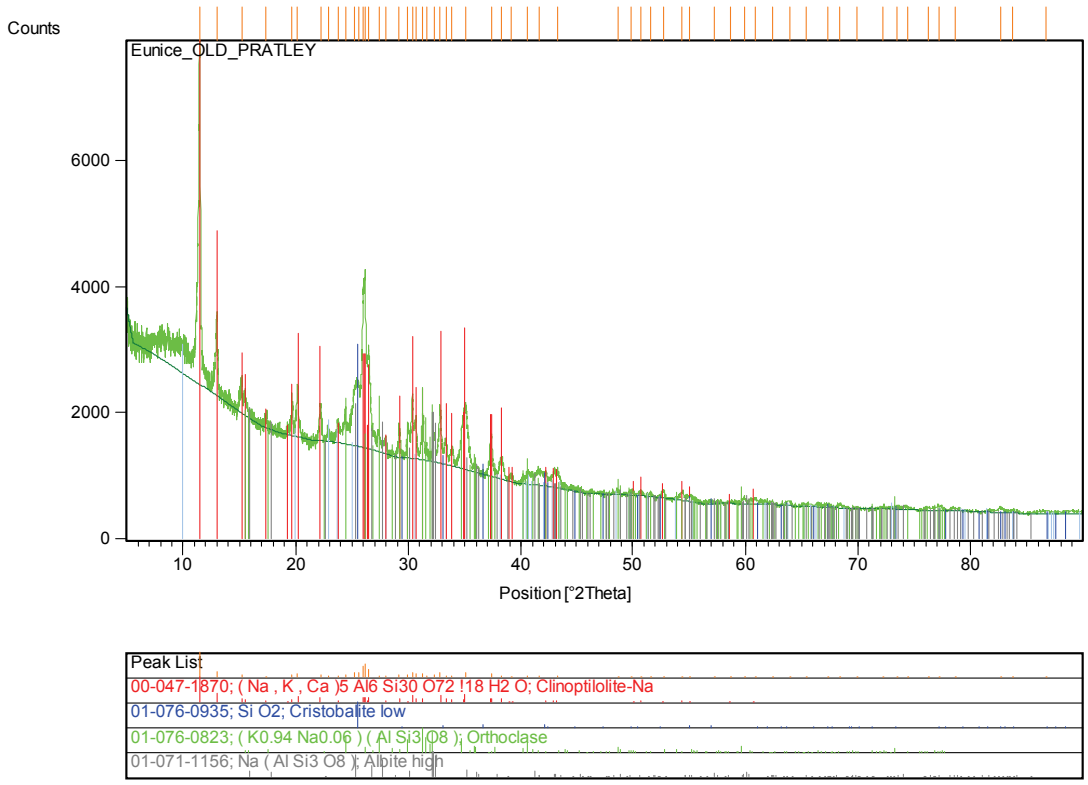

Figure 1: X-ray diffraction patterns of the Old Pratley clinoptilolite

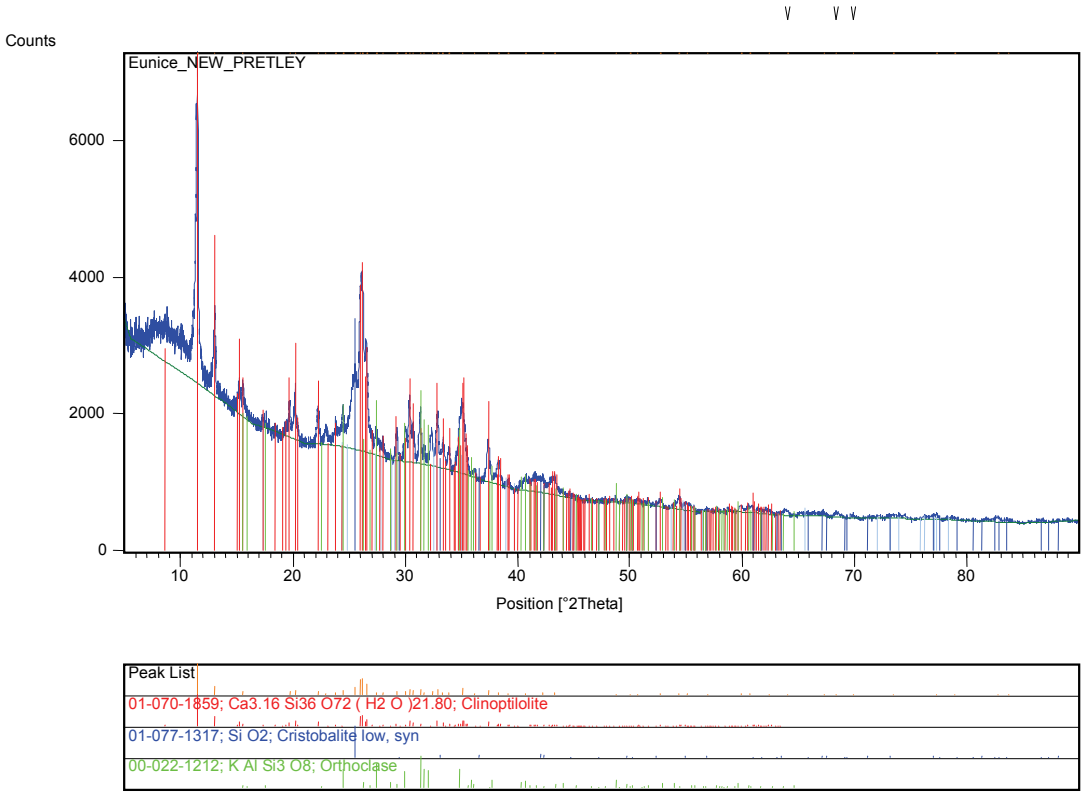

Figure 2: X-ray diffraction patterns of the New Pratley clinoptilolite

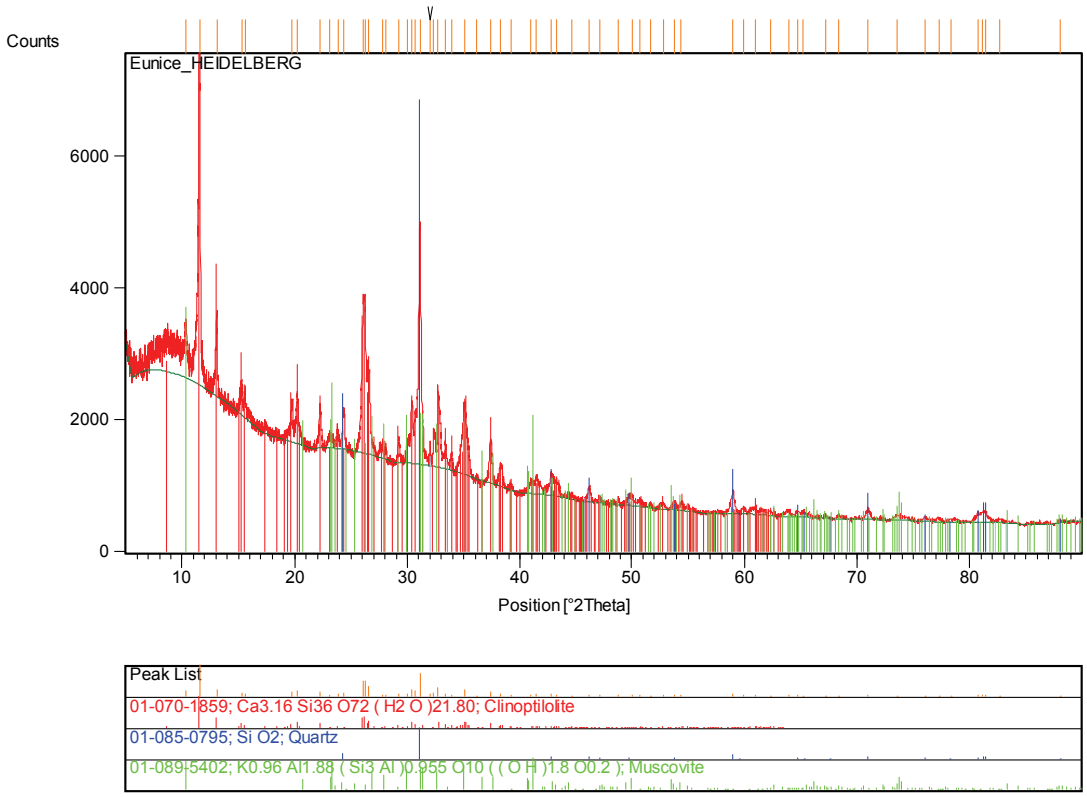

Figure 3: X-ray diffraction patterns of the Heidelberg clinoptilolite

APPENDIX D

Table D.1: Effect of contact time on ammonia-nitrogen removal

Time (Hours)	Unconditioned (Co = 4.9 mg/ℓ)		Unconditioned (Co = 10.2 mg/ℓ)		Unconditioned (Co = 20.1 mg/ℓ)	
	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)
0.25	2.4	2	5.4	4.9	12.4	12.1
0.5	2.1	1.8	5.2	4.4	11.5	11.6
1	2	1.4	5	3.9	10.9	10.3
2	1.8	1.6	4.5	3.6	9.8	9
3	1.5	1	4.3	3.5	9.2	8.1
4	1.2	0.9	3.8	3.1	8.2	8
5	1.1	0.9	3.7	3.1	8.1	7.8
6	1	0.9	3.6	3	8	7.8

Table D.2: Effect of contact time on ammonia-nitrogen removal

Time (Hours)	Conditioned (Co = 5.2 mg/ℓ)		Conditioned (Co = 9.8 mg/ℓ)		Conditioned (Co = 20.5 mg/ℓ)	
	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)
0.25	2	1.7	4.8	4.5	11.9	11.2
0.5	1.8	1.6	4.5	4.1	11.1	10.8
1	1.6	1.2	3.9	3	10.5	10.1
2	1.3	1	3.2	2.8	9.2	9
3	1.2	0.7	2.6	2.2	8.4	8.1
4	1	0.6	2	1.9	8	7.7
5	0.9	0.6	1.9	1.7	7.9	7.4
6	0.8	0.5	1.8	1.7	7.8	7.4

Table D.3: Effect of contact time on removal efficiency.

Time (Hours)	Unconditioned (Co = 4.9 mg/ℓ)		Unconditioned (Co = 10.2 mg/ℓ)		Unconditioned (Co = 20.1 mg/ℓ)	
	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)
0	0	0	0	0	0	0
0.25	51	59.2	47.1	52	38.3	39.8
0.5	57.2	63.3	49	56.9	42.8	42.3
1	59.2	71.4	51	61.8	45.8	48.8
2	63.3	77.6	55.9	64.7	51	55.2
3	69.4	79.6	57.8	65.7	54	59.7
4	75.6	81.6	62.7	69.6	59.2	60.2
