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OPTIONS FOR SEPERATE TREATMENT OF URINE

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PREFACE

Human urine contains 80% of the total nitrogen, 70% of the potassium and around 50% of the total phosphorous of the total loads in municipal wastewater. Urine represents less than 1% of the total wastewater volume and can be collected undiluted with modern no-mix toilets or waterless urinals. The effects and benefits of partial urine separation on advanced biological nutrient removal plants have already been illustrated and quantified previously. However, the treatment of separated urine has not yet been developed into marketable processes.

Menselijke urine bevat 80% van de totaal stikstofvracht, 70% van het kalium en rond 50% van het totaal fosfaat vracht in huishoudelijk afvalwater. Het volume van urine bedraagt minder dan 1% van het totaal afvalwater volume en kan met moderne "no-mix" toiletten of waterzuinige urinoirs onverdund worden ingezameld. De effecten en voordelen van gescheiden urine inzameling op gevorderde rioolwater zuiveringsinrichtingen (rwzi) zijn reeds uitgewerkt en gekwantificeerd. De behandeling van brongescheiden urine is echter nog niet in marktklare processen ontwikkeld.

Author of this report is; Jac Wilsenach (TU-Delft). The project steering group consisted of: ir. Harm Baten (Hoogheemraadschap van Rijnland), ir. Elbert Majoor (Waterschap Veld en Vecht), ir. Ruud Schemen (Hoogheemraadschap van het Hollands Noorderkwartier) en Bert Palsma (STOWA).

De technieken zijn beschikbaar, de toepassingen zijn veelbelovend; wij zijn hard op zoek naar mogelijkheden om praktijkervaring op te doen.

Utrecht, Juni 2005
De directeur van de STOWA
Ir. J.M.J. Leenen

ABSTRACT

Human urine contains 80% of the total nitrogen, 70% of the potassium and around 50% of the total phosphorous of the total loads in municipal wastewater. Urine represents less than 1% of the total wastewater volume and can be collected undiluted with modern no-mix toilets or waterless urinals. The effects and benefits of partial urine separation on advanced biological nutrient removal plants have already been illustrated and quantified previously. However, the treatment of separated urine has not yet been developed into marketable processes.

Using urine directly as fertiliser presents a few problems. Transport of liquid is expensive in typical Dutch situations where great distances have to be covered from densely populated urban areas to farmland. Furthermore, urine produced in the Netherlands contains only around 10-15% of the nutrients produced in animal manure. The technological and highly specialised character of modern agriculture also undermines the assumption that urine or animal manure can be easily used as fertilisers. More innovative ways have to be developed to recycle nutrients. Recovery of nutrients in a solid fertiliser, for example, would be an improvement.

Struvite can be recovered effectively from urine as either $MgNH_4PO_4.6H_2O$ or $KMgPO_4.6H_2O$. A reactor was developed that includes settling (liquid/solids separation). This was found to be a robust and reliable reactor, with an absolute minimum of moving parts. In the case of untreated urine, with a high pH, supersaturation of struvite occurs with addition of Mg and primary nucleation has preference. If ammonia is first removed from urine (e.g. biologically) the pH has to be increased for struvite precipitation. This can be done in such a manner that supersaturation is limited and better crystal growth occurs, which improves settling. However, lower supersaturation also leads to lower phosphate recovery efficiency. It is doubtful whether the slight improvement in settling characteristics justifies the lower removal efficiency.

Biological nitrogen removal from urine was possible in different reactor configurations. The most promising combination was two continuous stirred tank reactors with recycle for nitritation and denitrification. This system converted COD and NH_4^+ in urine into an NH_4NO_2 solution, with up to 30% of the influent nitrogen removed as nitrogen gas. This effluent liquid could be treated in a biofilm anammox reactor, at a high rate of 2,200 $gN/m^3_{react}.d$ and 85% total nitrogen removal. Anammox on carrier material proved to be more resistant to high concentrations of nitrite or oxygen, compared to available literature. Clogging was never a serious problem, owing to the slow growth rate of anammox organisms. If urine were diluted by 50% (e.g. some toilet flush water), all biological treatment techniques would be improved with less inhibition due to free ammonia and nitrous acid (especially nitritation) and the relatively high salt concentration of urine. Still, undiluted urine could better be mixed with supernatant from anaerobic digestion. This strategy has the double advantage of treating a bigger waste stream with more efficient technology. In such a case, urine should be collected undiluted, for transport and process efficiency. With longer storage, urea hydrolysis (which limited the reaction rates in some of the experiments from this study) could also be expected to be complete.

Despite its conceptual interest, a single reactor system (CANON) in this study performed worse than the two-reactor system (SHARON/Anammox). The control of a CANON system

requires intensive supervision. Operation of anammox in a fixed bed under anaerobic conditions (this study) was more robust, required almost no control and in the end was more efficient. Our results suggest that an overall removal rate for the combined SHARON/Anammox process of between 900 - 1000 $gN/m^3_{react}.d$ (based on 85% N_2 removal in the anammox process) is possible.

The impact of separate urine collection and treatment was illustrated in a model study, where an Integrated Urine an Wastewater Treatment Process was defined, with struvite recovery and SHARON/Anammox as N-removal process. This model study demonstrated that if 50% or more of urine were collected separately, wastewater treatment performance could be greatly improved. More compact and energy efficient processes for integrated treatment of urine and wastewater are feasible. The main advantage of urine separation is not the production of better effluent quality, for there are processes capable of producing very good effluent quality. The main advantage of integrated wastewater and urine treatment is the production of very good effluent quality (2 – $3gN/m^3$) with a substantial saving in resources and even net production of primary energy.

Further research to improve the wastewater treatment system should be focussed towards other aspects, such as logistics, economic feasibility, interest of investors and construction companies, etc. The next step should be implementation of techniques on a pilot scale, integrated within existing systems.

STOWA IN BRIEF

The Institute of Applied Water Research (in short, STOWA) is a research platform for Dutch water controllers. STOWA participants are ground and surface water managers in rural and urban areas, managers of domestic wastewater purification installations and dam inspectors. In 2002 that includes all the country's water boards, the provinces and the State.
These water controllers avail themselves of STOWA's facilities for the realisation of all kinds of applied technological, scientific, administrative-legal and social-scientific research activities that may be of communal importance. Research programmes are developed on the basis of requirement reports generated by the institute's participants. Research suggestions proposed by third parties such as centres of learning and consultancy bureaux, are more than welcome. After having received such suggestions STOWA then consults its participants in order to verify the need for such proposed research.

STOWA does not conduct any research itself, instead it commissions specialised bodies to do the required research. All the studies are supervised by supervisory boards composed of staff from the various participating organisations and, where necessary, experts are brought in.

All the money required for research, development, information and other services is raised by the various participating parties. At the moment, this amounts to an annual budget of some six million euro.

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SAMENVATTING

Menselijke urine bevat 80% van de totaal stikstofvracht, 70% van het kalium en rond 50% van het totaal fosfaat vracht in huishoudelijk afvalwater. Het volume van urine bedraagt minder dan 1% van het totaal afvalwater volume en kan met moderne “no-mix” toiletten of waterzuinige urinoirs onverdund worden ingezameld. De effecten en voordelen van gescheiden urine inzameling op gevorderde rioolwater zuiveringsinrichtingen (rwzi) zijn reeds uitgewerkt en gekwantificeerd. De behandeling van brongescheiden urine is echter nog niet in marktklare processen ontwikkeld.

Het gebruik van urine direct als meststof kent een aantal problemen. Vervoer van vloeistof is duur in het geval van de Nederlandse randstad, waar grote afstanden tussen woonwijken en steden enerzijds en landerijen anderzijds liggen. Verder bevat urine in Nederland geproduceerd maar ongeveer 10 – 15% van de mineralen vracht die in mest van veehouderijen afkomstig zijn. De technologisch en hoogs specialistische aard van moderne landbouw betekent ook dat urine niet gemakkelijk kan worden ingezet als plaatsvervanger voor industriele kunstmest. Meer innovatieve methoden zijn nodig voor het hergebruik van mineralen. Terugwinning van mineralen als vaste stof zal veel voordeliger zijn.

Struviet kan efficiënt worden teruggewonnen uit urine als of $MgNH_4PO_4.6H_2O$ of $KMgPO_4.6H_2O$. Een reactor is ontwikkeld waarbij bezinking is geïntegreerd (vloeistof/vaste stof scheiding). Onderzoek wees dat dit, mede dankzij de minimum bewegende delen, een robuuste en betrouwbare reactor opstelling is. In het geval van onbehandeld urine, waarbij een hoge pH kenmerkend is, ontstaat oververzadiging van struviet na toevoeging van Mg, waarbij primaire deeltjesvorming voorkeur heeft. Indien ammonium wordt verwijderd (bijvoorbeeld biologisch) moet de pH verhoogd worden alvorens struviet gaat precipiteren. Dit kan op zo’n wijze wordt uitgevoerd dat de oververzadiging beperkt blijft waardoor een betere kristalgroei kan plaatsvinden, hetgeen de bezinking bevordert. Lagere oververzadiging van struviet leidt echter ook direct tot een slechtere effluent kwaliteit en minder terugwinning. Het is twijfelachtig of het slechtere effluent kwaliteit wordt gerechtvaardigd door een iets betere bezinking.

Biologische stikstof verwijdering van urine is onderzocht in verscheiden reactor configuraties. Het meest belovende combinatie bleek twee volledige gemengde reactoren met recirculatie, voor nitrificatie en denitrificatie. Binnen dit systeem werden CZV en NH4+ in urine omgezet naar een NH4NO2 mengsel, waarboven zoveel als 30% van het influent stikstof is verwijderd als stikstofgas. Dit effluent samenstelling is succesvol behandeld in een biofilm anammox reactor, met een hoge omzetsnelheid van 2,200 $gN/m^3_{react}.d$ en 85% totaal stikstof verwijdering. Anammox op dragermateriaal is bewezen als zeer bestand tegen hoge concentraties nitriet en zuurstof, vergeleken met ander bronnen uit de literatuur. Geen problemen met dichtslibben van de reactor waren tegengekomen, mee dankzij de lage groeisnelheid van anammox organismen. Indien urine met 50% wordt verdund (d.w.z. inclusief een beetje spoelwater) kunnen allen biologische processen worden verbeterd van wegen minder inhibitie door vrij ammoniak en nitriet zuur. Dit geldt vooral voor ammoniak oxidatie. Verdunning verlaagt ook de zoutconcentratie, die remmend inwerkt voor zowel ammonium oxideerders als anammox organismen. Wel kan urine beter onverdund wordt ingezameld en met slibgistingswater wordt vermengd. Bij deze strategie worden voordelen gehaald het beter

behandelen van een grotere afvalstroom. Vervoer en opberging zijn uiteraard meer efficiënt bij minder verdunde urine. Opberging heeft ook als voordeel dat ureum splitsing volledig is verlopen tegen het tijd dat urine behandeld wordt. Deze studie heeft aangetoond dat in sommige gevallen, ureum splitsing in bicarbonaat en ammonium de proces snelheid beperkt.

Ongeacht zijn conceptuele belang, heeft een enkel reactor systeem (CANON) in deze studie veel slechter gepresteerd dan de tweestap systeem (SHARON/Anammox). Het beheer van een CANON proces vergden intensieve toezicht. Bedrijf van een anammox systeem op drager materiaal onder anaerobische toestanden was in deze studie veel meer robuust en vergden bijna geen procesbeheer en was over het algemeen meer efficiënt (m.b.t. reactor volume en reactie snelheid, inclusief de SHARON processtap). De resultaten lieten zien dat het gecombineerd SHARON/Anammox proces een omzetsnelheid van 900 – 1000 $gN/m^3_{react}.d$ goed mogelijk is (gebaseerd op 85% N_2 verwijdering in de anammox proces).

De impact van gescheiden urine inzameling en behandeling op het afvalwater systeem is met behulp van een modellenstudie gedaan. Hierbij is een geïntegreerde urine en afvalwaterzuivering behandelingsproces gedefinieerd, met struviet terugwinning en N verwijdering via SHARON/Anammox. Deze modellenstudie demonstreerden gevallen waar 50% (of meer) urine gescheiden is ingezameld. Meer compacte en energiezuinige processen zij dan mogelijk. Het grote voordeel van urine scheiding is niet een betere effluent kwaliteit, aangezien deze al mogelijk is binnen het huidige systeem. Het grootste voordeel is dat een zeer goeie effluent kwaliteit mogelijk (2 – 3 gN/m^3) is met een groot besparing in hulpbronnen en zelfs netto productie van primaire energie.

Ten einde het afvalwatersysteem verder te verbeteren, dient het onderzoek zich te verplaatsen naar andere aspecten die tot nu niet echt aan bod kwamen. Hierbij moet men denken aan logistiek, economische haalbaarheid, belang van projectondernemers, bouwbedrijven, enz. Een volgende stap moet zijn de implementatie van technieken op demonstratie niveau, geïntegreerd binnen bestaande systemen.

DE STOWA IN HET KORT

De Stichting Toegepast Onderzoek Waterbeheer, kortweg STOWA, is het onderzoeksplatform van Nederlandse waterbeheerders. Deelnemers zijn alle beheerders van grondwater en oppervlaktewater in landelijk en stedelijk gebied, beheerders van installaties voor de zuivering van huishoudelijk afvalwater en beheerders van waterkeringen. Dat zijn alle waterschappen, hoogheemraadschappen en zuiveringsschappen en de provincies.

De waterbeheerders gebruiken de STOWA voor het realiseren van toegepast technisch, natuurwetenschappelijk, bestuurlijk juridisch en sociaal-wetenschappelijk onderzoek dat voor hen van gemeenschappelijk belang is. Onderzoeksprogramma's komen tot stand op basis van inventarisaties van de behoefte bij de deelnemers. Onderzoekssuggesties van derden, zoals kennisinstituten en adviesbureaus, zijn van harte welkom. Deze suggesties toetst de STOWA aan de behoeften van de deelnemers.

De STOWA verricht zelf geen onderzoek, maar laat dit uitvoeren door gespecialiseerde instanties. De onderzoeken worden begeleid door begeleidingscommissies. Deze zijn samengesteld uit medewerkers van de deelnemers, zonodig aangevuld met andere deskundigen.

Het geld voor onderzoek, ontwikkeling, informatie en diensten brengen de deelnemers samen bijeen. Momenteel bedraagt het jaarlijkse budget zo'n zes miljoen euro.

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DESAR OPTIONS FOR SEPERATE TREATMENT OF URINE

CONTENTS

CHAPTER 1

SEPARATE COLLECTION AND TREATMENT OF URINE AND NEW POTENTIALS FOR WASTEWATER TREATMENT

CONTENTS

1

BACKGROUND

Human urine contains 80% of the total nitrogen, 70% of the potassium and around 50% of the total phosphorous of the total loads in municipal wastewater (Larsen and Gujer, 1996). Urine represents less than 1% of the total wastewater volume and can be collected undiluted with modern no-mix toilets or waterless urinals (STOWA, 2002). The effects of partial urine separation on advanced biological nutrient removal plants have already been illustrated and quantified previously. Partial urine separation would increase treatment capacity by 30% for raw wastewater treatment and up to 100% for pre-settled wastewater. The total nitrogen effluent quality of existing municipal wastewater treatment systems could be improved to 2 - 3 gN/m^3 (Wilsenach and van Loosdrecht, 2003). In parallel to research, different water boards in the Netherlands are investigation options of improving wastewater treatment through introduction of urine separation. Recently, two water boards Rijnland and Delfland commissioned preliminary studies to test the feasibility of urine separation (Rijnland, 2004 and Delfland, 2004). However, the treatment of separated urine has not yet been developed into marketable processes.

