



THE SHARON PROCESS: AN INNOVATIVE METHOD FOR NITROGEN REMOVAL FROM AMMONIUM-RICH WASTE WATER

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ABSTRACT

A new biological process for ammonia removal from flows containing hundreds to thousands milligrams NH_4^+ per litre has been developed at the Delft University of Technology. The SHARON process operates at a high temperature (30-40 °C) and pH (7-8). The process is performed without sludge retention. This enables the prevention of nitrite oxidation, leading to lower operational costs. Denitrification is used to control the pH. A full scale plant was designed (1500 m³) based on kinetic and stoichiometric parameters determined at 1.5 l. scale and model predictions. Total costs are estimated at about \$1.7 per kg removed $\text{NH}_4^+\text{-N}$. The first full scale SHARON plant will be operational at the Dokhaven waste water treatment plant in Rotterdam in the beginning of 1998. This contribution focuses on the principles of the process and evaluates conditions for which application seems feasible. © 1998 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Adsorption-Belebungs verfahren; denitrification; modelling; nitrification; nitrite; SHARON; waste water treatment.

INTRODUCTION

New European legislation for reducing the total N-content in the effluent of wastewater treatment plants stimulates research towards new strategies for upgrading existing plants. Specific treatment of internal recycle flows gets much attention nowadays (Kollbach, 1996). On request of the water authority Hollandse Eilanden en Waarden, the Delft University of Technology developed a new approach for treating recycled water from the sludge digesting unit at Sluisjesdijk, being part of the two stage A/B process (Böhnke, 1978) Dokhaven in Rotterdam (470.000 p.e.). This recycle flow accounts for about 15% of the ammonium load in the influent of the waste water treatment plant. An evaluation of mass balances over the plant, that currently operates with an overloaded B-stage, showed that 85% ammonia reduction in the recycle flow will shift the operation of the B-stage from oxygen limited to ammonium limited, reducing total nitrogen in the effluent (currently 24 mg/l) by 25%. The new SHARON process concept was developed for treating this recycle flow, exploiting its specific temperature and composition. SHARON is an acronym for Single reactor High activity Ammonia Removal over Nitrite.

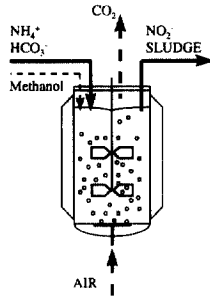


Fig. 1. The SHARON process in a well mixed continuous flow reactor

Table 1. Year average composition of the centrifuged sludge digestion effluent (1994)

component	unit	value
COD	mg/l	810
BOD	mg/l	230
N-Kj	mg/l	1053
NH ₄ ⁺ -N	mg/l	1000
P-tot	mg/l	27
SS	mg/l	56
HCO ₃ ⁻	mg/l	4080
HCO ₃ ⁻ /N ratio.	mol/mol	1.1
pH	-	8.1-8.4
Temperature	°C	30

CONCEPTS OF THE SHARON PROCESS

The SHARON process was initially developed for the treatment of ammonium rich centrifugate, rejected by the direct dewatering of warm digested sludge. For the studied case, the composition of this centrifugate is given in table 1. As can be seen, the liquid contains about 1 g NH₄⁺-N per litre, on molar basis a similar

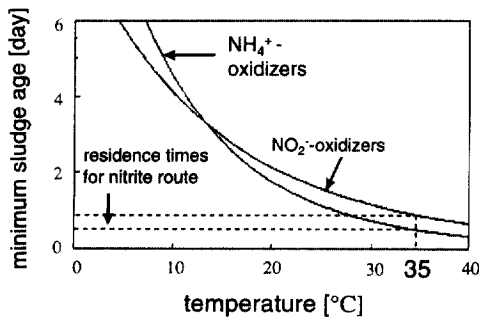


Fig. 2. Minimum residence time for ammonium and nitrite oxidisers as function of the temperature

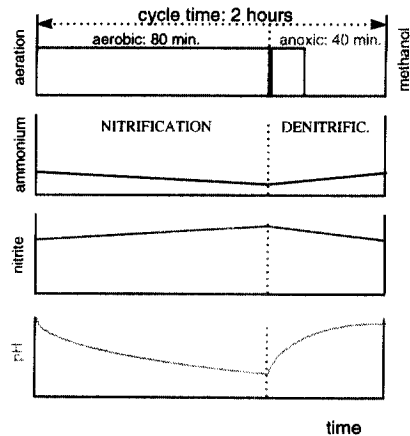


Fig. 3. Transient medium conditions due to intermittent aeration

bicarbonate content, has a temperature of 30 °C and a pH of 8.1-8.4. The SHARON process especially takes advantage of the high temperature, enabling high specific growth rates, so that no sludge retention is required. The process can be carried out in a simple continuous stirred tank reactor (Fig. 1).