5	77.6	81.6	63.7	69.6	59.7	61.2
6	79.6	81.6	64.7	70.5	60.2	61.2

Table D.4: Effect of contact time on removal efficiency.

Time (Hours)	Conditioned (Co = 5.2 mg/ℓ)		Conditioned (Co = 9.8 mg/ℓ)		Conditioned (Co = 20.5 mg/ℓ)	
	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)	Concentration mg/ℓ (Pratley 1)	Concentration mg/ℓ (Pratley 2)
0	0	0	0	0	0	0
0.25	61.5	67	51	54	41	45
0.5	65.4	69	54	58	46	47
1	69.2	77	60	69	49	51
2	75	81	67	71	55	56
3	77	87	73	78	59	60
4	81	88	80	81	61	62
5	83	88	81	83	62	64
6	85	90	82	83	62	64

APPENDIX E

Detail results for the sorption isotherms.

Table E.1 Batch adsorption experiment 2.1: 3 hr samples: Calculation of contaminant concentration sorbed on the solid

Clino (g)	C_0 (mg/ℓ)	C (mg/ℓ)	x (mg)	q (mg NH_3-N/g clino)
1.00	10.18	6.40	1.89	1.89
2.00	10.18	5.90	2.14	1.07
3.00	10.18	4.71	2.73	0.91
4.00	10.18	4.19	2.99	0.75
5.00	10.18	4.14	3.02	0.60

Table E.2 Batch adsorption experiment 2.1: 3 hr samples: Calculation of variables to plot

q	C	$1/q$	$1/C$	$\log q$	$\log C$
1.89	6.40	0.529	0.156	-0.277	0.806
1.07	5.90	0.935	0.170	-0.029	0.771
0.91	4.71	1,099	0.212	-0.041	0.673
0.75	4.19	1.333	0.239	-0.125	0.622
0.60	4.14	1.667	0.242	-0.222	0.617

Table E.3 Batch adsorption experiment 2.2: Ammonia concentration of analysed samples (0.25-0.7 mm diameter particles)

NH_3-N conc. after:		Bottle 1 (1 g clino)	Bottle 2 (2 g clino)	Bottle 3 (3 g clino)	Bottle 4 (4 g clino)	Bottle 5 (5 g clino)	Control
(mg/ℓ)	3 hrs	5.044	4.430	3.726	3.197	2.957	8.418

Table E.4 Batch adsorption experiment 2.2: 3 hr samples: Calculation of contaminant concentration sorbed on the solid