Udert *et al.* (2003a) already demonstrated that a 1:1 ammonium nitrate fertiliser solution could be produced in a biofilm reactor. This liquid fertiliser would have high phosphate and potassium concentrations, including micro-nutrients such as magnesium and calcium. Aeration of urine before application to fields is necessary for two reasons:

- Biological nitrification lowers the pH to 6.5 and thereby prevents ammonia volatilisation.
- Nitrate is the form in which plants mostly take up nitrogen. Ammonium nitrate fertilisers, rely on bacteria in the aerobic layer of topsoil to oxidise the NH_4^+. Application of only ammonium, or injection of ammonia below the aerobic surface, may result in ground water pollution through leaching.

Using urine directly as fertiliser implies transport of liquid. This would be costly where great distances have to be covered, typically from densely populated urban areas to farmland. Still, the treated urine would have to compete with animal manure as a potential recycled fertiliser. The technological and highly specialised character of modern agriculture undermines the assumption that urine or animal manure as fertilisers are desired, or even accepted. More sophisticated and inventive ways to recycle nutrients would have to be developed. Recovery of nutrients in a solid fertiliser would therefore be advantageous.
Nitrogen is not a finite mineral, but abundantly present in atmosphere. Recovery of ammonia from urine requires almost as much energy as the combined energy required for industrial ammonia production and nitrogen removal via SHARON/Anammox (Maurer *et al.*, 2003, Wilsenach *et al.*, 2003). Other ammonia recovery or nitrogen removal techniques are possible (Maurer *et al.*, 2003). Ammonia adsorption to zeolites have already been studied for urine (Lind *et al.*, 2000). When compared to recovery of ammonia, industrial ammonia production is inexpensive at around €200/tonN. If ammonia were recovered from urine and sold, based on this price, it would mean an economic gain of only around €1 per person per year, which

is unlikely to cover the costs of industrial grade ammonia recovery. Conventional biological N removal costs around €3600/tonN (assuming 40% of the total wastewater treatment cost is related to N removal). Ammonia recovery techniques are more expensive, around €5000/tonN (STOWA 96-01). With the load of ammonia produced through animal husbandry and the lack of farmland near cities, efficient nitrogen removal could prove a more feasible option than recovery (at least in large urban areas).

Phosphate and potassium are both finite resources. The amounts of these minerals in human excreta are, however, quite small when compared to the total economical throughput in society. In the Netherlands for example, 14 kt P and 24 kt K enter municipal wastewater treatment plants annually. The nutrient input through industrial fertiliser is 14 kt P/year and 30 kt K/year. Still, the amounts produced by animal manure exceed these by far: 80 kt P/year and 200 kt K/year (STOWA, 2001-39). The possible contribution of nutrient recovery from municipal wastewater seems limited (10 – 15% of the total throughput). It is unlikely that recycle of minerals will result in any economic benefit for treatment plants. Nevertheless, the recovery of phosphate and potassium will be essential in sustainable societies. Magnesium ammonium phosphate (struvite) precipitation is a well-known technique for P removal from wastewater side-streams. The N:K:P molar ratio in urine is roughly 27:2:1. Therefore, less than 4% of the ammonia in urine could be recovered with struvite. If ammonia were first removed effectively, potassium struvite could be precipitated.

In this study, three main questions were investigated:

1 Recovery of phosphate (and potassium) from source separated urine in a simple and robust reactor
2 Removal of nitrogen from source separated urine in different biological reactors
3 Integration of these process units with existing or new centralised wastewater treatment processes, where sustainability of different treatment options is quantified in terms of effluent quality and energy consumption.

2

PHOSPHATE AND POTASSIUM RECOVERY

Conditions controlling phosphate precipitation and scaling have been studied for different purposes:

- efficient phosphate removal in wastewater treatment
- operation and maintenance strategies, to prevent pipe scaling
- recovery of struvite to be used directly as fertiliser in agriculture

Struvite formation and recovery is well-described. This research was aimed at operating a simple and robust reactor, with a minimum of moving parts and little requirements for maintenance.

The calf manure treatment plant at Putten (Schuiling and Anrade, 1999) has continuously produced potassium struvite for the past five years. Although they have not developed the produced KMP into a marketable product (it is given to farmers for free), struvite recovery is used as the cheapest way of phosphate removal.

Recovery of struvite (magnesium ammonium phosphate) as part of urine treatment has gained interest recently (Lind *et al.*, 2000 and Ronteltap *et al.*, 2003). Urine from low flush toilets could have a phosphate concentration of around 500 mg/l. In this research, recovery of $MgNH_4PO_4.6H_2O$ (MAP) from untreated synthetic urine was investigated. Recovery of KMgPO4.6H2O (KMP) from synthetic urine first treated in bioreactors for N removal was also studied.

A simple technique for struvite precipitation in a continuous stirred tank reactor (CSTR) with gravity separation, is described in this report. The outflow of struvite particles from precipitation/crystallisation reactors to liquid/solids separation devices could still be a major cause for operational breakdowns due to scaling and pipe blockage. We therefore designed a precipitator that incorporates the sedimentation of precipitated particles in a special internal compartment. As stated above, undiluted and stored urine would result in high supersaturation and almost immediate precipitation, producing many fines. However, in the case of biologically treated urine, alkalinity can be removed biologically. The pH therefore would have to be increased before precipitation will occur. If this pH were controlled at an optimum, supersaturation could be limited and more efficient crystal formation could be achieved. However, the lower pH leads to lower P-removal efficiency (effluent concentration of around 35 gP/m^3 for pH 9, but 75 gP/m^3 for pH 8.7). The improved settling of bigger crystals does not justify the lower removal efficiency, and one should rather allow extra storage volume. In general, MAP removal efficiency was better than KMP removal efficiency under similar conditions (effluent concentration of 15 gP/m^3 for pH 9).

3

BIOLOGICAL N REMOVAL FROM URINE

The load of nitrogen in urine is around 12 gN/p.d. This is in the form of urea, which has been found to hydrolyse in a couple of days in urine collection systems and tanks. Apart from the large nitrogen load, urine also contains 10g/p.d COD (Ciba Geigy, 1977). This COD consists of 90% soluble substances, of which 82% is readily biodegradable (Udert et al., 2003a).

Supernatant from anaerobic digesters has a high ammonium concentration, between 600 and 1200 mgNH_4-N/l, as well as a higher temperature (typically 30ºC) compared to normal wastewater. For these two conditions, alternative treatment options were developed, based on nitrogen removal via nitrite (STOWA 96-01). This process is based on the higher growth rate of ammonia oxidisers compared to nitrite oxidisers at temperatures above 25ºC. Operation in a reactor without sludge retention and hydraulic retention time of 1 - 1.5 days resulted in complete washout of nitrite oxidisers. The single reactor for high activity ammonia removal over nitrite (SHARON) was operated as a cyclic reactor on full scale. Methanol was dosed primarily for pH control at the end of aerobic cycles, but also served the purpose of denitrification via nitrite. Effluent from the SHARON process can be treated in an Anammox process, or anaerobic ammonium oxidation (Van Dongen et al. 2001 a, b). The oxygen demand of the combined SHARON/Anammox process is 42% of conventional nitrification. Moreover, no organic carbon is required for denitrification. A major disadvantage is the low growth rate of anammox organisms.

In this study we showed that a different set of process parameters control the presence of nitrifiers at very high ammonium and nitrite concentrations (typical for urine). Free ammonia and free nitrous acid could both contribute to the complete inhibition of nitrite oxidisers. This makes nitritation possible at lower temperature (20ºC) and at higher sludge age (20-30 days) for a more stable process. However, if undiluted urine were collected, inhibition of the ammonium oxidisers could also occur. We also showed that partial denitrification in urine is possible via nitrite. With the COD present in urine, around 30% of the nitrogen load could be removed. The remaining liquid has a ammonium nitrite ratio of around 1, and would be a good influent for the anammox process.

A biofilm anammox reactor was started and operated successfully over a period of two years. The maximum removal rate of 2,200 $gN/m^3_{react}.d$, and the nitrogen removal efficiency of 85%, compares well to any anammox reactor yet reported. In this case, however, sub-optimal conditions were applied, such as high salt concentrations and relatively low temperatures (23-24ºC). Anammox on carrier material proved to be robust against nitrite concentrations normally inhibiting activity and growth, even above concentrations (> 100 mgN/l) thought to be irreversibly inhibitive (fatal). Almost all biomass was retained in this system, but clogging was not a problem. The simplicity of this reactor type, consisting only a submerged packed bed with liquid recycle, adds to the attractiveness of this process.

The nitritation and anammox processes have also been combined in a single reactor, at oxygen limited conditions, dubbed the CANON process (completely autotrophic nitrogen removal over nitrite). As in the case of Sliekers *et al.* (2003) we found that the nitrogen removal rate under aerobic conditions (limited oxygen) was only about 20-25% of the anaerobic N-removal rate.

Urine should be collected as undiluted as possible, e.g. with waterless urinals. The overall system, including storage tanks and reactors, could be smaller if the liquid were not diluted. If urine were transported by truck before treatment, the disadvantage of more dilute liquids is obvious. Phosphate recovery, e.g. as struvite precipitation, would also be more efficient at higher concentrations. Furthermore, urea hydrolysis and the resultant scaling of precipitants in collection pipes can be limited by keeping urine as concentrated as possible (Udert *et al.*, 2003b). In spite of these benefits, the high ammonium concentration could lead to inhibition of bacteria. This inhibition could also be used advantageously to suppress nitrite oxidisers. High salt concentrations of undiluted urine would also inhibit the growth rate of organisms. If urine were collected undiluted, it could be justified to transport it by truck and mix with digester supernatant before treatment. In this way, a higher nitrogen load is treated with more efficient technology, such as SHARON/denitrification, or SHARON/Anammox. The problem of inhibition, due to extreme ammonia and nitrous acid concentrations, is also excluded by dilution with supernatant.

4

INTEGRATION OF PROCESSES TO TREAT URINE AND WASTEWATER

The concentrations of nitrogen (N) and phosphorus (P) in municipal wastewater are generally higher than required for cell growth associated with organic carbon (COD) removal. Biological nutrient removal processes are specifically designed to remove these excess nutrients. Both nitrification and denitrification require a great deal of resources, relative to wastewater treatment as a whole. The aeration required for nitrification, accounts for almost 25% of the total energy demand in wastewater treatment plants. Furthermore, denitrification requires energy in the form of readily biodegradable organic carbon. Primary sedimentation is therefore excluded at treatment plants where complete denitrification is necessary. Consequently, organic carbon that could have been converted into natural gas (via anaerobic digestion) is converted directly into CO_2 and some biomass. Apart from the demand on resources, the conventional techniques for nitrogen removal face some other problems. Ammonia oxidising bacteria are slow growing organisms within the normal temperature range of wastewater treatment plants (typically 10 - 14°C in the Netherlands). The low growth rate necessitates long sludge ages, which in turn increases the size of single sludge treatment plants. Treatment plants are also exposed to ammonium peak loads and temperature shocks from varying influent and ambient conditions.

With complete or even partial urine separation, different treatment process would become possible. Nutrients (N and P) remaining in wastewater after partial urine separation could be removed by assimilation into cell mass via an A-stage like aerobic reactor. Short solids retention time in an aerobic reactor leads to high sludge production and would yield a high amount of methane in anaerobic digestion. Supernatant from the anaerobic digester is expected to have a high nutrient concentration. Results from the SHARON/Anammox reactor (investigated in laboratory reactor) suggested that lower salt and ammonium concentrations would improve the process. Digester supernatant could therefore be mixed with urine for N-removal in a combined treatment concept. Results from the research on struvite recovery suggested that the high phosphate concentration of urine is not crucial for good recovery. Lower phosphate concentrations would still be suitable for struvite recovery. Mixing of anaerobic digester supernatant with urine increases the total load of phosphate that can potentially be recovered as struvite.

This integrated wastewater and urine treatment (IntWUT) process was evaluated by means of a model study. Various urine separation efficiencies could be treated in different reactor configurations, and were compared to a BCFS process for conventional wastewater treatment. The results suggest that very low effluent concentrations are possible (e.g. N_{tot} = 2.5 gN/m^3). The resources required in the different processes (where an equal effluent quality is produced) give an indication of the relative sustainability of processes. Low energy demand and high methane production makes net energy generation possible, in a process half the size

of conventional treatment processes. Where the primary energy requirement for the BCFS process was 10 Watt/person (continuous average power demand), a net primary energy generation of 2 Watt/person was possible with the IntWUT process at 85% urine separation. This efficiency of the IntWUT process is sensitive to the amount of nutrient actually removed with sludge production, but this does not have much influence on the power demand.

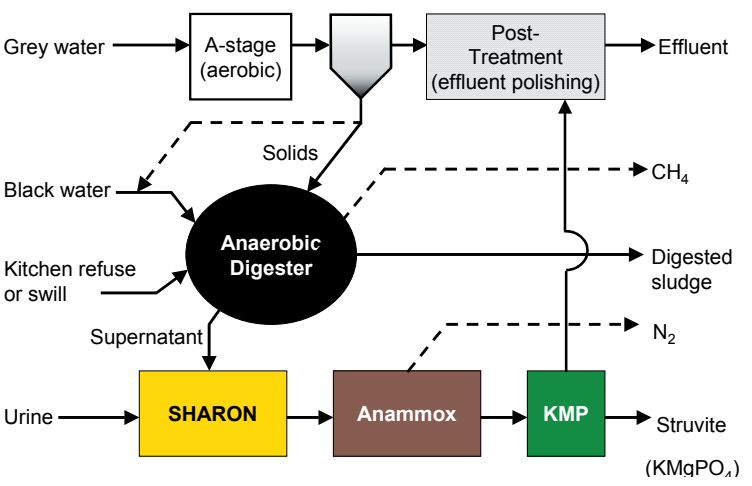
5

FUTURE WATER AND WASTE MANAGEMENT OPTIONS

A concept for treatment of separately collected black water, urine and grey water is shown in figure 1. This concept could be realised in the near future, integrating new neighbourhoods within the existing infrastructure without complete abandoning of the current system. It is foreseen that no-mix toilets will only later (if ever) be installed in private houses, but that urine separation systems in public places (e.g. hospitals, office blocks, sport stadium, etc.) will be easier to maintain. Experience from eco-villages has shown that roughly only 50% of toilet visits occur at home (Jönsson *et al.* 1997). It is then further assumed that black water from normal houses (toilet water with faeces and urine) could be collected separately in a fairly concentrated form, using modern water-saving toilets, typically 15 litres per person per day. Black water could in this way be transported to a central treatment plant with a dedicated pressure pipeline. This liquid would already be concentrated enough for direct anaerobic digestion, combined with some sludge from grey water treatment. Grey water, with a relatively high COD content and low nutrients content, could be treated by aeration in an A-stage reactor with short solids retention time, i.e. high sludge production. Grey water could also be treated locally. If that is the case, the produced sludge could be separated and transported with the black water (shown in figure 1 as an alternative). The concept can be improved further by adding kitchen refuse or swill to the anaerobic digester. This leads to increased methane production.