The high temperature has a second advantage. At normal temperatures in waste water treatment plants (5-20 °C) nitrite oxidisers grow faster than ammonium oxidisers, which means that ammonium is completely oxidised to nitrate. However, the reverse is true at elevated temperatures, as can be seen in Fig. 2, which is based on temperature coefficients found by Hunik (1993). The use of a system without sludge retention has

the advantage that the sludge residence time (SRT) is controlled by the hydraulic residence time (HRT), so that by carefully selecting the HRT, nitrite oxidisers can be washed out, while ammonium oxidisers are retained in the reactor.

Due to nitrification at this high concentration level, the pH will decrease significantly. Per mole of NH_4^+ two moles of H^+ are produced. For approximately 50% these can be neutralised by stripping CO_2 formed from the bicarbonate that is present in centrifuged sludge digestion effluent. To compensate for the remaining acid, denitrification or base addition can be used. For denitrification a COD source, for example methanol, should be added here. Using the nitrite route, costs for methanol dosage are 40-50% lower than for NaOH addition, so that the first option was chosen. Note that this way, pH regulation depends on the CO_2 stripping efficiency of the reactor, which is a scale dependent feature. To what extent denitrification is necessary depends on the buffering capacity of the medium and on the required pH. The pH determines the microbial conversion rates, as is explained later. This is essentially a cost optimisation problem. For simplicity, nitrification and denitrification are performed in one reactor, by switching the aeration on and off.

The effluent of the SHARON reactor contains suspended solids typically in concentrations well below 1 g/l. This is irrelevant when treating internal recycle flows. For the studied case, the effluent nitrite concentration is not relevant either, as denitrification will afterwards occur in the A-stage of the A/B process.

KEY PROCESS CONDITIONS

Experimental set-up

The SHARON process was operated at lab. scale (1.5 l) for 2 years, in a continuously stirred tank reactor (CSTR), fed with centrifuged effluent from the sludge digestion (table 1). The reactor was operated in cycles of 2 hours: 80 minutes aerobic and 40 minutes anoxic. The hydraulic residence time was set to 1.5 days. In Fig. 3, the concentration profiles are sketched for one nitrification-denitrification cycle. From the observed turnovers, stoichiometric parameters could be obtained. Kinetic parameters were determined in respirometric experiments with samples taken from this reactor. It is important to recognise that the SHARON process conditions are quite extreme compared to those in the classical municipal waste water treatment plants. Especially the high dilution rate puts a selection pressure upon the system for fast growing micro-organisms rather than for organisms with a high affinity for substrate, which is the case in conventional installations operating at low nutrient concentration levels. For that reason most kinetic and stoichiometric coefficients were determined experimentally. An average ammonium conversion in the order of 80-85% could be obtained. The process was stable in the sense that the nitrite route could be maintained. At lab. scale, growth of nitrite oxidisers on the glass wall and static objects was prevented by cleaning the reactor daily.

Temperature

The temperature dependency of the nitrification rate was determined with respiration experiments (Fig. 4). Due to biomass degradation at higher temperatures, always a temperature optimum is found, in this case 40°C. To ensure process stability a working temperature of 35 °C was chosen. The corresponding maximum specific growth rate for ammonium oxidisers was 2.1 d⁻¹. For the considered process conditions, the exothermic reaction leads to a net temperature increase of 9 °C, which means that the reactor can easily be controlled at the optimum temperature by cooling.

pH

The pH turned out to be a very important process parameter. Due to the high ammonium conversion rates and the alternating nitrification (proton production) and denitrification (proton consumption), the process pH varies about one pH unit in one N/D cycle. Therefore, the pH influence on the conversion rates has to be taken into account explicitly, which is not common in modelling municipal waste water treatment plants, using for example the IAWQ model. In order to reduce experimental effort, it was important to distinguish