Clino (g)	C_0 (mg/ℓ)	C (mg/ℓ)	x (mg)	q (mg NH_3-N/g clino)
1.00	9.98	5.04	2.47	2.47
2.00	9.98	4.43	2.78	1.39
3.00	9.98	3.73	3.13	1.04
4.00	9.98	3.20	3.39	0.85
5.00	9.98	2.96	3.51	0.70

Note: Amount of ammonia removed, x, calculated: $x = (\text{Volume})*(C_0 - C) = (0.5)*(9.98 - C)$

Table E.5 Batch adsorption experiment 2.2: 3 hr samples: Calculation of variables to plot

q	C	$1/q$	$1/C$	log q	log C
2.47	5.04	0.405	0.198	0.392	0.702
1.39	4.43	0.719	0.226	0.143	0.646
1.04	3.73	0.962	0.268	0.017	0.572
0.85	3.20	1.177	0.312	-0.071	0.505
0.70	2.96	1.429	0.338	-0.155	0.471

Table E.6 Batch adsorption experiment 2.3: Ammonia concentration of analysed samples (powdered clino)

NH_3-N conc. after:		Bottle 1 (1 g clino)	Bottle 2 (2 g clino)	Bottle 3 (3 g clino)	Bottle 4 (4 g clino)	Bottle 5 (5 g clino)	Control
(mg/ℓ)	3 hrs	5.022	3.389	3.341	2.909	2.188	11.17

Table E.7 Batch adsorption experiment 2.3: 3 hr samples: Calculation of contaminant concentration sorbed on the solid

Clino (g)	C_0 (mg/ℓ)	C (mg/ℓ)	x (mg)	q (mg NH_3-N/g clino)
1.00	10.7	5.02	2.86	2.86
2.00	10.7	3.39	3.67	1.84
3.00	10.7	3.34	3.70	1.23
4.00	10.7	2.91	3.91	0.98
5.00	10.7	2.19	4.28	0.86

Note: Amount of ammonia removed, x, calculated: $x = (\text{Volume})*(C_0 - C) = (0.5)*(10.7 - C)$

Table E.8 Batch adsorption experiment 2.3: 3 hr samples: Calculation of variables to plot

q	C	$1/q$	$1/C$	log q	log C
2.86	5.02	0.350	0.199	0.456	0.701
1.84	3.39	0.545	0.295	0.265	0.530
1.23	3.34	0.813	0.299	0.090	0.524
0.98	2.91	1.020	0.344	-0.009	0.464
0.86	2.19	1.163	0.457	-0.066	0.340

APPENDIX F

Table F.1 The NH_4-N concentration of analysed effluent samples from the beaker tests to establish the efficiency of untreated and regenerated powdered clinoptilolite for the removal of ammonia-nitrogen from Pretoria tap water spiked with NH_4Cl to approximately. 20 and 10 mg/ℓ NH_3N

The Data obtained using untreated Old Pratley powdered clino				
	Concentration (mg/ℓ)			
Amount of clino (g)	Run 1 (Co= 19.1)	Run 2 (Co= 9.5)	Run 3 (Co= 20) Regenerated	Run 4 (Co= 9.4) Regenerated
1	14	8.94	10.4	6.5
2	12.8	8.1	9.5	5.6
4	12.3	6.7	6	5.4
8	8.5	5.3	4.2	1.8
16	5.8	5.26	2.6	1.7

Table F.2 The NH_3-N concentration of analysed effluent samples from the beaker tests to establish the efficiency of powdered clinoptilolite for the removal of ammonia-nitrogen from Sunderland ridge secondary effluent with different initial effluent concentrations

The Data obtained using untreated Old Pratley powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
	13.3	2	12.7	12.3	12.1
2	13.3	4	12.3	9.6	9.5
3	13.3	6	9.6	8.2	8.3
4	13.3	8	8.2	6.6	6.4
5	13.3	10	6.2	5.5	6.0
6	13.3	0	13.3	13.3	13.3
The Data obtained using regenerated Old Pratley powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
1	13.0	2	11.2	8.7	8.0
2	13.0	4	9.0	6.8	6.9
3	13.0	6	7.7	6.1	6.8
4	13.0	8	4.6	5.0	4.7
5	13.0	10	4.9	3.9	3.7
6	13.0	0	13	13	13

The Data obtained using un-treated New Pratley powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
1	12.0	2	7.4	8.5	8.3
2	12.0	4	4.3	3.9	3.9
3	12.0	6	2.9	3.6	3.9
4	12.0	8	2.3	2.1	2.6
5	12.0	10	1.2	1.7	1.3
6	12.0	0.0	12.0	12.0	12.0
The Data obtained using regenerated New Pratley powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
1	9.4	2	5.1	4.0	3.5
2	9.4	4	3.4	3.1	2.7
3	9.4	6	2.1	2.7	2.4
4	9.4	8	1.6	1.5	1.4
5	9.4	10	1.4	1.07	0.9
6	9.4	0.0	9.4	9.4	9.4

The Data obtained using un-treated Heidelberg powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
1	9.6	2	6.5	6.0	5.5
2	9.6	4	4.9	3.6	3.7
3	9.6	6	3.7	2.7	2.4
4	9.6	8	2.5	1.8	1.5
5	9.6	10	1.5	1.3	1.1
6	9.6	0.0	9.6	9.6	9.6
The Data obtained using regenerated Heidelberg powdered clino					
			Concentration mg/ℓ NH_3N		
Beaker (500 mℓ)	Initial con (mg/ℓ NH_3N)	Amount of clino (g/ℓ)	after 15 min	after 30 min	after 1 hr
1	9.6	2	6.5	6.0	5.1
2	9.6	4	3.7	3.1	2.4
3	9.6	6	2.7	2.7	2.2
4	9.6	8	2.0	1.8	1.3
5	9.6	10	1.5	1.3	1.2
6	9.6	0.0	9.6	9.6	9.6

APPENDIX G

Packed column studies to establish the effect of the different operation parameters, which may affect the ion-exchange capacity.

Effect of different flow rates and particle sizes

Table G.1: Column experiment 1, run 1 [5 BV/h]: NH_3-N concentration of analysed effluent samples (*Note: Dashes indicate that the NH_3-N concentration of the sample was found to be too low to analyse with the method used.)

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
10	-	-	120	-	-	230	-	-
20	-	-	130	-	-	240	-	-
30	-	-	140	-	-	250	0.381	-
40	-	-	150	-	-	260	-	-
50	-	-	160	0.325	-	270	-	-
60	-	-	170	0.509	-	280	-	-
70	-	-	180	-	-	290	0.989	0.457
80	-	-	190	-	-	300	1.500	1.054
90	-	-	200	-	-	310	5.074	5.114
100	-	-	210	-	-	320	6.207	6.026
110	-	-	220	-	-			

Table G.2: Column experiment 1, run 2 [5 BV/h]: NH_3-N concentration of analysed effluent samples (*Note: Dashes indicate that the NH_3-N concentration of the sample was found to be too low to analyse with the method used.)