Typical ammonium and phosphate concentrations from this digester could be around 800 gN/m^3 and 100 gP/m^3 respectively. Addition of 50% separately collected urine would increase these concentrations up to 1,400 gN/m^3 and 160 gP/m^3 respectively. These concentrations are sufficiently high for effective phosphate recovery as struvite and nitrogen removal via SHARON/Anammox.

FIGURE 1 **CONCEPT: TREATMENT OF SEPARATELY COLLECTED GREY WATER, BLACK WATER, KITCHEN REFUSE AND URINE**



With vacuum transport, the amount of water used for transport of toilet waste is further reduced, which increases nutrient concentrations further. Typical ammonium and phosphate concentrations in the effluent from an accumulation reactor investigated by Wageningen University was 1,500 gNH_4^+-N/m^3 and 100 gPO_4^{3-}-P/m^3. When 50% separately collected urine is added to this supernatant, ammonium and phosphate concentrations can be increased to around 2,500 gNH_4^+-N/m^3 and 300 gPO_4^{3-}-P/m^3 respectively. The P and N concentrations without any separate urine collection are high enough for the struvite recovery and SHARON/Anammox processes. Still, higher concentrations would improve efficiency of both processes (removal efficiency, size, etc). In this scheme, struvite precipitation follows after nitrogen removal (and not before it, as suggested elsewhere). This is believed to be an improvement for two main reasons. Firstly, ammonia that is not removed in the SHARON/Anammox process would be removed completely with struvite (i.e. a kind of polishing step for better effluent quality). Secondly, potassium can also be recovered to some extent, if ammonia were removed adequately in the SHARON/Anammox process. Addition of MgO would be sufficient for pH increase and struvite crystallisation.

Biodegradability of influent COD where black water and kitchen refuse is combined, is higher than normal wastewater sludge digestion, between 80-90% of the influent COD is removed. This could improve the energy generation potential, which would have to be high enough to justify the use of vacuum sewers, which are energy intensive relative to the other processes in this wastewater treatment scheme.

This proposed system seems to be technically feasible, based on research done by TU Delft, Wageningen University and Research and other institutions. Aspects which could still influence the overall feasibility of such a system, includes at least the following:

- economies of scale (e.g. pressure line for black water)
- shared (or overlapping) interests of those responsible for wastewater transport (municipalities) and those responsible for wastewater treatment (water boards).
- willingness and interest of investors and construction companies to take part in such initiatives.
- logistics regarding collection and transport of urine or swill

All these aspects could be investigated (and clarified to some extent) within the current system, by means of pilot studies. It is unlikely that further experimental work or desktop studies will add much extra insight to these aspects.

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CHAPTER 2

RECOVERY OF PHOSPHATE AND POTASSIUM FROM SOURCE SEPARATED URINE THROUGH STRUVITE PRECIPITATION

CONTENTS

1

INTRODUCTION

Phosphate has to be removed from wastewater to prevent eutrophication of surface waters. During the past then years, biological P removal has become almost standard practice for new wastewater treatment plants in the Netherlands. A clearer understanding of phosphate accumulating organisms (PAOs) has ensured stable operation of these plants. In a specially controlled environment, PAOs accumulate in a mixed sludge population and take up excess phosphate to form storage products. Practically all soluble phosphate can be removed from the main wastewater stream, producing very good effluent quality. However, excess phosphate is often released again during sludge treatment, especially in anaerobic digestion. Up to 50% of the phosphate in wastewater treatment plant influent could originate in the return flows from sludge treatment (Ueno and Fuji, 2001). If these return flows have supersaturated phosphate concentrations, precipitation and scaling will occur. Scaling disrupts the operation of plants, leading to poor performance, increased pump heads, decreased flow rates, costly repairs etc. (Neethling and Benisch, 2004). Many options have been investigated to deal with scaling, but with little success. Smooth pipe surfaces, for example, prevent struvite at first, but scaling would ultimately develop if the liquid were supersaturated (Parsons and Doyle, 2004). The most efficient prevention of scaling is removal of phosphate in a dedicated side-stream reactor.

Phosphate is a finite resource that should be recovered and recycled where possible. Apart from phosphate, municipal wastewater also contains potassium that could potentially be recycled. These amounts are, however, not large when compared to the total economical throughput. In the Netherlands for example, 14 kt P and 24 kt K enter municipal wastewater treatment plants annually. The nutrient input through industrial fertiliser is 14 kt P/year and 30 kt K/year. Still, the amounts produced by animal manure exceed these by far: 80 kt P/year and 200 kt K/year (STOWA, 2001-39). The possible contribution of nutrient recovery from wastewater seems limited (10 – 15% of the total throughput) and will unlikely result in substantial economic benefit for treatment plants.

Of the total loads in municipal wastewater, urine contains 80% of the total nitrogen, 70% of the potassium and around 50% of the total phosphorous (Larsen and Gujer, 1996). Urine represents less than 1% of the total wastewater volume and can be collected undiluted with modern no-mix toilets or waterless urinals. The N:K:P molar ratio in urine is roughly 27:2:1. Therefore, less than 4% of the ammonia in urine could be recovered with magnesium ammonium phosphate (struvite) precipitation. Other ammonia recovery or nitrogen removal techniques are possible (Maurer *et al.*, 2003). Nitrogen is not a finite mineral and industrial ammonia production does not require much more energy than the recovery of ammonia from urine (Wilsenach *et al.*, 2003). With the load of ammonia produced through animal husbandry and the lack of farmland near cities, efficient nitrogen removal could prove a more feasible option than recovery.

Partial urine separation would increase treatment capacity and effluent quality of existing municipal wastewater treatment systems (Wilsenach and van Loosdrecht, 2003). Future treatment systems could consist of a SHARON/Anammox process for N removal, which also allows that more energy can be recovered from anaerobic digestion (Chapter 4 of this report). Improved efficiency of phosphate and potassium recovery, due to high mineral concentrations, would be additional benefits of urine separation. Urine from low flush toilets could have a phosphate concentration of around 500 mg/l. Recovery of struvite (magnesium ammonium phosphate) as part of urine treatment has gained interest recently (Lind *et al.*, 2000 and Ronteltap *et al.*, 2003). We report on experiments to recover $MgNH_4PO_4.6H_2O$ (MAP) as well as $KMgPO_4.6H_2O$ KMgPO4.6H2O (KMP) from urine, in batch tests and a specially designed continuous stirred tank reactor (CSTR).

2

PROCESS CHOICE AND DESCRIPTION

Phosphate can be recovered in crystallisation processes. In a liquid with high supersaturation, primary nucleation (precipitation) of phosphate minerals will occur in the presence of suitable cations. Supersaturation increases with increasing alkalinity, according to reaction 1:

$$H_3PO_4 \rightarrow H_2PO_4^- + H^+ \rightarrow HPO_4^{2-} + 2H^+ \rightarrow PO_4^{3-} + 3H^+ \quad (1)$$

Two different techniques are currently available for phosphate crystallisation, i.e. via calcium phosphate or struvite.

The Crystalactor is a fluidised bed reactor where milk of lime is added in sufficient quantities to maintain pH 8.5 (Eggers *et al.*, 1991). However, before this step, the liquid is dosed with sulphuric acid to remove bicarbonate to prevent precipitation of calcium carbonate instead of calcium phosphate. Sand is introduced as seed material and kept in suspension by special flow regulation. This process is not only complex, but also expensive. Although the product is an excellent substitute for raw phosphate rock, the low price of phosphate rock (around €30/ton $Ca_3P_2O_5$) does not make this process profitable. The price of phosphate rock is not expected to rise considerably in the near future.

A fluidised bed reactor could also be used to crystallise struvite, of which the best example is perhaps at a wastewater treatment plant in Japan (Ueno and Fuji, 2001). Magnesium hydroxide is added with the inflow at the bottom of the fluidised bed, with sodium hydroxide to maintain a pH between 8.2 and 8.8. Struvite granules of 0.5 to 1 mm are formed, which can be easily separated by screening. Phosphate removal of around 90% was achieved form an influent concentration of 110 gP/m^3.

Seckler *et al.* (1991) established the relationship between supersaturation (related directly to pH) and efficiency of crystal growth. A higher pH leads to improved total P removal (through precipitation), but at the same time producing relatively more fines, which settle poorly. At a lower pH, primary nucleation is prevented and crystal growth becomes the major mechanism of P removal. An optimum pH exists for every P concentration where maximum crystallisation efficiency is achieved with good total removal. At high phosphate concentrations (above 150 mg/l), high localised supersaturation occurs and leads to more primary nucleation. It seems that higher phosphate concentration improves removal, but provides difficulties regarding separation and drying of precipitant. The combined high alkalinity and phosphate concentration of undiluted stored urine (pH 9 – 9.4, P = 500 mg/l) could result in high supersaturation and primary nucleation, causing havoc in fluidised bed reactors.

A much simpler technique is precipitation in a continuous stirred mixed reactor (CSTR) after which struvite is separated in a settling tank. The calf manure treatment plant at Putten (Schuiling and Anrade, 1999) has constantly produced potassium struvite for the past five years.

The outflow of struvite particles from precipitation/crystallisation reactors to liquid/solids separation devices could still be a major cause for operational breakdowns due to scaling and pipe blockage. To solve these issues, we designed a precipitator that incorporates the sedimentation of precipitated particles in a special internal compartment. As stated above, undiluted and stored urine would result in high supersaturation and almost immediate precipitation, producing many fines. However, in the case of biologically treated urine, alkalinity is removed biologically. The pH therefore would have to be increased before precipitation will occur. If this pH were controlled at the optimum, supersaturation could be limited and more efficient crystal formation could be achieved.

3

MATERIALS AND METHOD

3.1 SYNTHETIC URINE MIXTURE

Synthetic urine was prepared (Griffith, 1976). Nutrient concentrations were as follows, P = 31 mM (955 mgP/l), total N = 705 mM (9870 mgN/l) and K = 52 mM (2050 mgK/l). Small amounts of urease enzyme were added. This was apparently sufficient for complete urea hydrolysis, increasing pH to 9.3. Natural precipitation occurred (with Mg and Ca in urine) leaving a P concentration around 750 mgP/l. In the case of biological treatment prior to struvite crystallisation, the same mixture was used. This mixture had more or less the same salt composition as urine.

3.2 BATCH TESTS

Batch tests were performed to investigate the use of different magnesium additives to recover magnesium ammonium phosphate (MAP) from synthetic urine. MAP precipitation was investigated in 250ml stirred and unstirred flasks, adding MgO and $MgCl_2$ at different Mg:P ratios. The decrease in PO_4 and NH_4 concentrations over time were measured. We used Dr. Lange spectro-photometer .

In a second set of experiments, synthetic urine was first treated in a combined Sharon/Anammox process to remove nitrogen biologically. This effluent was used to investigate potassium magnesium phosphate (KMP) precipitation, with MgO and $MgCl_2$ as additives. Bio-reactor effluent had a pH of 7.3, the P concentration was around 460 mgP/l and NH4 was around 40 mgN/l. The potential for MAP precipitation was therefore practically excluded. The pH was initially increased from 7.4 to 9.4 by addition of 25 mmol NaOH per flask. With MgO addition, the pH increased to 9.4 without the need of an additional hydroxide source.

3.3 PRECIPITATION REACTOR

Figure 1 shows two alternative mechanisms for liquid/solid separation in a single continuous stirred tank reactor. The reactor shown on the left hand was used in the first experiments. This was later replaced with the reactor shown in the right hand, believed to be an improved design. Figure 2 shows the experimental set-up with bench scale precipitator, including motor for mixer, pumps and pH control probes.

FIGURE 1 **SCHEMATIC DIAGRAM OF THE PRECIPITATION REACTOR WITH SETTLING COMPARTMENT**

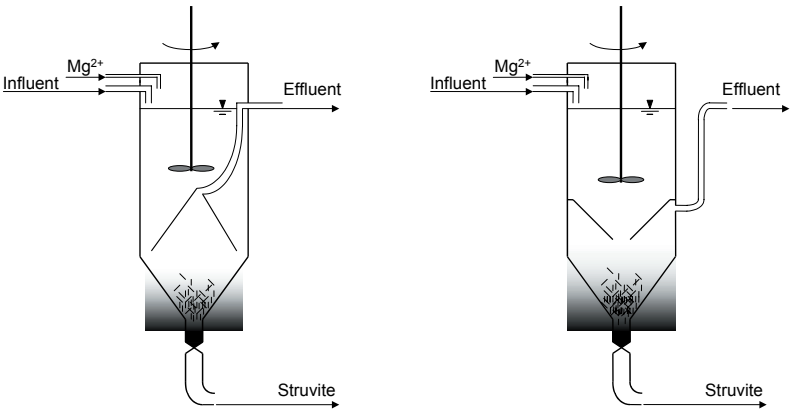
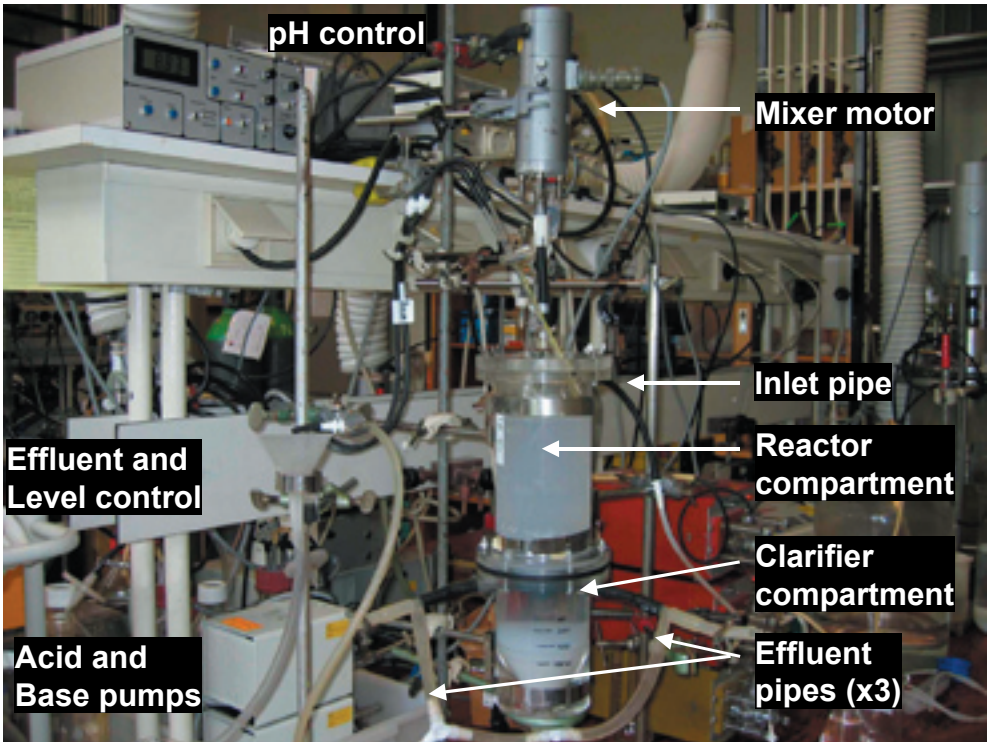


FIGURE 2 **EXPERIMENTAL SET-UP OF STRUVITE PRECIPITATOR**



The reactor had height of 300mm and diameter of 100mm. The volumes of the precipitation section and the settling section were both 0.77l.