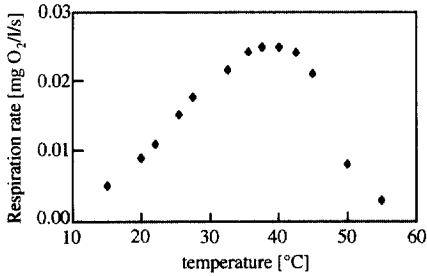


Fig. 4. Temperature dependency of the maximum growth rate of ammonium oxidisers

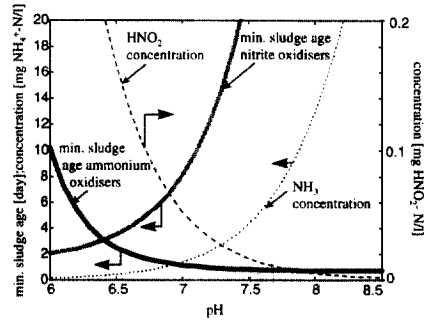


Fig. 5. Estimation of the pH influence on the growth rates of ammonium and nitrite oxidisers for 130 mg NH₄⁺-N/l and 300 mg NO₂⁻-N/l at 35 °C

the biochemically active form of the compounds that are subject to the chemical acid-base equilibria. For ammonium oxidisers NH₃ is the actual substrate rather than NH₄⁺, and HNO₂ is the inhibiting component (Anthonisen, 1976). The following equation was therefore used to express the specific growth rate for ammonium oxidisers:

$$\mu^{\text{amm}} = \mu_{\text{max}}^{\text{amm}} * \frac{C_{\text{NH}_3}}{K_{\text{NH}_3}^{\text{amm}} + C_{\text{NH}_3}} * \frac{C_{\text{O}_2}}{K_{\text{O}_2}^{\text{amm}} + C_{\text{O}_2}} * \frac{K_{\text{I,HNO}_2}^{\text{amm}}}{K_{\text{I,HNO}_2}^{\text{amm}} + C_{\text{HNO}_2}} \quad (9)$$

Experimentally, it was shown that K_{NH_3} is indeed constant at about 7 mg/l NH₃-N for the pH range 6.5-8.5 at 30 °C (Brouwer, 1995). At 35 °C the same value can be used (Lochtman, 1995). At typical effluent (and thus medium) concentrations of 130 mg NH₄⁺-N per litre, the NH₃ concentration ranges from 0.14 mg/l at pH 6 to 13.1 mg/l at pH 8, which indicates the important effect of the pH on the ammonium conversion rate. No inhibition of ammonia was found up to concentrations of 6000 mg NH₄⁺-N/l at pH 7 and 40 °C (Brouwer, 1995). The inhibition constant for nitrous acid was established at 0.2 mg/l HNO₂-N so that at higher pH the inhibition effect of HNO₂ is limited (the HNO₂ concentration at nitrite concentrations of about 300 mg/l ranges from 0.53 to 0.00525 mg/l in the pH range of 6-8).

Nitrite oxidisers use HNO₂ as their substrate as well (Anthonisen, 1976), with K_{HNO_2} =0.26 mg HNO₂/l (Wiesmann, 1994):

$$\mu^{\text{nit}} = \mu_{\text{max}}^{\text{nit}} * \frac{C_{\text{HNO}_2}}{K_{\text{HNO}_2}^{\text{nit}} + C_{\text{HNO}_2}} * \frac{C_{\text{O}_2}}{K_{\text{O}_2}^{\text{nit}} + C_{\text{O}_2}} \quad (10)$$

Their growth rate varies between 0.17 d⁻¹ and 0.02 d⁻¹ in the pH range 7-8. The pH dependency of the growth rates of both the ammonium and the nitrite oxidisers is illustrated in Fig. 5, for an ammonium concentration of 130 mg NH₄⁺-N/l and a nitrite concentration of 300 mg NO₂⁻-N/l. It must be stressed that the inhibition constant for HNO₂ (0.2 mg HNO₂-N/l) was determined at pH 7 only. Nevertheless, it is clear that the margins in the required residence times to maintain ammonium oxidisers and washout nitrite oxidizers, are much larger at higher pH values, than is suggested in Fig. 2. In the low pH range nitrite oxidisers are predicted to grow faster than the ammonium oxidisers. It was important to recognise that the pH influence on the process performance could completely be covered by taking the effect of the chemical equilibria into account.