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
10	0.911	0.576	90	0.900	0.102	170	0.190	-
20	0.813	0.384	100	1.129	0.156	180	0.419	-
30	0.857	0.245	110	1.473	0.172	190	2.838	0.189
40	0.857	0.242	120	1.254	0.013	200	4.271	0.720
50	0.643	0.167	130	1.314	0.037	210	5.200	1.962
60	0.622	0.139	140	1.850	0.125	220	6.590	2.904
70	0.733	0.056	150	2.375	0.034			
80	0.800	0.035	160	3.517	0.101			

Table G.3: Column experiment 1, run 3 [10 BV/h]: NH_3-N concentration of analysed effluent samples

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
20	0.736	0.251	100	1.679	0.080	180	5.146	0.916
40	0.615	0.137	120	2.997	0.086	200	7.775	2.000
60	0.727	0.111	140	2.682	0.132	220	8.372	4.169
80	0.991	0.089	160	3.785	0.266			

Table G.4: Column experiment 1, run 4 [15 BV/h]: NH_3-N concentration of analysed effluent samples

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
20	0.783	0.172	100	4.011	0.175	180	7.522	3.586
40	0.998	0.170	120	5.909	0.354	200	8.356	4.747
60	1.484	0.152	140	6.589	1.103	220	10.973	6.838
80	2.496	0.172	160	6.681	2.000			

Effect of different initial feed concentrations on different particle sizes

Table G.5: Column experiment 2, run 1 [10.2 mg/ℓ]: NH_3-N concentration of analysed effluent samples

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
20	1.057	0.703	160	2.608	0.395	300		0.045
40	1.031	0.602	180	2.175	0.567	320		0.012
60	0.917	0.529	200	2.881	0.633	340		1.386
80	1.022	0.380	220	3.097	0.549	360		1.919
100	1.140	0.459	240	3.862	0.739	380		3.873
120	1.211	0.471	260	3.594	0.799			
140	1.787	0.381	280	4.911	1.619			

Table G.6: Column experiment 2, run 2 [19.1 mg/ℓ]: NH_3-N concentration of analysed effluent samples

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
20	0.736	0.251	100	1.679	0.080	180	5.146	0.916
40	0.615	0.137	120	2.997	0.086	200	7.775	2.000
60	0.727	0.111	140	2.682	0.132	220	8.372	4.169
80	0.991	0.089	160	3.785	0.266			

Table G.7: Column experiment 3, run 3 [42.9 mg/ℓ]: NH_3-N concentration of analysed effluent samples

Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ		Sample (BV)	mg/ℓ	
	A	B		A	B		A	B
20	1.695	0.731	60	5.951	0.509	100	8.835	1.136
40	3.154	0.505	80	7.902	0.549	120		4.731

Effect of different initial feed pH's

Table G.8: Column experiment 4, run 4 to 7 different initial feed pH's, initial feed concentration apprx.20 mg/ℓ NH_3-N. Concentration of analysed effluent samples collected every 20 BV.

	Concentration mg/ℓ			
BV	pH 9.01	pH 8.00	pH 6.98	pH 5
20	2.8	0.9	1.1	1.6
40	3.5	1.1	1.1	1.6
60	4.6	1.4	0.9	1.2
80	4.9	2.3	1.1	1.4
100	5.4	2.8	1.4	2.1
120	6.6	3.9	1.5	3.9
140	6.8	4.3	3.3	4.1
160	7.1	5.3	4.4	5.6
180	9.8	6.5	4.8	6.3
200	8.8	7.4	6.6	7.2
220	10.7	7.9	6.7	7.7

APPENDIX H

Table H.1: The data for the elution curves (the 0.1 M NaCl regenerant prepared using Pretoria tap water).

BV	Concentration (mg/ℓ)	
	Regeneration cycle 4	Regeneration Cycle 5
0	15.8	6.5
0.83	81	99.6
1.66	196	325.2
2.5	306.8	310
5	276.7	274.5
7.5	263.5	208.7
10	174	173.2
12.5	172.3	174.2
15	142.9	145.5
17.5	108.2	113.4
20	83.2	112.6
22.5	98.9	101.1
25	86.3	92.6
27.5	82.1	80
30	83.2	77.9

Table H.2: The breakthrough curve data of the runs conducted with Pretoria tap water spiked with NH_4Cl to concentration of approximately 20 mg/ℓ NH_4N.

BV	Concentration (mg/ℓ)				
	Run 1	Run 2	Run 3	Run 4	Run 5
20	3.3	1.5	0.02	0.2	0.99
40	4.7	1.1	0.08	0.1	0.75
60	5.7	1.1	0.04	0.4	1.01
80	6.1	0.7	0.9	0.04	1.4
100	8.6	0.9	1.2	0.1	1.5
120	9.9	1.06	2.37	1.6	1.66
140	8.4	1.3	2.4	3.6	2.8
160	11.4	1.9	2.44	3.7	3.9
180	10.8	3.6	3.7	4.2	5.8
200		3.4	3.4	3.8	6.42
220		4.7	3.5	7.4	10.4

Table H.3: The breakthrough curve data of the runs conducted with Sunderland ridge secondary effluent, at varying initial feed concentrations.

	Concentration (mg/ℓ)							
BV	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13
20	0.2	0.8	1	1	0.3	0.2	0.7	0.9
40	0.9	1.1	1.5	1.3	0.5	0.1	0.8	1.25
60	1.1	1.5	2.2	1.4	0.7	0.2	0.7	1.66
80	1.5	1.6	2.2	1.02	0.5	1	0.8	2.0
100	2.3	2.5	2.6	1.3	0.6	1.6	1.6	2.1
120	7.2	3.3	3.9	1.9	0.6	2.8	2.8	3.4
140	4.1	4.1	3.2	2.1	0.4	2.9	3.1	5.4
160	3.9	7.5	4.8	2.5	1.2	3.7	4.6	6.5
180	4.4	8.6	8.6	4.9	2.09	3.9	6.4	6.5
200	8.9	8.7	7.4	3.6	1	4.3	6.9	6.7
220	9.3	9.5	8.1	3.9	1.6	5.6	7.4	7.0