The effects of different hydraulic retention times and mixing velocities on reactor performance were investigated. The redox potential was observed for different conditions. The robustness of the reactor was also investigated by operating the reactor continuously for a long as possible. Precipitants from the batch tests and the reactor were identified using X-ray diffraction (XRD) analysis.

4

RESULTS AND DISCUSSION

4.1 BATCH TESTS

Figure 3 shows the phosphate removal efficiency for different MgO:P and $MgCl_2$:P ratios for untreated synthetic urine. With a MgO:P ratio of 1.1, more than 90% of phosphate was removed in the stirred flask. From figure 3a it is clear that stirring greatly increases the removal efficiency. An increase in pH was observed with the increasing amounts of MgO, although the effect is not significant. When $MgCl_2$ was used (figure 3b), all phosphate was removed with a Mg:P ratio of 1.1. A slight decrease in pH was observed with increasing $MgCl_2$ additions, but without any practical implication.

FIGURE 3 RESULTS FROM MAP BATCH EXPERIMENTS WITH DIFFERENT MG^{2+} ADDITIVES

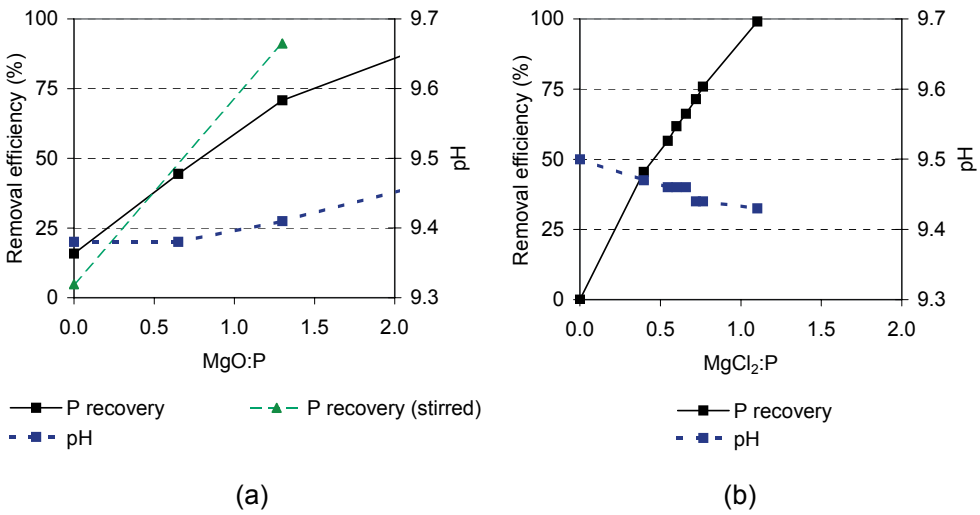
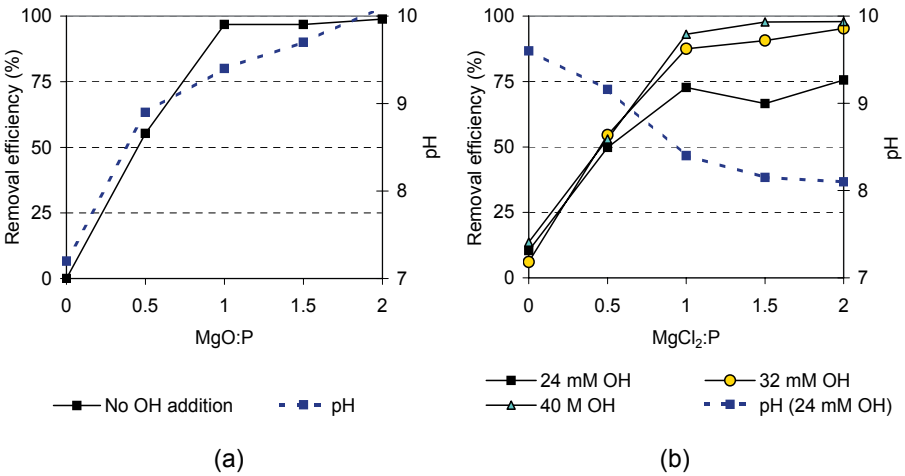


Figure 4 shows the phosphate removal efficiency for different MgO:P and $MgCl_2$:P ratios where effluent from the bio-reactor was used. With MgO as additive, the pH rose with increasing amounts of MgO. The pH rose to 9.2 at Mg:P = 1 (figure 4a), and almost all phosphate was removed under these conditions (stirred flask). With extra MgO additions, the pH increased further, without further effect on the P removal efficiency (remains almost 100%). Figure 4b shows the pH profile where the liquid had a pH 9.4 without any $MgCl_2$ addition. With higher $MgCl_2$ additions, as KMP is precipitated, the pH also decreased. The decrease in the pH to 8.2 resulted in low phosphate removal, even with an overdose of magnesium (P removal is only 75% with Mg:P = 2). The pH profile is similar to the trend observed earlier (figure 3b). In this case (figure 4b), the lack of the bicarbonate buffer in the anammox effluent caused the pH to drop significantly with phosphate removal. When more NaOH was added to pH 9.4 again, the P removal efficiency increased.

FIGURE 4 **RESULTS FORM KMP BATCH EXPERIMENTS WITH DIFFERENT MG^{2+} AND OH^- ADDITIVES**



In all four cases, described above, almost all phosphate was removed at Mg:P = 1, regardless of magnesium source or whether ammonium or potassium struvite is precipitated. As with other research, a pH of 9 was crucial for precipitation and complete phosphate removal.

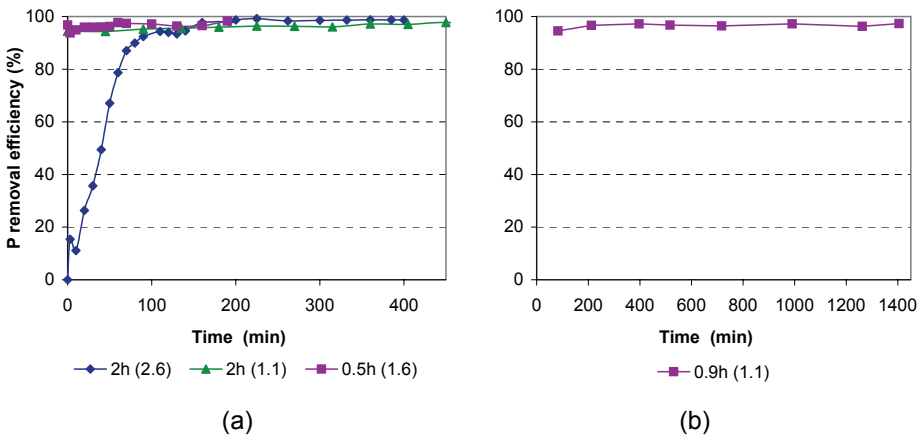
4.2 PRECIPITATION REACTOR WITH UPRIGHT SEPARATOR - $MGNH_4PO_4.6H_2O$ REMOVAL

The precipitation and settling of struvite in a single reactor was successfully achieved in most experiments. Figure 5a clearly shows the struvite precipitation in the reactor section of the reactor. Struvite deposition on the impeller, walls and outlet pipe can also be seen. In figure 5b, struvite crystals can be seen in the settling section (powdery white substance in the inverted cone). The reactor was further tested under different conditions to optimise performance.

After starting with the CSTR full of untreated liquid, steady state was reached within 3 hours of continuous urine and soluble $MgCl_2$ influent in all experiments (figure 6a). Figure 6a also shows that hydraulic retention time down to 0.5 h had no effect on the removal efficiency (based on soluble P). The measured Mg:P ratio is shown in brackets behind the HRT in the legend. At steady state, the soluble P effluent concentration remained around 10 mgP/l (removal efficiency of 97%). Figure 6b shows the removal efficiency during continuous operation over 24 hours during which no operational breakdowns occurred. Eventually, the effluent pipe became blocked.

FIGURE 5 STRUVITE FORMATION (A) AND SETTLING (B) IN THE PRECIPITATION REACTOR

FIGURE 6 SOLUBLE PHOSPHATE REMOVAL EFFICIENCY OF THE PRECIPITATION REACTOR AT DIFFERENT HYDRAULIC RETENTION TIMES



Some precipitant was always present in the effluent, reducing the total removal efficiency to around 92%. Scaling on reactor wall and the effluent pipe occurred in all experiments. Higher mixing velocity in general reduced the amount of precipitate on reactor wall and effluent pipe. However, at the same time mixing power was transferred to the settling compartment, resulting in outflow of some precipitant.

FIGURE 7 **EFFECTS OF MIXING INTENSITY ON P REMOVAL PERFORMANCE AND SETTLING**

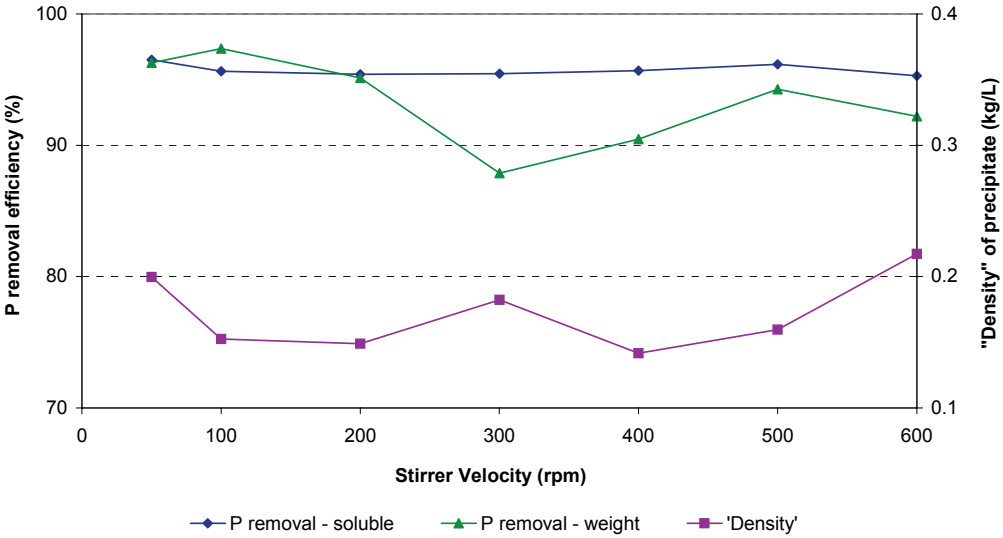
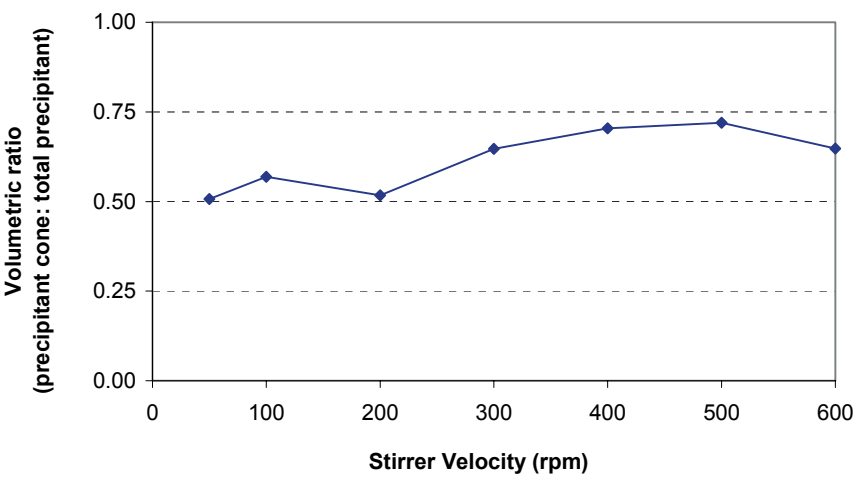


Figure 7 shows the difference between total phosphate removal (based on total weight) and soluble phosphate removal. The difference between these two efficiencies indicates the amount of fines that escaped with the reactor effluent. At 300 rpm, the lowest removal efficiency was measured. It is not yet clear why less precipitant leaves the reactor at still higher mixing velocities (400, 500 and 600 rpm). There seems to be an inverse relationship between the “density” of precipitant and total removal efficiency. The “density” of precipitant was simply measured as the mass of precipitant/crystals occupying a certain volume of the settling compartment. The peak at 300 rpm could indicate that more fines escaped the settling compartment with effluent, leaving only crystals to settle, thus yielding a higher “density”. It would seem that at still higher mixing intensities, precipitants are suspended longer in the precipitation compartment, reducing the primary nucleation and increasing crystal growth.

Figure 8 shows that higher mixing intensity led to relatively more precipitant/crystals in the settling compartment. In all batches, precipitant still occurred on reactor walls and impeller blades. Precipitant that still attached on the reactor walls in the precipitation compartment at higher mixing intensities, was more difficult to remove.

FIGURE 8 **EFFECTS OF MIXING INTENSITY ON POSITION OF PRECIPITANT SETTLING**



The XRD analysis showed that precipitant was predominantly struvite, with some chloride salts. Needle shaped crystals, typical of struvite, were observed under a microscope (x60), but no granules.