From these data it follows that a high pH is preferable to outcompete nitrite oxidisers and obtain a lower effluent NH_4^+ concentration. An increased pH however, requires a higher degree of denitrification, hence more methanol.

FULL SCALE PROCESS SIMULATION

Process performance depends strongly on the pH -varying due to the cyclic process operation-, the liquid-gas mass transfer rate of CO_2 and the denitrification level. To deal with these complex and non-linear interactions, a dynamic computer model has been written in MATLAB/SIMULINK (The Mathworks, Inc) for simulating process simulation at full scale. The model was used to evaluate the variable process costs (oxygen and methanol supply) for maintaining a year average NH_4^+ conversion of 85% using a simple control strategy. As will be shown below, variable costs account for 60% of the total processing costs. For the influent flow rate and composition, daily average data for one year were used that had been measured in 1994. From Fig. 6 it is clear that the process load highly fluctuates especially due to large flow rate variations. The model consisted of 13 non-linear differential equations for gas and liquid phase expressing the accumulation of the involved compounds as a function of the influent load and the microbial conversion rates. At any point in time, the concentrations of the non-protonated and protonated form of the compounds had to be calculated, which was done by iteratively solving the set of chemical equilibrium equations in combination with the charge balance (Hellings *et al.*, 1997). All involved chemical equilibrium constants could be obtained from the literature. In the model, the reactor was operated as a continuous reactor with constant volume. Consequently, the effluent flow rates varied along with the influent flow rates, so that the residence time was not truly constant. On year average basis both the aerobic and anoxic residence times were 1.3 days. The residence time was higher than strictly necessary, because the foreseen reactor volume (a previous post thickening tank of 1500 m^3) is oversized. In simulation, the aerators were simply turned on and off every 2 hours despite the influent load, and a fixed amount of methanol was added during the first half hour of the anoxic period. Note that in case of longer residence times, the anoxic residence is increased, while the oxic period remains close to 1 day to prevent nitrite oxidation. Experimentally, hardly any biomass decay was observed when the reactors were not fed for a period of more than one week. As a complete interruption of the influent flow never lasted for more than 4 days in the measurement period, no biomass degradation was included in the model. Simulation results are summarised in table 2 for a dosage of 1 kg methanol per kg converted $\text{NH}_4^+\text{-N}$, giving 60% denitrification. A yearly average ammonium conversion of over 85% is then predicted. Of the methanol, only 70% was effectively used for denitrification. On basis of the cost evaluation for the studied case, that is presented below, potential yearly savings for methanol addition are in the order \$ 40.000 when more sophisticated control is applied.

Table 2. Predicted year average effluent concentrations for a methanol dosage of 1 kg/kg influent $\text{NH}_4^+\text{-N}$

quantity		influent	effluent
NH_4^+	[mg N/l]	972	130
NO_2^-	[mg N/l]	-	345
NO_3^-	[mg N/l]	-	0.9
HCO_3^-	[mmol/l]	72.3	7.3
$\text{HCO}_3^- / \text{NH}_4^+$	[mol/mol]	1.1	0.78
pH	[-]	8.3	7.4
Temp	[°C]	30	35
Act.biomass	[g/l]	-	0.33

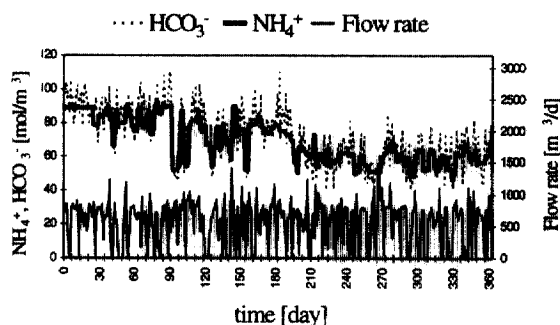


Fig. 6. Day average influent composition on molar basis and flow rate (1994). Used for the predictions in table 2.