Table H.4: The data for the breakthrough curves during regenerant re-use

	Concentration after Regeneration cycles (mg/ℓ NH_3N)			
BV	Loading after 1st re-use of regenerant Run 1	Loading after 2nd re-use of regenerant Run 2	Loading after 3rd re-use of regenerant Run 3	Loading after 4th re-use of regenerant Run 4
20	1.6	1.3	1.7	2.0
40	1.8	2.0	3.8	4.5
60	2.6	2.6	4.4	4.8
80	3.7	4.7	4.7	6.4
100	6.8	7.0	8.4	10.2
120	6.9	6.1	8.8	11.1
140	9.8	10.5	8.9	11.1
160	10.9	10.6	10.9	12.9
180	11.2	11.3	12.9	14.1
200	12.9	13.6	14.0	13.8
220	13.2	15.0	15.1	14.7

Table H.5: Concentrations vs. regeneration data

BV	Concentration (mg/ℓ)				
	Loading after Regeneration with 1.0 M NaCl	Loading after Regeneration with 0.1 M NaCl	Loading after 1st Regenerant reuse	Loading after 2nd Regenerant reuse	Loading after 3rd Regenerant reuse cycle
20	0.7	0.1	1.9	1.8	2.4
40	0.7	0.2	2.3	2.1	4.5
60	0.9	0.3	3.1	4.3	3.4
80	1.3	0.7	2.8	4	6.8
100	1.4	3.7	3.9	6.4	4.6
120	2.8	6.1	4.2	9.5	4.7
140	2.9	6.9	4.7	8.8	8.8
160	3.4	10.1	5.7	10.5	9
180	4.5	10.9	6	9.6	9.8
200	5.3	12.5	6.3	13.4	12.4
220	6.4	12.9	7.1	15.2	14.7

Table H.6: Air-stripping experiment: concentration of analysed samples after continuous air stripping

Air-stripping (with Raschig rings)		Air-stripping (porous diffuser)	
Total hours air-stripping	NH_3-N mg/ℓ	Total hours air stripping	NH_3-N mg/ℓ
0	65.0	0	65.8
4	35.1	3	36.0
8	12.6	6	20.2
12	6.5	24	9.0
16	3.6		
20	1.8		
24	1.5		
28	1.0		

Table H.7: Air-stripping after regenerant reuse (porous diffuser)

Time of sample collection	Concentration NH_4N in regenerant	ConcentrationNH_4N in regenerant
0	119.5	112
0.25	110	98
0.5	99.9	84
1	95.5	77
2	88.4	65
3	74.5	55
4	66	42
6	57.2	40
8	50	32
10	41.2	25
12	30	19
24	9.25	8
30	2	1.5

Table H.8: Effect of regenerant reuse on run length using a particle size of 0.25-0.7 mm (Pratley 1)

BV	Concentration mg/ℓ						
	Run 1 (Co = 20.1 mg/ℓ)	Run 2 (Co = 20.5 mg/ℓ)	Run 3 (Regn reuse Run 1; Co = 16.8)	Run 4 (Regn reuse Run 2; Co = 20.4)	Loading after 3rd Reg reuse cycle; Co = 19.5	Loading after 4th Reg reuse cycle; Co = 22.6	Loading after 5th Reg reuse cycle; Co = 22.0
20	0.4	0.1	0.3	0.4	0.3	0.4	0.5
40	0.8	0.2	0.4	0.3	0.3	0.3	0.4
60	0.6	0.2	0.2	0.3	0.3	0.3	0.4
80	0.6	0.2	0.4	0.3	0.2	0.4	0.3
100	0.7	0.3	0.3	0.5	0.1	0.6	0.7
120	0.6	0.4	0.2	0.4	0.3	1.1	1.1
140	0.5	0.7	0.3	0.8	0.5	1.8	2.4
160	0.7	0.9	0.3	1.6	0.6	6.1	2.2
180	1.1	1	0.5	4.3	1.3	8.8	5.4
200	2.1	2	0.8	5.8	4.2	8.8	10
220	4.4	2.4	1.9	8	4.5	12.9	10.7

Table H.9: Effect of regenerant reuse on run length using a particle size of 0.25-0.7 mm (Pratley 1)

BV	Loading after 6th Reg reuse cycle: Co = 20.0	Loading after 7th Reg reuse cycle	Loading after 8th Reg reuse cycle
20	0.5	0.3	0.5
40	0.3	0.2	0.2
60	0.2	0.2	0.2
80	0.3	0.2	0.2
100	0.3	0.5	0.3
120	0.5	0.7	1
140	1.6	2.3	2
160	4	4.4	4.7
180	4.1	4.4	5
200	7.6	6.9	6.7
220	9.8	8.1	7.9

Table H.10: Effect of regenerant reuse on run length using a particle size of 0.25-0.7 mm (Pratley 2)

BV	Concentration mg/ℓ						
	Run 1	Loading after 1st regeneration reuse cycle	Loading after 2nd regeneration reuse cycle	Loading after 3rd regeneration reuse cycle	Loading after 4th regeneration reuse cycle	Loading after 5th regeneration reuse cycle	Loading after 6th regeneration reuse cycle
20	0.1	0.6	0.4	0.2	0.4	0.3	0.3
40	0.1	0.4	0.3	0.2	0.3	0.2	0.3
60	0.2	0.4	0.3	0.2	0.3	0.3	0.4
80	0.2	0.3	0.4	0.2	0.2	0.5	0.6
100	0.7	0.3	0.4	0.3	0.2	0.6	0.7
120	2.7	0.3	0.9	0.4	0.5	1	1.2
140	3.5	0.7	2.3	1.2	1.5	1.8	1.8
160	8.2	1.3	5.2	3.6	2.1	2.2	2.9
180	11.9	5	5.5	5.4	4.7	4.8	5.1
200	13.4	7.8	6.1	6.8	5.8	6.2	6.7
220	13.6	8.4	7	7.5	6.9	7.7	8.1

Table H.11: Effect of regenerant reuse on run length using a particle size of 0.25-0.77 mm (Pratley 2)

BV	Loading after 6th regeneration reuse cycle	Loading after 7th regeneration reuse cycle	Loading after 8th regeneration reuse cycle
20	0.3	0.2	0.3
40	0.3	0.1	0.4
60	0.4	0.1	0.4
80	0.6	0.1	0.2
100	0.7	0.4	0.8
120	1.2	1.2	1.4
140	1.8	1.9	1.6
160	2.9	4.1	3.8
180	5.1	6.6	5.9
200	6.7	6.5	6.6
220	8.1		8

Table H.12: Effect of regenerant reuse on run length using a particle size of 0.25-0.77 (Pratley 2)

Regenerated with 15 BV of 0.1 M NaCl; amount of 1 M NaOH = 40 mℓ; pH = 12.01
Amount of 1 M NaOH added to raise pH after 1st air-stripping = 40 mℓ; pH = 12.20.