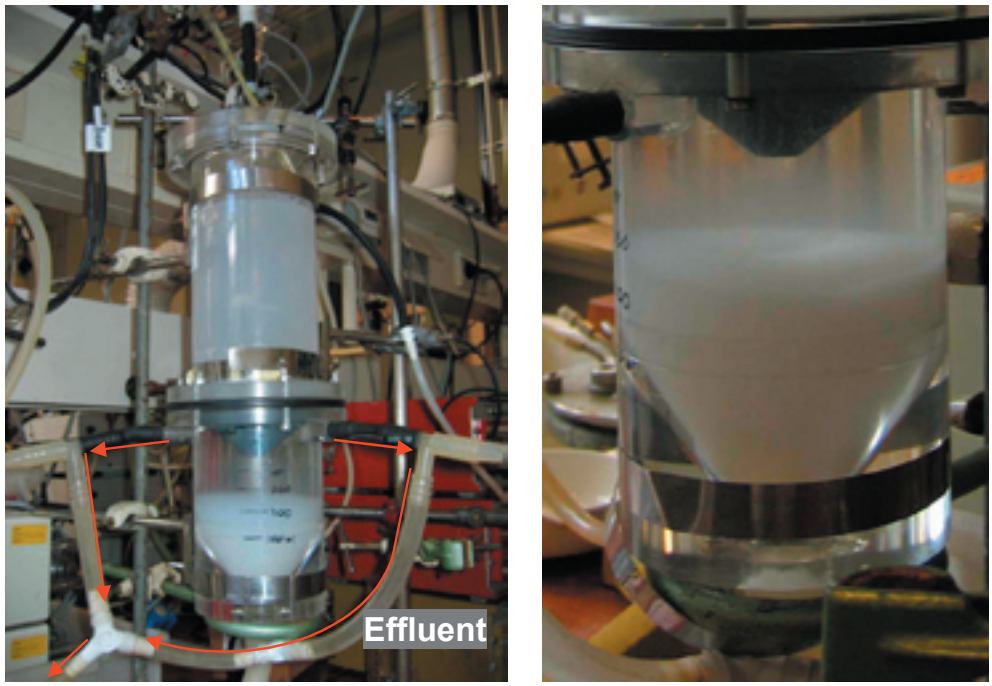
4.3 PRECIPITATION REACTOR WITH DOWNWARD SEPARATOR - $KMgPO_4.6H_2O$ REMOVAL

A few initial experiments with the separating device shown in figures 1b and 9 a, b were done to determine effect of mixing intensity and hydraulic retention time. Figure 9a clearly shows a murky reaction compartment with below it a clear liquid section, and at the bottom the settled potassium struvite crystals. Figure 9b shows a more detailed view of the separation during operation. In the centre, immediately below the downward cone, the liquid is less transparent due to settling crystals (coming through the cone from the reaction compartment above), while at the outer limits and to the top the liquid is clear, indicating efficient separation. In the case of the downward cone, almost no solids were lost in the effluent lines.

The downward cone (figure 1b, figures 9a,b) is believed to be an improvement on the upright cone (figure 1a, figures 5a,b) for two reasons:

- The effluent pipes are outside the reaction compartment, and where precipitant occurred without restraint on the effluent pipe with the upright cone (figure 5a), this is no problem in the downward cone.
- Almost no mixing energy is transferred between the reaction compartment and the separation compartment. This allows for better settlement of the particles.

FIGURE 9 PRECIPITATION REACTOR DURING POTASSIUM STRUVITE PRECIPITATION (A) AND SOLIDS/LIQUID SEPARATION COMPARTMENT WITH FUNNEL HOPPER FACING DOWN



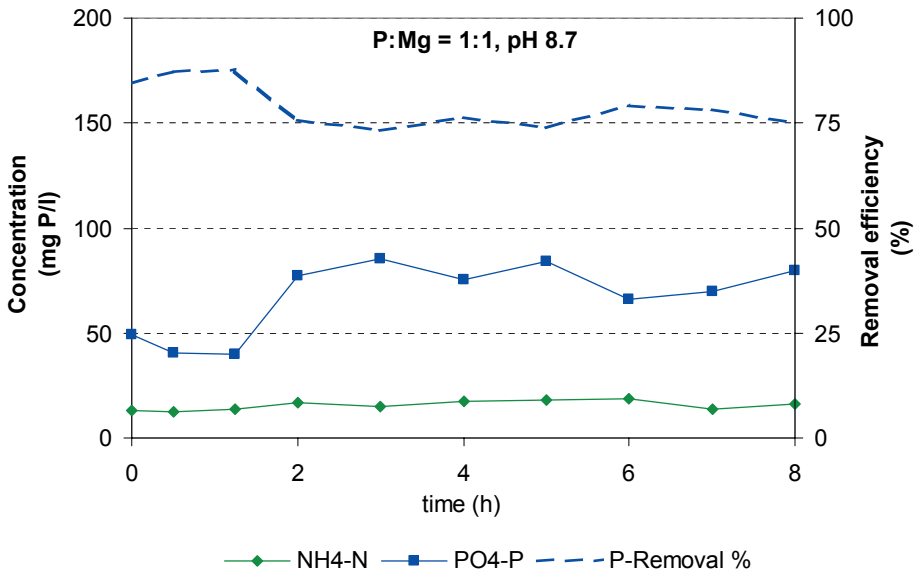
(a) (b)

The hydraulic retention time had little or no effect on the phosphate removal efficiency above 1.6 hours, as was the case with ammonium struvite precipitation in the reactor with upright cone. Effects of mixing intensity were not investigated to the full, but it is believed that an optimum has to be found. At a too high mixing intensity, centrifugal forces move phosphate

particles to the edges and crystal growth on the reactor walls become problematic. High mixing intensity also had the effect of forcing crystals through the opening in the downward cone. This could be observed visually, with an increase in crystal flow rate with an increase in the mixing intensity. The possibility of damaging and breaking up struvite crystals, which are brittle as individual crystals, is also not excluded. At a too low mixing intensity, not enough particles remain in suspension. This could lead to lower overall removal, because in this case the objective was also to limit supersaturation in order to promote crystal growth in favour of primary nucleation. We found an "optimum" at 100 rpm. Struvite crystals don't settle very well, compared to granules, for instance, and it is probable that the optimum mixing intensity would rather be on the low side than too high.

Figure 10 shows results for potassium struvite removal over time, with equimolar amounts of Mg and P in the influent, with a hydraulic residence time of 2 hours and ph controlled at 8.7. As compared to figure 6, the phosphate removal efficiency of potassium struvite at lower pH is much less than ammonium struvite under similar conditions. For ammonium struvite, a phosphate effluent concentration of 10 mgP/l was possible, but in this case it was only around 75 mgP/l. Almost all ammonium was removed, but the influent ammonium concentration was only 50 mgN/l. Therefore some 30% of potassium was also removed, keeping in mind an influent ratio, K:PO4 = 2.1:1.

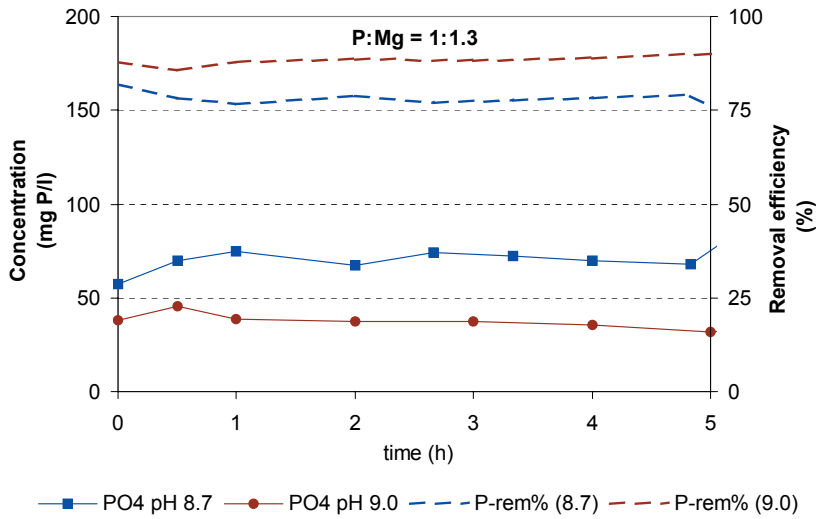
FIGURE 10 POTASSIUM STRUVITE REMOVAL OVER TIME, P:MG = 1:1



When the ratio of Mg:P in the influent was increased to 1.3:1, no real difference in removal efficiency was observed (figure 11). Figure 11 also shows the results for potassium struvite removal over time, at pH 9. There is a clear improvement of phosphate recovery. This confirms the statement that supersaturation of struvite is mostly determined by the phosphate speciation at different pH values, according to reaction 1.

However, the settling characteristics of the struvite formed at higher pH (9) was noticeably worse from that at the lower pH (8.7). Based on the volume occupied in the settler compartment, and the actual amount of phosphate removed, the struvite crystallised at a lower pH (8.7) had a density of 2.4 gP/l, while the struvite crystallised at a higher pH (9) had a density of 2.0 gP/l.

FIGURE11 POTASSIUM STRUVITE REMOVAL OVER TIME, P:MG = 1:1.3



The hypothesis that lower pH ensured lower supersaturation and therefore better crystal growth seems correct, but this comes at the price of reduced phosphate removal efficiency. The difference in settling characteristics probably does not justify the lower removal efficiency. This is already a compact process and more settling space should be provided.

Effects of solids in the influent (either biomass or a recycle of crystallised struvite) on crystal growth in the reaction compartment could still be evaluated.

5

CONCLUSIONS

Struvite can be recovered effectively from urine as either $MgNH_4PO_4.6H_2O$ or $KMgPO_4.6H_2O$. In the case of untreated urine, with a high pH, super saturation of struvite occurs with addition of Mg and primary nucleation has preference. If ammonia is first removed from urine (e.g. biologically) the pH has to be increased, and this can be done to limit super saturation, giving preference to crystal growth. However, the difference in settling characteristics was not spectacular.

Transfer of mixing power to the settling compartment has to be prevented. Furthermore, mixing power has to be kept at an optimum, which should be just sufficient to keep struvite crystals in suspension. Too high mixing power leads to increased scaling on reactor walls.

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CHAPTER 3

BIOLOGICAL NITROGEN REMOVAL FROM URINE

CONTENTS

1

INTRODUCTION

Nitrogen removal from household wastewater traditionally relies on two distinct biological processes:

i A group of autotrophic organisms oxidises ammonium to nitrite, after which a second group oxidises nitrite to nitrate,

ii Heterotrophic organisms reduce nitrate and/or nitrite to nitrogen gas.

Both of these processes require substantial resources, relative to wastewater treatment as a whole. The aeration required for nitrification accounts for almost 25% of the total energy demand in wastewater treatment plants. Furthermore, denitrification requires energy in the form of readily biodegradable organic carbon. Primary sedimentation is therefore excluded at treatment plants where complete denitrification is necessary. Consequently, organic carbon that could have been converted into natural gas (via anaerobic digestion) is converted directly into CO_2 and some biomass.

Apart from the demand on resources, the conventional techniques for nitrogen removal face other problems. Ammonia oxidising bacteria are slow growing organisms within the normal temperature range of wastewater treatment plants (typically 10 - 14ºC in the Netherlands). The low growth rate necessitates long sludge ages, which in turn increases the size of single sludge treatment plants. Treatment plants are also exposed to ammonium peak loads and temperature shocks from varying influent and ambient conditions.

Treatment of side streams, such as anaerobic digester supernatant, has gained interest during the past years for various reasons. Supernatant contributes some 10 – 20% of the ammonium load to activated sludge reactors. When plants are compelled to perform better, supernatant treatment is an attractive option. Supernatant has a much higher ammonium concentration, between 600 and 1200 mgNH_4^+-N/l, as well as a higher temperature (typically 25 - 35ºC) compared to wastewater. Under these two conditions, alternative treatment options become possible, which the STOWA investigated previously. These techniques include air/steam stripping of ammonia (STOWA 95-12), struvite precipitation (STOWA 95-13) and nitrogen removal with membrane bioreactors (STOWA 95-09). In the evaluation of these techniques, the production of residual substances with physical/chemical processes proved problematic (STOWA 95-08). In a following study, the removal of nitrogen via nitrite was investigated (STOWA 96-01). In this process, the higher growth rate of ammonia oxidisers compared to nitrite oxidisers at 35ºC is used to prevent nitrite oxidation. Operation in a reactor without sludge retention and a hydraulic retention time of 1.5 days resulted in complete washout of nitrite oxidisers. Reaction 1 describes the batch reactor dubbed SHARON (single reactor for high activity ammonia removal over nitrite). Methanol was dosed primarily for pH control at the end of aerobic cycles, but also served the purpose of denitrification (reaction 2):

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (1)$$

$$CH_3OH + 2NO_2^- + H^+ \rightarrow N_2 + 2H_2O + CO_2 + 2OH^- \quad (2)$$

In a comparison with physical/chemical techniques (mentioned above), the SHARON process was found the least expensive alternative (STOWA 96-01).

Recent studies have also proven the viability of treating effluent from the SHARON process in an Anammox process, or anaerobic ammonium oxidation (Van Dongen *et al*. 2001 a, b). This novel biological process can be described by reaction 3:

$$NH_4^+ + 1.32\ NO_2^- + H^+ \rightarrow 1.02\ N_2 + 0.26\ NO_3^- + 2H_2O + \text{biomass} \quad (3)$$

The resources required in the anammox process are substantially less than for conventional nitrogen removal. The oxygen demand of the combined SHARON/Anammox process is only 42% of conventional nitrification. Moreover, no organic carbon is required, because ammonium provides the energy source. A major disadvantage is the slow growth rate of anammox bacteria. Under optimum conditions (pH 7.5-8 and temperature range of 30-35^{o}C), the doubling time is nearly two weeks. Biomass retention is therefore crucial. The SHARON and Anammox processes have also been combined in a single reactor, at oxygen-limited conditions, dubbed the CANON process (completely autotrophic nitrogen removal over nitrite).

Urine is the main source of minerals and nutrients found in municipal wastewater. Up to 80% of the nitrogen, 70% of potassium and 50% of phosphate in wastewater originate from urine (STOWA 2001-39). The load of nitrogen in urine is around 12 gN/p.d. This is in the form of urea, which has been found to hydrolyse in a couple of days in urine collection systems and tanks:

$$NH_2CONH_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \quad (4)$$

Apart from the large nitrogen load, urine also contains 10g/p.d COD (Ciba Geigy, 1977). This COD consists of 90% soluble substances, of which 82% is readily biodegradable (Udert *et al*., 2003a). Although this is not enough COD for complete denitrification, it could be employed as a means of pH control during nitritation. It has already been demonstrated that source separated urine can be stabilised with biological nitritation (Udert *et al*., 2003a). Sequencing batch reactors as well as continuous stirred tank reactors were successful in oxidising maximally 50% of the ammonium in urine to nitrite (total N concentration 2 and 8 gN/l respectively). The same study showed the potential for biological N removal from urine with anammox bacteria in batch tests. However, 56% of ammonium has to be oxidised for complete N removal through this process.

Udert et al. (2003a) also showed that 1:1 ammonium nitrate solution could be produced in a biofilm reactor. This liquid would be a suitable fertiliser, with high phosphate and potassium concentrations. The lowered pH would also prevent ammonia volatilisation. However, while industrial ammonia production remains fairly inexpensive and the Netherlands remain a net importer of nitrogen (e.g. via animal fodder), urine fertiliser will receive little commercial interest. Moreover, nitrogen is not a finite mineral and energy required for recovery is often equal to the combined energy required for biological N removal (via SHARON/Anammox) and industrial ammonia production (Maurer et al., 2003). Nevertheless, separate collection and treatment of urine remains interesting because of the benefits to wastewater treatment,

which have already been discussed in depth (Wilsenach and Van Loosdrecht, 2003, 2004, STOWA 2001-39 and chapter 4 of this report).

It is generally thought that dilution of urine in separation systems has to be prevented. Primarily, the overall system (including storage tanks and reactors) could be smaller if the liquid is kept undiluted. If urine has to be transported by truck before treatment, the advantage of a less dilute liquid is obvious. Phosphate recovery, e.g. as struvite precipitation, would also be more efficient at higher concentrations. Furthermore, urea hydrolysis and the resultant scaling of precipitants in collection pipes can be limited by keeping urine as concentrated as possible (Udert et al., 2003b). If micro-pollutants have to be removed from urine in future, dilution would also reduce the efficiency. This last issue was not considered further in this study.