REACTOR DESIGN

Design of a full scale well stirred tank reactor is well covered in literature. As no gradients are present in the liquid phase, knowledge of the kinetic and stoichiometric microbial parameters is sufficient for calculating the turnover rates. Moreover, due to the relatively high power input and the fact that biomass is not selected for its settling properties, only small cell lumps are believed to be present, comparable to those in the small scale equipment. The important scale-up aspect is the height to diameter ratio of the reactor. The higher the reactor, the higher the average pressure in the gas phase. As CO_2 must be transferred from the liquid to the gas phase for pH control, a higher gas pressure counteracts this transport which is reflected by higher costs for denitrification, or even additional costs for base addition. Calculations showed that for a reactor of 1500 m^3 , a height of 4-5 meter does not give rise to such additional costs.

COST EVALUATION

On basis of the above mentioned design criteria, the process costs were evaluated for the full scale process, assuming a daily load of $1200 \text{ kg NH}_4^+\text{-N/day}$, an influent concentration of $1 \text{ g NH}_4^+\text{-N/l}$ and 85% conversion. These costs include fixed costs for e.g. construction (from scratch), maintenance and operation, and variable costs for energy, methanol and some NaOH supply (safety measure, table 3). The overall costs are estimated at about $\$1.7$ per kg removed $\text{NH}_4^+\text{-N}$. Power input (over 90% for aeration) accounts for 35% of the total costs and methanol dosage for 25%. Such calculations should be considered with care, because they are always location specific to some extent. Nevertheless, the order of magnitude indicates that the process is very competitive. A study for a comparable case (van der Zandt *et al.*, 1996) showed that costs for treating recycled water from a sludge digester using more conventional techniques, are in the order of US $\$5$ - 10 .

DISCUSSION

Process efficiency for different loads

The process aims at high ammonium conversion rates rather than at low effluent concentrations. The process efficiency (expressed as the percentage converted ammonium) depends solely on the influent ammonium concentration if the temperature, residence time and pH remain at their original values. This can be seen

Table 3. Estimated yearly costs for a load of $1200 \text{ kg NH}_4^+\text{-N/day}$ and an influent concentration of $1000 \text{ mg/l NH}_4^+\text{-N}$

Capital costs/ maintenance/exploitation	: \$ 226
Electricity (>90% aeration)	: \$ 225
Methanol	: \$ 162
NaOH	: \$ 32
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Total	\$ 645

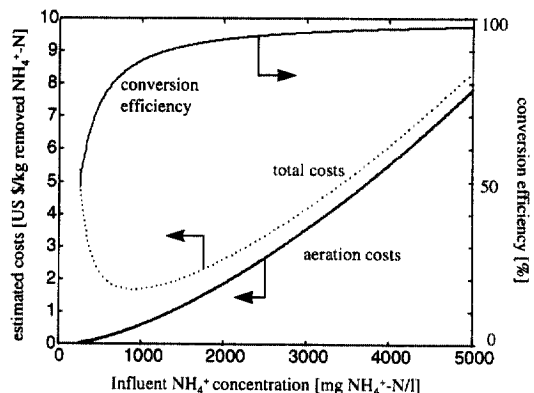


Fig. 7. Ammonium conversion efficiency and estimated costs as function of the influent NH_4^+ concentration

from equation 9 when a Monod term for ammonium is used for convenience. At pH 7 the measured value for K_{NH_3} (0.5 mg $\text{NH}_4^+\text{-N/l}$) is equivalent to a K_{NH_4} value of 64 mg $\text{NH}_4^+\text{-N/l}$. For a liquid residence time of 1 d⁻¹, the specific growth rate for the ammonium oxidisers obtains the same value in a system without sludge retention. For the realistic assumption that the product of the 2 rightmost terms of equation 9 possesses a value of 0.7, the Monod term for ammonium must be 0.68, given a maximum specific growth rate of 2.1 d⁻¹. This corresponds to an ammonium concentration of 130 mg $\text{NH}_4^+\text{-N/l}$. Depending on the influent concentration, the biomass concentration adjusts itself to a value where this medium, hence effluent, concentration is reached. For a range of influent concentrations, the conversion efficiency is depicted in Fig. 7, that decreases from over 97 % at an influent concentration of 5000 mg $\text{NH}_4^+\text{-N/l}$ to about 50% (at 250 mg $\text{NH}_4^+\text{-N/l}$). In the same figure, estimated costs per kg removed $\text{NH}_4^+\text{-N}$ are presented, based on the data in the previous section. It was assumed that methanol addition is proportional to the converted amount of ammonium. Aeration costs were calculated by using the equality $k_{\text{La}}=c*(P/V)^{0.4}$ that provides a rough estimate for the oxygen transfer coefficient as a function of the agitation power per unit volume in stirred tank reactors (van 't Riet en Tramper, 1991). The oxygen transfer rate is basically proportional to this k_{La} value. At low influent concentrations, overall costs are mainly determined by fixed costs. At higher influent concentration aeration costs become dominant. Alternative process design can however reduce aeration costs in this range. The current estimations reveal that total costs are about minimum for the conditions at the Dokhaven WWTP and that the costs are entering the usual range for N-removal at influent concentrations below 250 mg $\text{NH}_4^+\text{-N/l}$ and above approximately 3500 mg $\text{NH}_4^+\text{-N/l}$.