BV	Concentration mg/ℓ				
	Loading after 1st regeneration reuse cycle	Loading after 2nd regeneration reuse cycle	Loading after 3rd regeneration reuse cycle	Loading after 4th regeneration reuse cycle	Loading after 5th regeneration reuse cycle
20	1.4	1.2	1.1	1.8	1.7
40	1.3	1.2	1.4	2	2.1
60	1.1	1.3	1.6	3.1	2.9
80	1.1	1.5	2	3.9	4
100	1.4	1.7	2.5	4.8	5.2
120	2.4	2	3.1	6.7	7.3
140	3.7	2.9	3.9	8.1	8.5
160	4.9	3.8	4.8	9.7	10.1
180	9.9	9.2	8.9	10.9	11.8
200	12	11.3	11	12	12.9
220	12.6	12	11.9	12.7	13.3

APPENDIX I.

LOADING CYCLE: 10 BV/h Regeneration with 0.1 M NaCl pH 11.4

Flow BV (1 BVV=23ℓ)	LOADING CYCLE: 10 BV/h – PRODUCT WATER AMMONIA CONCENTRATION NH_3 (mg/ℓ)																
For 4500L add 85.82 g NH_3Cl to raise NH_3-N concentration by 5 mg/L	Lab	Pilot 3-Aug-08	Pilot 10-Aug-08	Pilot 12-Aug-08	Pilot 17-Aug-08	Pilot 19-Aug-08	Pilot 23-Aug-08	Pilot 26-Aug-08	Pilot 30-Aug-08	Pilot 3-Sep-08	Pilot 25-Nov-08	Pilot 9-Dec-08	Pilot 12-Dec-08	Pilot 16-Dec-08	Pilot 9-Jan-09	Pilot 15-Jan-09	Average
Secondary effluent		5.3	7.3	6.2	6.3	4.7	5.6	5.2	7.2	7	5.8	5.1	4.2	6.5	7.5	6.3	
Target		17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	
Ammonia added (NH_4Cl)		200.8	166.5	185.4	183.7	211.1	195.7	202.5	168.2	171.6	192.2	204.3	219.7	180.2	163.1	183.7	
Na(OH) added to pH11.4 (mL)	-	380.0	360.0	380.0	360.0	440.0	420.0	470.0	430.0	420.0	400.0	430.0	380.0	380.0	400.0	400.0	
Series Title	Lab Scale Results	Pilot Plant 1	Pilot Plant 2	Pilot Plant 3	Pilot Plant 4	Pilot Plant 5	Pilot Plant 6	Pilot Plant 7	Pilot Plant 8	Pilot Plant 9	Pilot Plant 10	Pilot Plant 11	Pilot Plant 12	Pilot Plant 13	Pilot Plant 14	Pilot Plant 15	Pilot Plant Average
Start	19.100	14.9	15.6	16.8	16.3	16.5	17	16.8	16.7	17	15.2	17.1	13.3	15.1	14.6	17.8	16.1
0	0.253	0.2	0.3	0.2	0.4	0.3	0.1	0.3	0.2	0.3	0.1	0.2	0.5	0.1	0.2	0.3	0.3
10	0.250	0.2	0.3	0.2	0.4	0.3	0.1	0.3	0.2	0.3	0.0	0.2	0.1	0.2	0.2	0.2	0.2
20	0.251	0.2	0.3	0.1	0.3	0.3	0.2	0.3	0.3	0.3	0.1	0.3	0.1	0.2	0.3	0.3	0.2
30	0.150	0.2	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.1	0.3	0.1	0.1	0.3	0.3	0.2
40	0.137	0.3	0.3	0.6	0.3	0.3	0.3	0.3	0.3	0.3	0.1	0.3	0.1	0.1	0.3	0.3	0.3
50	0.120	0.3	0.3	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.2	0.2	0.3	0.3
60	0.120	0.3	0.3	0.5	0.3	0.4	0.4	0.4	0.4	0.4	0.2	0.3	0.1	0.2	0.2	0.5	0.3
70	0.120	0.3	0.3	0.5	0.4	0.5	0.5	0.5	0.4	0.4	0.2	0.4	0.1	0.3	0.5	0.5	0.4
80	0.120	0.3	0.3	0.5	0.5	0.5	0.5	0.6	0.4	0.5	0.2	0.6	0.1	0.2	0.6	0.3	0.4
90	0.100	0.5	0.3	0.5	0.6	0.6	0.5	0.6	0.5	0.6	0.4	0.5	0.3	0.4	0.6	0.5	0.5
100	0.080	0.6	0.4	0.7	0.8	0.7	0.8	0.7	0.7	0.8	0.5	0.6	0.5	0.5	0.7	0.6	0.6
110	0.080	0.6	0.6	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.6	0.6	0.5	0.7	1.1	0.7	0.7
120	0.086	0.7	0.7	0.8	0.9	0.9	1.0	0.5	0.9	0.9	0.9	0.8	0.6	0.9	1.2	0.9	0.8
130	0.100	1.0	0.8	1.3	1.3	1.0	0.9	0.4	0.7	1.0	1.2	1.1	0.9	1.1	1.4	1.0	1.0
140	0.132	1.3	0.9	2.7	1.4	1.1	1.1	0.5	0.9	1.1	1.3	1.2	1.2	1.2	1.6	1.3	1.1
150	0.200	1.3	1.1	3.5	1.6	1.3	1.4	0.5	1.0	1.5	1.2	1.3	1.3	1.3	2.0	1.4	1.2
160	0.266	1.3	1.2	4.4	1.7	1.6	1.8	0.7	1.4	1.6	1.5	1.5	1.4	1.5	3.2	1.5	1.4
170	0.700	1.7	1.4	5.5	1.8	2.0	2.3	1.2	2.0	2.1	2.1	2.5	2.0	2.1	5.5	2.7	2.0
180	0.916	2.4	2.3	7.5	2.8	2.9	3.2	2.4	2.7	3.3	2.9	3.3	2.8	2.6	9.0	3.5	2.9
190	1.500	4.0	3.1	9.1	4.7	4.6	4.8	4.3	4.1	5.0	4.7	5.6	4.5	4.2	13.0	5.9	4.6
200	2.000	7.3	4.0	12.0	8.3	7.9	8.6	8.1	7.6	8.5	8.4	9.0	8.0	10.1	20.0	9.8	8.2
210	3.000																
220	4.169																
230	7.000																
NH_3 remaining in effluent to breakthrough (mg NH_3-N) (7)	1737.5	3109.6	2817.5	2323.0	3841.0	3668.5	3047.5	2633.5	2668.0	3070.5	2509.3	2953.2	2879.6	2594.4	3335.0	3098.1	2716.7
NH_3 without removal in equivalent volume to breakthrough (mg NH_3-N) (8)	60.0	61686.0	64584.0	54096.0	67482.0	68310.0	66470.0	69552.0	65297.0	66470.0	59432.0	66861.0	55062.0	59041.0	53728.0	69598.0	62951.0
NH_3 removed from effluent (g NH_3-N) (Capacity) (9)	86.1	58.6	61.8	51.8	63.6	64.6	63.4	66.9	62.6	63.4	56.9	63.9	52.2	56.4	50.4	66.5	60.2
Capacity of clinoptilolite (g NH_3-N/L Clinoptilolite)(10	3.7	2.5	2.7	2.3	2.8	2.8	2.8	2.9	2.7	2.8	2.5	2.8	2.3	2.5	2.2	2.9	2.6