In spite of the benefits from collecting undiluted urine, the high ammonium concentration could lead to the inhibition of bacteria. The inhibition of ammonia oxidisers could be either due to free ammonia at high pH (typical for stored urine), or due to nitrous acid at low pH (typical with high nitrite concentrations required of the nitritation process). This inhibition could also be used advantageously to suppress nitrite oxidisers. High salt concentrations of undiluted urine would also inhibit the growth rate of organisms.

The aims of this study were to assemble, start, operate and compare three different bench scale biological reactors for the nitrogen removal from urine:

i Ammonium oxidation to nitrite in a sequencing batch reactor
ii Ammonium oxidation to nitrite and denitrification via nitrite in two continuous stirred tanks reactors in series
iii Anaerobic ammonium oxidation, in a fixed bed biofilm reactor, with the option of partial nitrification in the same reactor

These processes had to be carried out in simple and robust reactors without process control (i.e. self regulating) that could potentially be used as part of local or de-central treatment systems. One could therefore expect sub-optimal bacterial conditions and probably inhibition of organisms.

2

MATERIALS AND METHOD

2.1 SUBSTRATE MIXTURE: SYNTHETIC URINE

Urine from separate collection systems is normally diluted and has changing characteristics. Synthetic urine (table 1) with known concentrations was used according to the formula by Griffith et al (1976). This mixture had more or less the same salt composition expected in urine (e.g. Ciba Geigy, 1976, STOWA 2001-39). Deviations from this feed mixture are discussed where relevant.

TABLE 1 **COMPOSITION OF SYNTHETIC URINE (AFTER GRIFFITH ET AL. 1976)**

Compound	g/litre	mM/litre
$CaCl_2.2H_2O$	0.65	Ca^{2+}, 4.3
$MgCl_2.6H_2O$	0.65	Mg^{2+}, 3.2
NaCl	4.60	
Na_2SO_4	2.30	SO_4^{2-}, 16
Na_3citrate.$2H_2O$	0.65	
Na_2oxalate	0.02	
KH_2PO_4	2.80	PO_4^{3-}, 21
KCl	1.60	
NH_4Cl	1.00	NH_4^+, 19
Urea	25.0	N, 834
Creatinine	1.10	
Total N	12.3	852
Total Na		118
Total K		42

pH = 5.7 – 5.8, without urea hydrolysis.

2.2 SEQUENCING BATCH REACTOR (SBR) FOR AMMONIUM OXIDATION TO NITRITE

A 10-litre reactor was filled with tap water and some mixed liquor from nitrifying activated sludge. Small amounts of NH_4Cl were added to obtain ammonium concentrations in the reactor of around 50mg/l. Trace element solution was also added. During start-up, an ADI 1030 bio-controller was employed to maintain a constant pH, with 4M KOH and 0.4M HCl solutions, but after start-up the pH was not controlled any more. An Applikon pH 0-12 electrode was used to monitor pH. Oxygen in the system was measured using an Ingold DO electrode with O_2-Amplifier. Temperature was not controlled, but varied between 18 and 20°C. Increasing loads of ammonium were added with each new batch. The nitrite and nitrate concentrations were measured after each batch. When nitrite oxidation was inhibited, the feed was changed to synthetic urine solution (Griffith et al., 1976). In the first set of experiments, amounts of urease were added to the synthetic urine mixture. After each batch, sludge from removed liquid was left to settle in an Imhoff cone and returned to the reactor. Sludge age was in excess of 40 days. In a following set of experiments, no urease was added to the synthetic mixture. The effluent ammonium nitrite solution was stored for later treatment in an Anammox reactor.

2.3 CONTINUOUS STIRRED TANK REACTORS (CSTR) IN SERIES FOR NITRITATION/DENITRIFICATION

A 50% dilution of synthetic urine solution was prepared according to Griffith et al. (1976). The solution was fed continuously into a 2 litre CSTR that was closed to the atmosphere and through which nitrogen gas was bubbled. From this reactor, effluent was pumped into a 1.5 litre aerated CSTR from which final effluent was removed. Liquid was recycled from the aerated reactor back to the unaerated reactor at a ratio of recycle:influent flow ratio of around 10. Figure 1 shows a schematic drawing of the reactors. An Applikon pH 0-12 electrode was used with the ADI 1030 bio-controller only to monitor pH. Temperature was initially controlled at 30°C with a RM6 LAUDA recycling warm water through the double wall reactor. When nitritation increased the temperature control was stopped. Temperature was further monitored. Figure 2 shows the experimental set-up.

After a start-up phase of around three months, when the system was running stably, a new feed mixture was introduced. The initial feed mixture (Griffith et al., 1976) contained only creatinine as COD substrate, but in reality the COD load in urine could be ten times higher (Giba Geigy, 1977).

FIGURE 1 SCHEMATIC DRAWING OF TWO CONTINUOUS STIRRED TANK REACTORS FOR PARTIAL NITRIFICATION AND DENITRIFICATION VIA NITRITE

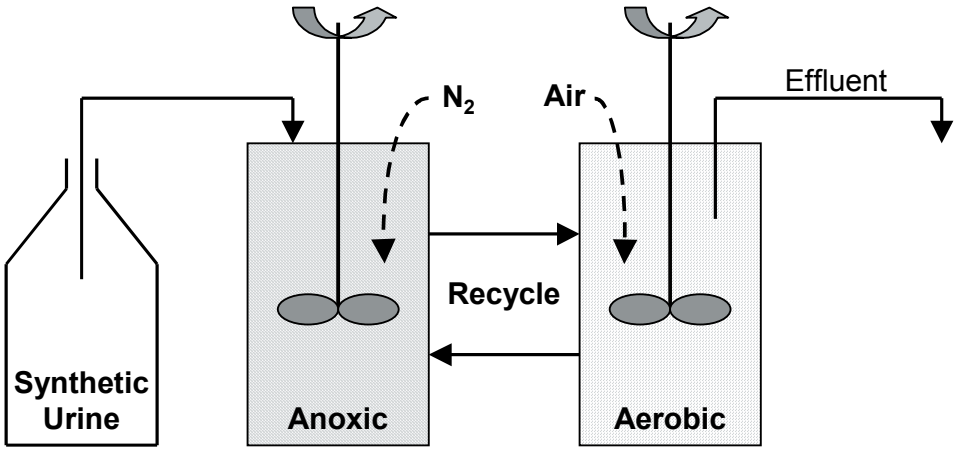
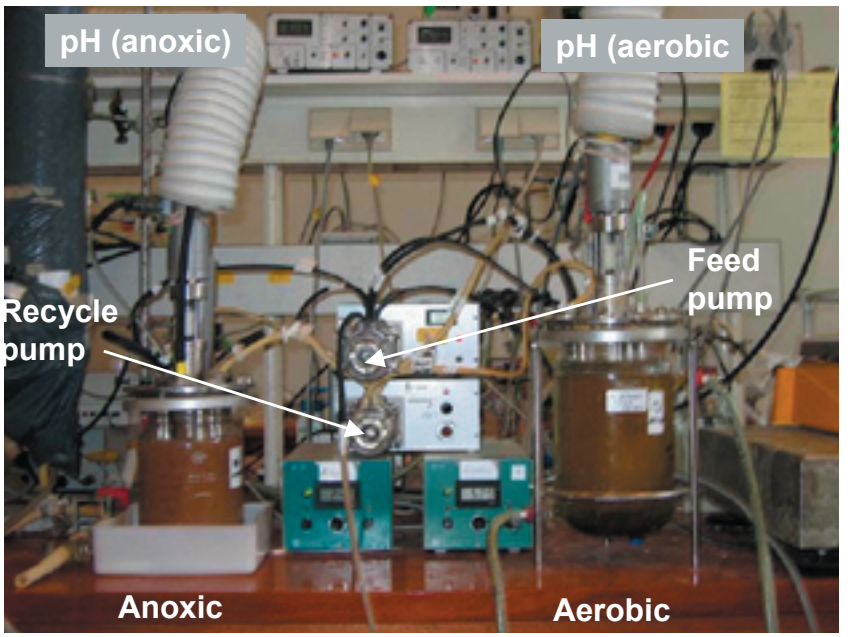


FIGURE 2 EXPERIMENTAL SET-UP FOR CONTINUOUS STIRRED TANK REACTORS



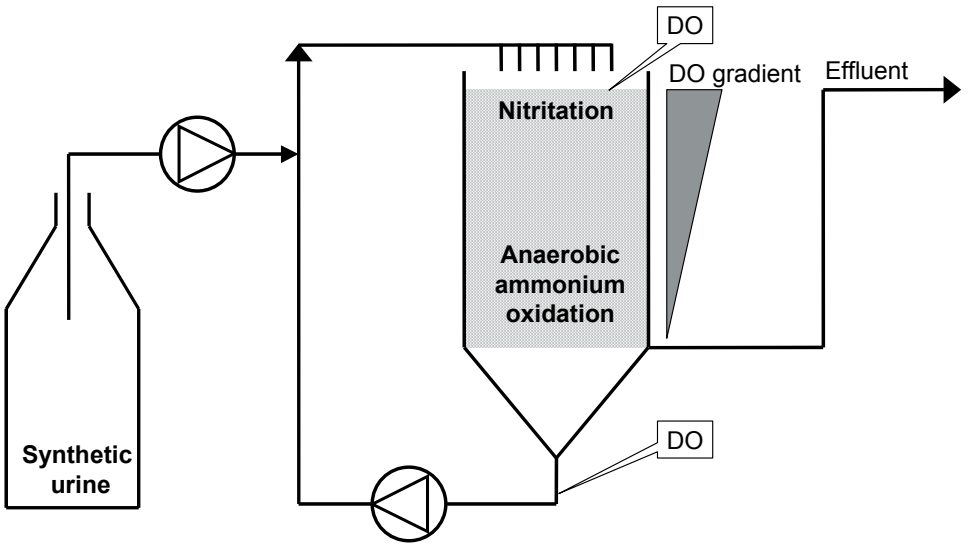
The exact COD composition of urine is complex and made up of a myriad of different organic substances and acids, all in the mg/l range (e.g. Thompson and Markey, 1975, and Chalmers *et al*. 1976). No formula for complete COD substitution in synthetic urine could be found. A yeast extract and some valeric acid were added to water with creatinine to yield a total COD concentration of around 10 g/l. This was added to the mixture described by Griffith et al. (1976) so that N_{tot}:COD_{tot} = 1 (N_{tot} at 50% dilution was 6 g/l). Although Udert et al (2003a) reported COD:N_{tot} =0.88, others have reported higher values up to 1.2 (Fittschen and Hahn, 1998). Urease was added to the feed mixture to ensure urea hydrolysis.

2.4 FIXED BED BIOFILM REACTOR (FBBR) FOR ANAEROBIC AMMONIUM OXIDATION (ANAMMOX) AND COMPLETE AUTOTROPHIC NITROGEN REMOVAL (CANON)

2.4.1 ASSEMBLY AND START-UP OF REACTOR (ANAEROBIC)

A fixed bed biofilm reactor (FBBR) was chosen for maximal sludge retention. A 6-litre glass column was filled with carrier material; plastic balls with a diameter of 17 mm and spiralling grooves. The carrier material was encaged in an aluminium grid structure, to prevent flotation due to nitrogen gas entrapment in the biofilm structure (e.g. Strous et al. (1997)). A pump with a continuous capacity between 0.5 and 1.5 l/min was used for recycling and mixing the liquid. The feed mixture was pumped into the reactor at 0.5 – 3.5 l/day at different stages of operation. The outlet level of the effluent pipe determined the liquid level inside the column. The reactor was first inoculated with a mixture of bacteria from different sources to operate under anaerobic conditions. Anammox sludge from a laboratory reactor in Delft together with anammox sludge, which had been stored for a year at 4ºC, was mixed with some nitrifying sludge.

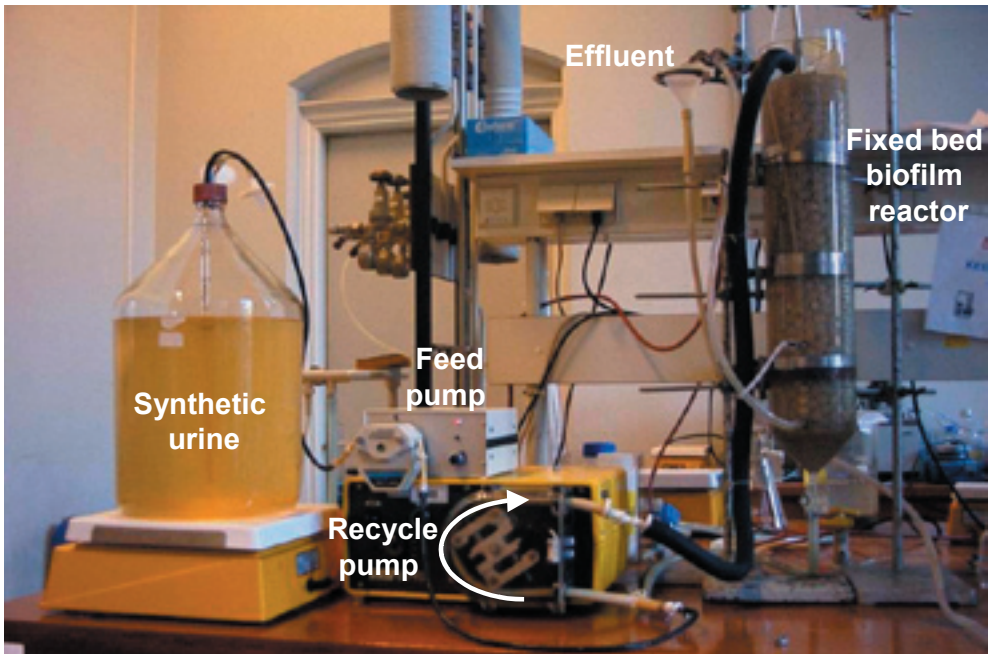
FIGURE 3 SCHEMATIC DRAWING OF ANAMMOX/CANON BIOFILM REACTOR, WITH POSITIONS OF DISSOLVED OXYGEN (DO) PROBES



The temperature inside the reactor equalled room temperature, which normally varied between 22 and 24ºC. The pH was not controlled, except at one occasion, described below. Figure 3 shows a schematic drawing of the reactor. Figure 4 shows a photograph of the reactor during the start-up phase. The column was, unlike shown in this photograph, covered in black plastic to prevent oxygenation by algae.

In the first stage of the start-up, only anammox bacteria were cultivated. A feed solution was prepared according to Strous et al. (1999), using tap water. The concentrations of $(NH_4)_2SO_4$ and $NaNO_2$ in this medium were increased according to the conversion rate in the reactor. This medium was later replaced with diluted synthetic urine (Griffith et al., 1976). In the synthetic urine, the urea, Na_2SO_4 and some of the NaCl were substituted with a mixture of $(NH_4)_2SO_4$, NH_4Cl, $NaNO_2$ and $NaHCO_3$. The concentrations of NH_4Cl and $NaNO_2$ were further increased according to the conversion rate in the reactor. The concentration of salts in the medium was increased with each new feed batch until the salt composition of synthetic urine was reached (119 mM Na^+ and 134 mM Cl^-).