Process efficiency for lower effluent concentrations

Increasing the residence time lowers the ammonium contents of the effluent. Note however that the process is not developed to meet strict effluent standards, as the effluent will still contain suspended solids and nitrite/nitrate (although more denitrification can be introduced). If effluent concentrations well below 130 mg $\text{NH}_4^+\text{-N/l}$ are to be reached, nitrite oxidizers may grow into the reactor. However, first calculations suggest that at high pH values a substantial increase in residence time is possible before this occurs. For lower effluent concentrations, costs rise due to higher investments for the larger reactor volume, and possibly due to the larger demands for oxygen (+25%) and COD source (+40%). Cost estimations are further complicated by fact that the presented kinetic parameters do not necessarily apply to much lower concentration levels when biomass is selected for lower growth rates and higher substrate affinity. This might lead to a better effectiveness than would be predicted on the basis of the presented data. A study for the Utrecht WWTP in the Netherlands revealed that the SHARON process is feasible indeed for a comparable load at an influent concentration of 500-600 mg/l $\text{NH}_4^+\text{-N}$. For strongly deviating conditions, additional research is required.

CONCLUSIONS

The SHARON concept seems to be most feasible for substantial ammonium reduction in waste water with a relatively high ammonium content (hundreds to thousands mg $\text{NH}_4^+\text{-N/l}$) and with an elevated temperature. Investment costs are low because a simple well mixed tank reactor of modest dimensions without a sludge retention system is sufficient. Variable costs are reduced by stopping the oxidation at nitrite and using denitrification for pH control. 2 years of laboratory experiments revealed that the nitrite route can be maintained at 35 °C using 1 day aerobic and 0.5 day anoxic residence time. Biomass inactivation due to lack of substrate for more than one week was limited. The reactor height to diameter ratio should be kept low in order to ensure high mass transfer rates for carbon dioxide, thus reducing costs for pH regulation.

Simulations showed that simple time based control and straightforward methanol supply are sufficient to maintain high conversion rates and stable process operation despite large influent fluctuations. For the situation at the Dokhaven WWTP, total costs for 85% ammonium conversion are estimated at about \$1.7 per kg removed $\text{NH}_4^+\text{-N}$ (load: 440 tons $\text{NH}_4^+\text{-N/year}$; influent concentration 1 g $\text{NH}_4^+\text{-N/l}$). Further cost reduction especially for methanol addition is possible by adjusting the supply rate to the ammonium load.

The conversion efficiency is basically determined by the influent NH_4^+ concentration. For a given load, more conversion, or lower effluent concentrations, can only be obtained if the hydraulic residence time is increased. It is not yet clear at which point complete oxidation to nitrate will occur, leading to higher costs for aeration and COD addition. First calculations reveal however, that at sufficiently high pH the HRT may be increased considerably before nitrite oxidation starts. Whether nitrite oxidation occurs or not, the concept may still be feasible under such conditions. At high influent concentration levels, processing costs are getting in range with alternative processes due to the high aeration costs.

The effluent contains suspended solids, which is irrelevant when treating internal recycle flows. In the studied case, the nitrite in the effluent (about 300 mg/l NO_2^- -N) is denitrified in the A-stage of the A/B process. For other applications, more complete denitrification can be introduced into the SHARON process.

The Grontmij consultants have a patent pending on the process. The first full scale SHARON process will be operational early 1998.

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