Capacity of clinoptilolite (meq NH_3-N/L Clinoptilolite)	0.267	0.182	0.192	0.161	0.198	0.201	0.197	0.208	0.195	0.197	0.177	0.198	0.162	0.175	0.157	0.207	0.187
Capacity of clinoptilolite (mg NH_3-N/g Clinoptilolite) (11)	4.304	2.927	3.087	2.587	3.180	3.230	3.170	3.344	3.130	3.168	2.845	3.194	2.608	2.821	2.518	3.323	3.010

Notes:

(1) 0.25-0.7 mm Pratley Clinoptilolite;
(2) 10 BV/h Regeneration;
(3) p48 Experimental data;
(4) Pilot plant test results;
(5) Breakthrough is selected as when the NH_3 in the effluent > 2 mg/ℓ NH_3-N;
(6) Total = NH_3 concentration at start x volume to breakthrough;
(7) Total mass of NH_3 remaining in effluent that was passed through column. The total is taken as all NH_3 in effluent until breakthrough has been reached and represents the area below the Concentration – Volume curve;
(8) This row represents the total NH_3 that would have remained in the effluent if no NH_3 was removed. The volume corresponds to the volume passed through the column until breakthrough inn (7). This calculation is an interim step to calculate the capacity of the column;
(9) The total NH_3 removed from the effluent and represents the capacity of the column (measured to breakthrough);
(10) Reduced capacity of the clinoptilolite represented as mass NH_3 removed per volume of clinoptilolite. (Only applicable to the specific clinoptilolite used – origin and size as in (1);
(11) Bulk Density of Clinoptilolite 0.25 mm-0.7 mm-0.87 g/mℓ.

Trapezoidal integration:

$h/2 * (y_1 + 2y_2 + 2y_3 \ldots\ldots 2y_{n-1} + y_n)$

APPENDIX J

Flow BV (1 BVV = 23ℓ)	LOADING CYCLE: NH_3-N (mg/ℓ)		
For 4500L add 85.82 g NH_3Cl to raise NH_3-N concentration by 5 mg/L	**Pilot** 27-Sep-08	**Pilot** 20-Dec-08	**Pilot** 22-Dec-08
Series Title	**Pilot Plant Average 5 BV/h**	**Pilot Plant Average 10 BV/h**	**Pilot Plant Average 15 BV/h**
Start	**16.1**	**16.2**	**16.2**
0	0.1	0.3	0.2
10	0.1	0.2	0.3
20	0.1	0.3	0.3
30	0.1	0.3	0.3
40	0.1	0.3	0.3
50	0.1	0.3	0.4
60	0.1	0.3	0.4
70	0.1	0.4	0.4
80	0.1	0.4	0.4
90	0.1	0.5	0.7
100	0.1	0.6	0.9
110	0.1	0.7	1.1
120	0.2	0.8	1.4
130	0.2	0.9	1.7
140	0.2	1.1	2.3
150	0.3	1.2	3.2
160	0.5	1.4	4.5
170	0.9	2.0	6.2
180	1.2	2.9	7.4
190	1.8	4.6	9.7
200	2.5	8.0	12.2
210	4.99		
220			
230			
NH_3 remaining in effluent to breakthrough (mg) (7)	2044.3	2780.5	2672.6

NH_3 without removal in equiv. volume to breakthrough (mg) (8)	74213.3	63276.8	52164.0
gNH_3 removed from effluent (g) (Capacity) (9)	72.2	60.5	49.5
Capacity of Clinoptilolite (g NH_3 / ℓ Clinoptilolite) (10)	3.1	2.6	2.2
Capacity of Clinoptilolite $meqNH_3$-N/ℓ Clinoptilolite	0.224	0.188	0.154
Capacity of Clinoptilolite $mgNH_4$-N/g Clinoptilolite (11)	3.607	3.023	2.473

APPENDIX K

Elution Curve

	REGENERATION: 10 BV/h – NH_3-N (mg/ℓ)			
	Pilot 25-Nov-08	**Pilot** 09-Dec-08	**Pilot** 12-Dec-08	**Pilot** 16-Dec-08
	10	**11**	**12**	**13**
	Curve 1 following cycle 10	**Curve 2 following cycle 11**	**Curve 3 following cycle 12**	**Curve 4 following cycle 13**
	1	9	8	15
	431	352	335	283
	496	391	349	311
	420	238	287	249
	344	217	226	211
	244	189	172	150
	152	140	130	102
	123	77	66	82
	90	64	41	72
	66	53	38	45
	54	31	22	20
	39	25	20	10
	85.83	62.97	54.44	54.41

APPENDIX L

Flow BV (1 BVV = 150 mℓ)	NH_3-N (mg/ℓ)	
	Lab Cycle 4	Lab Cycle 5
0	15.8	6.5
0.83	81	99.6
1.66	196	325.2
2.5	306.8	310
5	276.7	274.5
7.5	263.5	208.7
10	174	173.2
12.5	172.3	174.2
15	142.9	145.5
17.5	108.2	113.4
20	83.2	112.6
22.5	98.9	101.1
25	86.3	92.6
27.5	82.1	80
30	83.2	77.9

APPENDIX M

Flow BV (1 BVV = 23ℓ)	**REGENERATION: 10 BV/h – NH_3-N (mg/ℓ)**				
	Pilot 25-Nov-08				
Series Title	NH_3-N	Na	K	Ca	Mg
0.00	1	22	5.2	11	5
0.83	431	2405	308	792	172
1.67	496	3851	3116	436	64
2.50	420	3981	261	254	34
3.33	344	3886	168	197	22
5.00	244	3408	143	116	10
7.50	152	2594	87	77	5
10.00	123	2001	61	53	3
15.00	90	1656	35	33	2
20.00	66	1444	22	24	2
25.00	54	1396	16.5	19	2
30.00	39	1309	15.3	16	2