FIGURE 4 EXPERIMENTAL SET-UP DURING START-UP OF ANAMMOX BIOFILM REACTOR



The nitrogen removal capacity of the FBBR was calculated from the sum of ammonium and nitrite removed minus nitrate produced (from anammox metabolism), based on the known influent concentrations, influent flow rate and measured effluent concentrations.

2.4.2 EFFECTS OF LOW PH ON N-REMOVAL RATE

Anammox activity was evaluated at sub-optimal pH values of 7.0, 6.7 and 6.5 under anaerobic conditions. The pH was controlled with an ADI 1030 bio-controller and 0.6M HCl solution. The influent flow rate was increased until a nitrite concentration of around 40 mgN/l was reached, after which the influent was stopped and the decrease in nitrite concentration measured. Experiments were repeated.

2.4.3 INFLUENCE OF VARYING SALT CONCENTRATIONS ON ANAMMOX BACTERIA (BATCH TESTS)

Anammox sludge was taken from the FBBR and from a different anammox SBR, operating well over 4 years (not further described here). Batch flasks were prepared containing;

i) sludge from FBBR in urine solution (marked SaltSalt),
ii) sludge from FBBR in fresh solution (marked SaltFresh),
iii) sludge from the SBR in urine solution and (marked FreshSalt),
iv) sludge from SBR in fresh solution (marked FreshFresh).

Air was replaced by N_2 gas in the tests flaks to ensure anaerobic conditions. The flasks were left overnight in shakers at a constant temperature of 30°C before spiking with nitrite. The decrease in nitrite concentration was measured after extracting samples under airtight conditions. All batch tests were done in duplicate.

2.4.4 PARTIAL NITRITATION AND COMPLETE AUTOTROPHIC N REMOVAL

In a further stage of experimentation, the reactor was inoculated with nitrifying sludge from an existing granulated column reactor to investigate complete autotrophic N removal according to the principle illustrated schematically in figure 3. The water level in the column was dropped slightly and gradually to allow for natural aeration through trickling. Recycle flow was aerated and distributed at the top of the column with the mechanism shown in figure 5a. The feed mixture was changed to that described before (Griffith et al., 1976) with the only exception of some $NaNO_2$ still being added. The reactor was later re-inoculated with ammonium oxidisers from the SBR (described below). The oxygen concentration was measured on-line in the recycle pipe and at the top of the reactor, using two Ingold electrodes connected to O_2-Amplifiers (positions indicated in figure 3).

Finally, the reactor was fed with the effluent from the SBR (described in paragraph 2.2), with a NH_4^+:NO_2^- ratio of 5:2. Complete autotrophic N removal under oxygen limitation was further investigated. In this experiment, a different mechanism of natural aeration was employed (figure 5b). Recycle liquid was pumped into a vertical open tube of about 75mm (20mm diameter) with a cone-shaped bottom. The tube was filled with plastic balls to create a cascade for better aeration. During this experiment, the liquid level was not dropped to obtain better mixing of oxygenated return liquid at the top of the reactor.

FIGURE 5 NATURAL AERATION MECHANISMS FOR ANAMMOX/CANON BIOFILM REACTOR

A) DURING FIRST TWO EXPERIMENTAL PERIODS WITH LOWERED LIQUID LEVEL,

B) DURING LAST EXPERIMENT WITHOUT LOWERING LIQUID LEVEL.

2.5 ANALYTICAL METHODS

All measurements of NO_2^-, NO_3^-, NH_4^+ and N_{tot} were done with a Dr Lange spectrophotometer. In the case of NO_2^-, samples were diluted up to 1/500. Although the accuracy is questionable, the method was justified by measuring the prepared feed solutions (which had exact known concentrations) and comparing results. For low nitrite concentrations (below 10 mgN/l), Merckoquant analytical tests were used.

NO_3^- in the SBR and CSTR was measured after addition of sulfonic acid to remove NO_2^-, which otherwise shows up in NO_3^- measurement. Throughout most of the experiments, tests strips were used to detect NO_3^- and only in a few cases were Dr. Lange equipment used as control.

3

RESULTS

3.1 AMMONIUM OXIDATION TO NITRITE (NITRITATION) IN A SEQUENCING BATCH REACTOR

The SBR was initially operated for more than 40 days, with a volume exchange rate of 10% (1 litre in 10 replaced with each batch). Some nitrate was initially produced, but after the start-up period almost no nitrate was produced. Nitrite was produced in fairly high concentrations (more than 2 gN/l). However, the low volume exchange rate makes good quantification of ammonium oxidation (nitritation) rates difficult, because the differences between initial and final nitrite concentrations, for example 1.9 gN/l and 2 gN/l, cannot be measured accurately.

FIGURE 6 INCREASE IN NITRITE CONCENTRATION IN SBR WHEN 5 LITRES OF INFLUENT CONTAINING UN-HYDROLYSED UREA WAS EXCHANGED (BATCHES 10 AND 11)

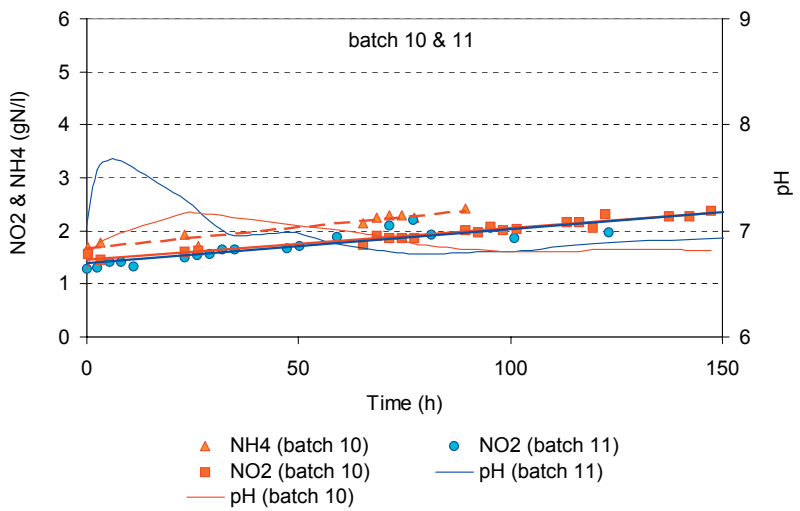
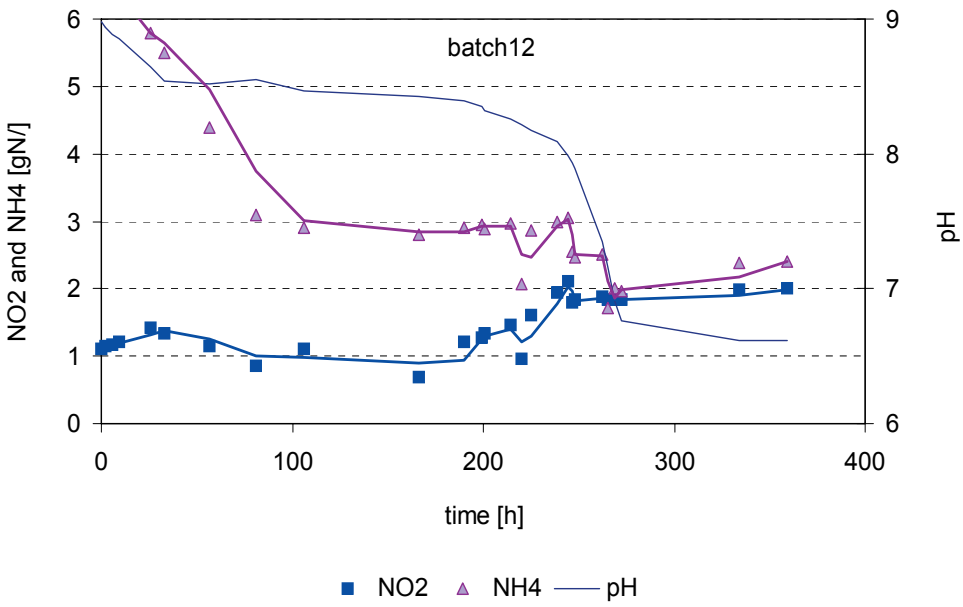


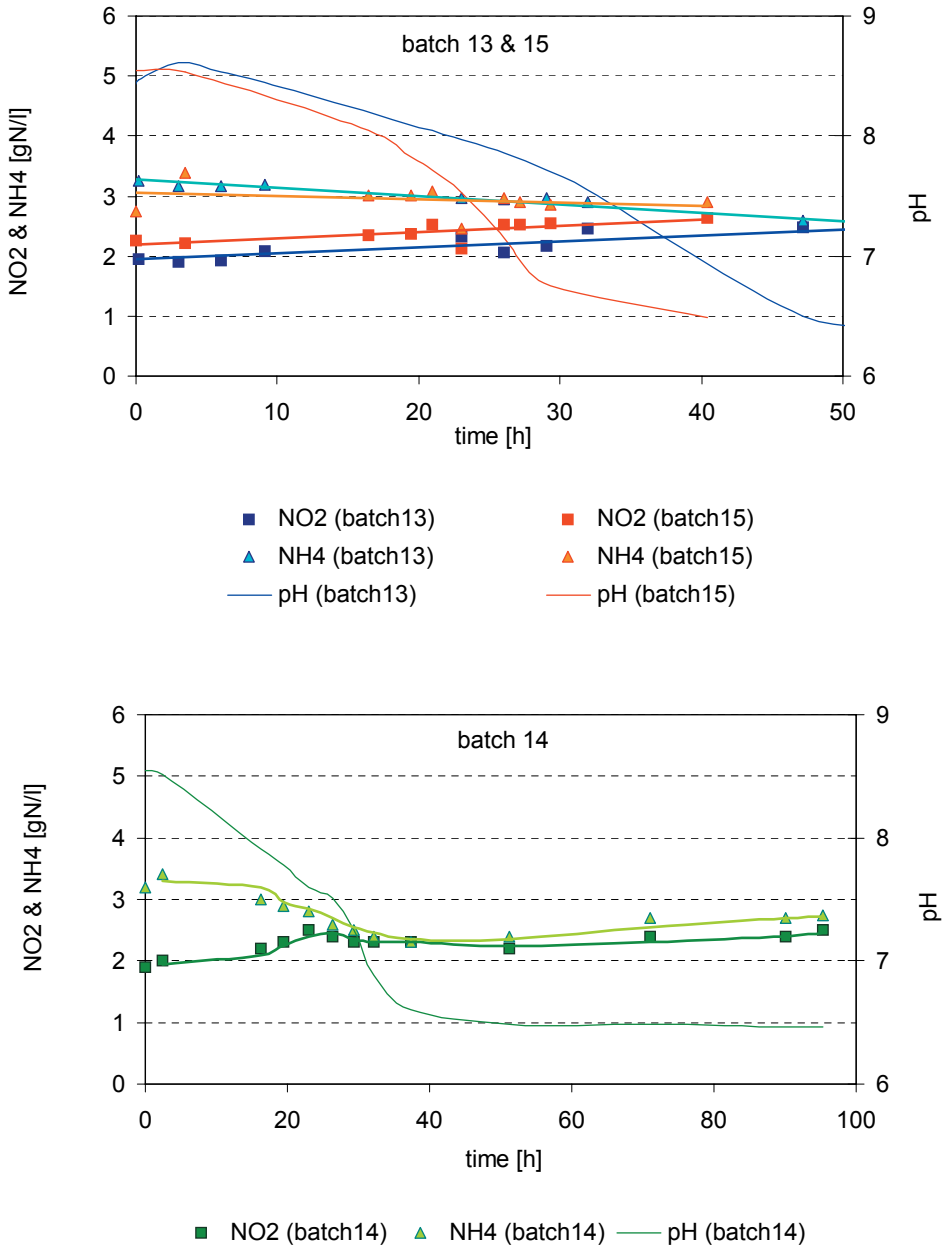
Figure 6 shows results from two batch tests where 5 litres of influent was changed for each batch. The influent contained un-hydrolysed urea to prevent a high pH and high ammonia concentration. The urea should then hydrolyse inside the reactor and nitritation should occur simultaneously. The pH increased initially, but then decreased and remained constant around 6.7 - 6.8. The concentration of ammonia (shown here only for batch 10) actually increased with time, instead of decreasing as would normally occur with nitritation. The difference between the ammonium and nitrite concentrations remained almost constant (i.e. equal slopes for ammonium and nitrite concentration over time). These two observations (constant pH and slowly increasing ammonium concentration) suggest that the rate of urealysis was equal to or less than the nitritation rate. Linear relationships with good correlation were observed for increases in nitrite and showed an equal nitritation rate for batches 10 and 11. However, from these results alone it cannot be concluded whether the nitrite production rate is a function of only the nitrifiying organisms or whether the rate was restrained in some way, due to slower urealysis and substrate limitation.

FIGURE 7 **RESULTS FROM SBR WHEN 5 LITRES OF INFLUENT CONTAINING HYDROLYSED UREA WAS CHANGED FOR BATCH 12**



For batch 12, 5 litres of influent was exchanged, but unlike the previous batch the urea in this influent was already fully hydrolysed after addition of urease. Figure 7 shows that the pH increases to around 9 at the start of the batch. Although a slight increase in nitrite was observed over the first day of operation, the rate of ammonium decrease was much higher. The ammonium concentration kept decreasing until around 3 gN/l (after 4 days). Nitrite was constant or slightly decreasing from day 2 to day 7. After the first day, the pH was also constant. No nitrate was formed. The loss in nitrogen can only be ascribed to ammonia stripping. At the same time, nitritation was inhibited. After 160 hours, total organic carbon tests from SBR samples revealed very low concentrations of active biomass. Extra biomass was added to the SBR (from CSTR effluent) and the pH started decreasing almost immediately, while nitrite increased again. However, when the pH was between 6.5 and 7 (after 260 hours) no further nitritation occurred, with ammonium and nitrite concentrations equal. The high pH and total ammonium (and/or nitrous acid) concentrations of undiluted urine seemed to be inhibiting nitritation.

FIGURE 8 INCREASES IN NITRITE AND DECREASE IN AMMONIA WHEN 2 LITRES OF INFLUENT CONTAINING HYDROLYSED UREA WAS CHANGED FOR BATCHES 13, 14 AND 15



For batches 13, 14 and 15, only 1 litre of influent was exchanged, but still with influent urea already hydrolysed. The pH increased to 8.5 after addition of influent, and then decreased rapidly between to pH 8 and pH 7 and remained constant at around pH 6.5. Nitrite increased linearly while ammonium decreased linearly. Figure 8 shows that nitritation rates for batches 13 and 15 were equal for all practical purposes, around 250 mgN/l_{react}.d. This is twice as high as the nitritation rate observed in batches 10 and 11.