Flow BV (1 BVV = ?ℓ)	**NH_3-N (mg/ℓ)**			
	Cooney	**Cooney**	**Cooney**	**Cooney**
Series Title	**NH3-N**	**K**	**Ca**	**Mg**
Cooney	NH3	K	Ca	Mg
0.8	150	27	55	28
1.8	635	300	249	169
2.3	680	275	268	168
2.8	413	141	153	90
3.3	318	142	120	55
3.9	269	125	107	47
4.7	253	112	102	43
5.9	207	104	90	36
8.6	146	90	76	31
11.5	113	72	58	26
19.5	54	63	53	18

APPENDIX N

Measured Backwash Flow Rate

Flow Rate		Bed Depth	Expansion
L/h	BV/h	m	%
0	0	1.300	0.0
150	7	1.306	0.5
200	9	1.315	1.2
250	11	1.340	3.1
300	13	1.380	6.2
400	17	1.500	15.4
500	22	1.675	28.8
650	28	1.963	51.0

APPENDIX O

Loading Cycle: 10 BV/h **Regeneration with 0.4 M NaCl pH7-pH8**

Flow BV (1 BVV = 23ℓ)	PRODUCT AMMONIA CONCENTRATION NH_3 (mg/ℓ)				
For 4500L add 85.82 g NH_3Cl to raise NH_3-N concentration by 5 mg/L		**Pilot** 03-Feb-09	**Pilot** 07-Feb-09	**Pilot** 12-Feb-09	**Average**
Secondary effluent		7.2	7.4	7.2	
Target		17	17	17	
Ammonia added (NH_4Cl)		168.2	164.8	168.2	
Alkalinity added to maintain pH 8.0 (4)		113.0	105.0	85.0	101.0
Series Title	**Average Air Stripped Regen.**	**Pilot Plant 16**	**Pilot Plant 17**	**Pilot Plant 18**	**Average Biological Restored Regen.**
Start	**16.1**	**16.4**	**16.1**	**17.1**	**16.5**
0	0.3	0.4	0.5	0.3	0.4
10	0.2	0.3	0.4	0.3	0.3
20	0.2	0.3	0.3	0.3	0.3
30	0.2	0.4	0.4	0.4	0.4
40	0.3	0.4	0.4	0.4	0.4
50	0.3	0.3	0.4	0.4	0.4
60	0.3	0.4	0.4	0.4	0.4
70	0.4	0.4	0.4	0.4	0.4
80	0.4	0.6	0.6	0.5	0.6
90	0.5	0.6	0.7	0.6	0.6
100	0.6	0.8	0.7	0.6	0.7
110	0.7	1.0	0.9	0.8	0.9
120	0.8	1.0	1.1	1.0	1.0
130	1.0	1.1	1.2	1.1	1.1
140	1.1	1.4	1.2	1.1	1.2
150	1.2	1.6	1.8	1.4	1.6
160	1.4	1.9	2.0	1.8	1.9
170	2.0	2.4	2.2	2.5	2.4
180	2.9	3.5	3.0	3.9	3.5
190	4.6	7.0	9.0	8.2	8.1
200	8.2	13.0	16.0	14.2	14.4
210					

220					
230					
NH_3 remaining in effluent to breakthrough (mg NH_3-N) (7)	2716.7	3475.1	3537.2	3254.5	3422.2
NH_3 without removal in equivalent volume to breakthrough (mg NH_3-N) (8)	62951.0	64124.0	62951.0	66861.0	64645.3
NH_3 removed from effluent (g NH_3-N) (Capacity) (9)	60.2	60.6	59.4	63.6	61.2
Capacity of Clinoptilolite (g NH_3-N/ℓ Clinoptilolite) (10)	2.6	2.6	2.6	2.8	2.7
Capacity of Clinoptilolite meqNH_3-N/ℓ Clinoptilolite	0.187	0.188	0.185	0.198	0.190
Capacity of Clinoptilolite mgNH_3-N/g Clinoptilolite (11)	3.010	3.031	2.969	3.179	3.060

Notes:
(1) Biologically restored regenerant;
(2) 10 BV/h Regeneration;
(3) Regenerant made up by inoculating secondary effluent with activated sludge from the Daspoort WwTW –nitrification reactor;
(4) The secondary effluent was used instead of tap water to make up the regenerant because the nitrifying bacteria need nutrients absent in tap water for cell growth.
(4) Alkalinity as a % of the stoichometric requirement.

APPENDIX P

AquaPlan cc
Reg no: Ck 95/56139/23
Watertreatment Engineering

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Attn:	Prof Japie Schoeman	**E-mail address:**	japie.schoeman@up.ac.za
From:	Guido Bieseman	**Nr. of Pages:**	01
		Reference:	E/2117/09

SUBJECT **Clinoptinolite Plant for Removal of Ammonia from Process Water**

A. Cost consideration for a 50 m^3/day plant:

1. Capital cost to provide a plant without recovery of ammonia.
   Budget Price: R 250 000,00 (ex-works JHB) — R 250 000,00

2. Cost of Chemicals per day.
   NaOH (flake form), to raise pH to 11,3 = 2,4 kg as 100 % / day at R 5,00/kg = R 12,00
   NaCl top up only = 12,5 kg as 100 % / day at 70c/kg = R 8,75
   R 20,75

3. Running cost, electricity only / day.

Main feed pump:	R 4,80
Chemical dosing pump:	R 0,25
Recirculation pump during regeneration:	R 1,00
Airfan:	R 0,75
	R 6,80

R 6,80

4. Semiskilled operator input (Labour)
   1 hour per production shift, to make up chemicals and start and stop the plant. — R 30,00

B. Same for a 100 m^3/day plant:

1.	Capital:	R 350 000,00
2.	Chemicals:	R 41,50
3.	Electricity:	R 13,60
4.	Labour:	R 30,00

C. 50 m^3/day with recovery of ammonia
(This will produce a 10 % $(NH_4)_2SO_4$ solution for use as fertiliser.)

1. Capital cost: R 290 000,00 — R 290 000,00

2. Chemical cost:

NaOH	R 12,00
NaCl	R 8,75
H_2SO_4 2,45 kg	R 2,95

R 23,70

3. Running cost:

Main feed pump	R 4,80
2 × Chemical dosing	R 0,50
2 × Recirculation pump	R 2,00
1 × Fan	R 0,75

R 8,05

4. Labour: R 30,00

5. Possible value of ammonium sulphate as fertiliser (at R 5/kg)
3,25 kg/day × R 5/kg R 19,50 / day

D. 100 m^3/day with recovery of ammonia

1.	Capital:	R 390 000,00
2.	Chemicals:	R 47,40
3.	Electricity:	R 16,10
4.	Labour:	R 30,00
5.	Recovery value $(NH_4)_2SO_4$:	R 39,00

Kind Regards
Guido Bieseman