One of the phenomena seen in batch 12 was observed again in batch 14, i.e. after the pH drops below 7, nitritation slows down, or stops completely. A further increase in nitrite depends on (slow) urealysis, which makes more alkalinity available, but which is also immediately consumed in nitritation, and the pH remains constant at 6.5. The second graph in figure 8 shows this phenomenon, with more or less constant ammonium and nitrite concentrations between 35 and 100 hours of operation.

In most of the batch experiments, the total nitrogen concentration was significantly higher than the sum of ammonium and nitrite concentrations, while nitrate was negligible. All effluent was stored in a single vessel and after collecting 20 litres concentrations were measured again. Although little nitrite was lost (presumably through normal denitrification), ammonium concentrations increased so that no real difference remained between the sum of ammonium and nitrite and the total nitrogen. It can be concluded that urealysis continued in the effluent vessel and indeed seems to be limiting the nitritation rate in some cases (e.g. batches 10 and 11). This could be a special condition of using synthetic urine, as most experiences with urine collection systems suggest that urea is always hydrolysed completely within a few days (Hanæus et al., 1997, Hellström et al., 1999 and Udert et al., 2003a).

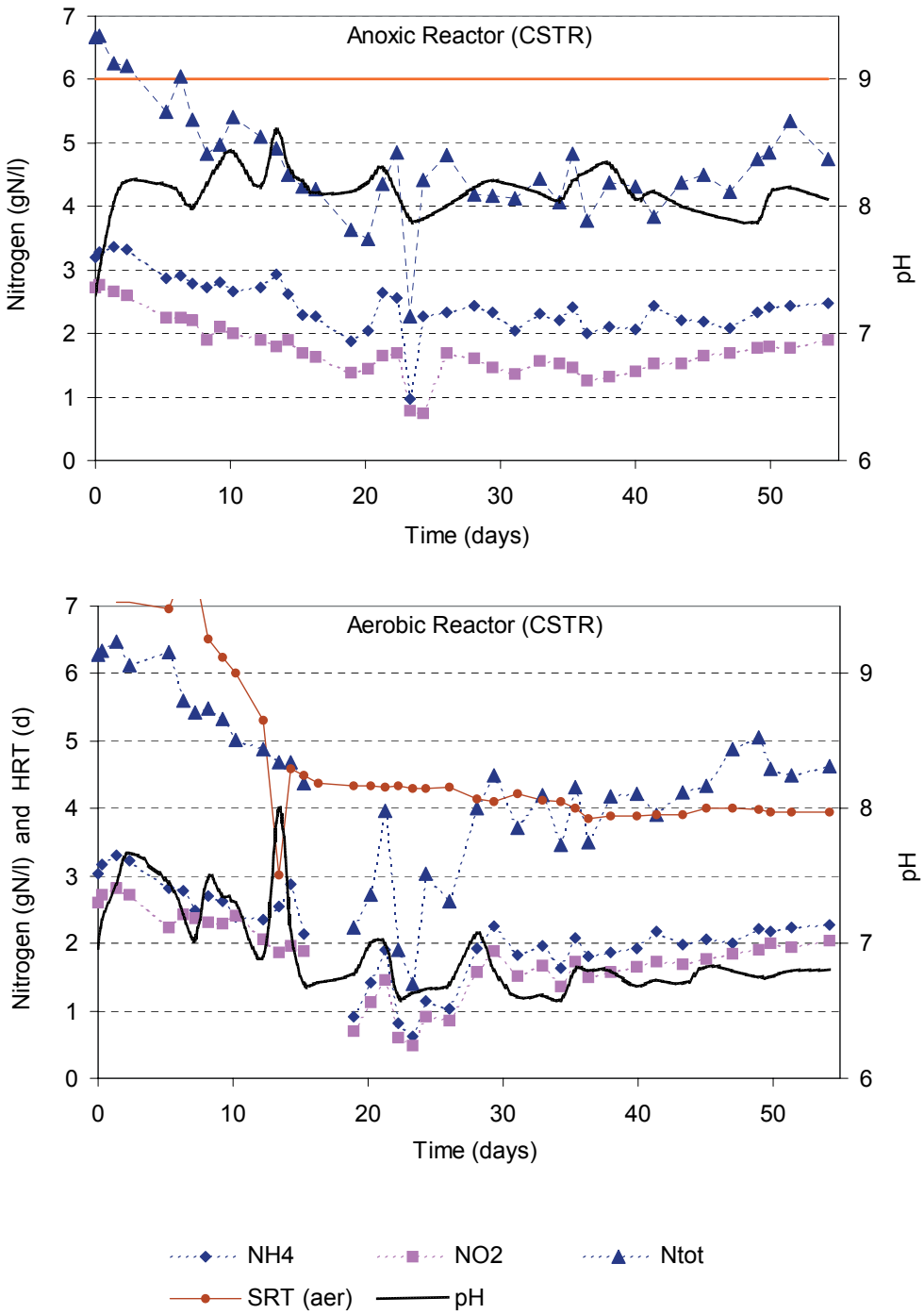
3.2 NITRITATION/DENITRIFICATION IN TWO CONTINUOUS STIRRED TANK REACTORS

Figure 9 shows the results from the CSTRs over a period of 60 days. In this period, the COD: N_{tot} ratio of 1 allowed for more denitrification than during start-up. After initial total nitrogen concentrations of 6.2 gN/l (aerobic) and 6.6 gN/l (anoxic), the total nitrogen concentration decreased until it reached around 4 gN/l in both reactors.

An erroneous increase in pump rate is reflected by the sharp increase in pH (in the aerobic reactor) around day 13. Some other operational problems were experienced due to pipe blockages and pump malfunction. At day 23, recycle back to the aerobic reactor ceased which consequently half-emptied the aerobic reactor. The reactor was filled with old effluent and pumps replaced. After these incidents, mechanical operation was stable.

In the CSTR, a nitritation rate of 1.1 gNH_4^+-N/l_{react}.d (based only on the aerobic reactor volume, where ammonium is converted) was maintained at the end of the experimental period. Udert et al (2003a) reported 0.8 gNH_4^+-N/l_{react}.d with more dilute urine (i.e less salt inhibition) and at a higher temperature (30°C).

FIGURE 9 RESULTS FROM CONTINUOUS STIRRED TANK REACTORS (FIGURES 1 AND 2), SHOWING NITROGEN REMOVAL AND EFFLUENT COMPOSITION (INFLUENT N = 6 G/L)



The removal of nitrogen in the anoxic zone of this set-up maintains a more neutral pH, and at the same time, the lower nitrogen (nitrite) concentration should increase the nitritation rate. However, an ideal influent solution for the anammox process could still not be produced, with NH_4^+:NO_2^- in the aerobic reactor effluent having a ratio of around 2:1.8. Virtually no nitrate was produced. The total suspended solids and volatile suspended solids concentrations were: 1.65 gTSS/l, 1.45 gVSS/l, at day 40 of operation, and 1.59 gTSS/l, 1.47 gVSS/l, at day 50 of operation.

At day 45 the recycle rate was increased from 8 l/d to 12 l/d, while the influent flow rate remained 0.4 l/d. This increase in the recirculation rate could not improve the NH_4^+:NO_2^- ratio. If anything, COD was less well utilized for denitrification (see total N concentration). When the recycle rate was turned down to 6 l/d, total N decreased somewhat.

After the reactors were decommissioned, the COD in the influent was measured again, and found to be only 4 gCOD/l, whereas at the beginning of the experiment it was 6 gCOD/l. It also had a foul smell, whereas at the beginning of the experiment it had a more "chemical" smell. Conditions were never sterile, and anaerobic digestion could have occurred. This decrease in COD (for whatever reason) would explain the steady increase in nitrite concentrations from day 40 onward, after the initial decrease.

3.3 ANAEROBIC AMMONIUM OXIDATION AND COMPLETE AUTOTROPHIC NITROGEN REMOVAL IN A FIXED BED BIOFILM REACTOR

3.3.1 START-UP OF ANAMMOX REACTOR

An overview of the FBBR's operation, from start-up until the end of the project, is presented in figure 10. Nitrogen removal capacity is expressed as milligrams nitrogen removed per day for each litre of reactor volume (mgN/l_{react}.d). After an initial period of little activity, N removal rate started to increase steadily from day 100 onwards. Influent salt concentrations were increased stepwise with each batch of feed mixture, and increases resulted in decreased activity (seen at days 121, 148 and 169). In these cases, the decreased removal rate also led to accumulation of nitrite in the system (at constant feed rate), which further decreased (or stopped) the N removal. Inhibition due to nitrite is discussed later. At normal salt composition (according to Griffith, 1976) the N removal capacity was 1000 mgN/l_{react}.d at day 194. During the start-up the temperature remained at around 24°C, while pH fluctuated between 7.5 and 8.0, depending on the influent pH. Biological growth during this period is illustrated by the difference between figure 11a (carrier material with some inoculum) and figure 11b (carrier material covered in biomass - day 230).

FIGURE 10 OVERVIEW OF N-REMOVAL PERFORMANCE OF THE FIXED BED BIOFILM REACTOR, FROM START-UP FOR ANAEROBIC AMMONIUM OXIDATION AND OPERATED WITH LIMITED AERATION BETWEEN DAYS 200 – 300 AND 400 – 500 (OPEN CIRCLES WITH LINES SHOW REMOVAL RATES UNDER ANAEROBIC CONDITIONS, WHILE DIAMONDS SHOW REMOVAL RATES UNDER ANAEROBIC CONDITIONS)

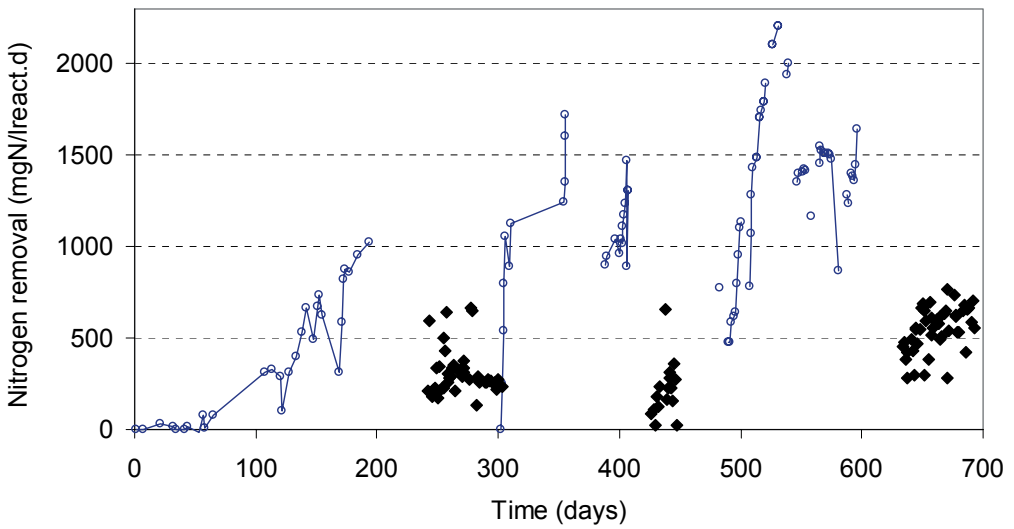
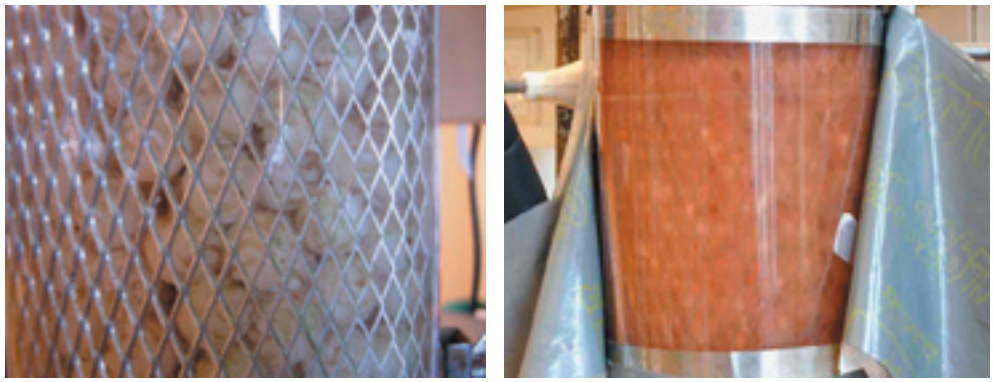


FIGURE 11 DETAIL OF CARRIER MATERIAL AND BACTERIA; A) SHORTLY AFTER START-UP, SHOWING LITTLE ANAMMOX BACTERIA, BUT ABUNDANCE OF ALGAE; B) BIOFILM GROWTH EIGHT MONTHS AFTER START-UP (DAY 230).



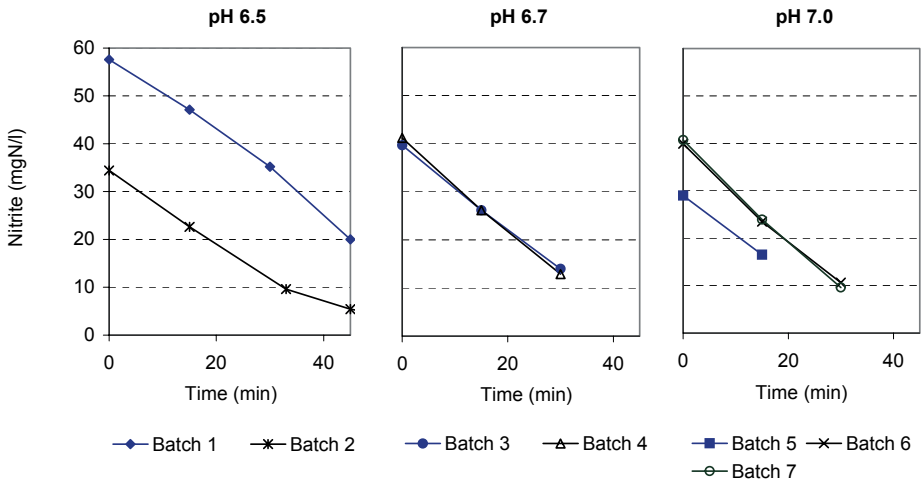
(a) (b)

From day 200 to 300, the FBBR was aerated as shown in figures 3 and 5a. During a period of 100 days, some nitritation occurred and nitrogen was removed. At this low pH (less than 7), ammonia evaporation can be excluded and no decrease in nitrate was measured, also ruling out heterotrophic denitrification. The N removal rate from the FBBR was only 300 mgN/l_{react}.d on average, but the values were too scattered to be conclusive. Nonetheless, simultaneous nitritation and anaerobic ammonium oxidation took place. This process was again attempted between days 400 and 500, but without improvement in the N removal rate.

3.3.2 EFFECTS OF PH ON ANAMMOX ACTIVITY AND N REMOVAL RATE

Between days 300 and 400, some experiments were done to determine the effect of pH on the FBBR as a whole. Anammox bacteria are known to have an optimum pH range of between 7 and 8.5. Outside this pH range, the activity drops drastically (Strous et al, 1997). Without any pH control during the nitritation of urine, a pH between 6.0 and 6.5 could be expected, as reported by Udert et al. (2003a). This was also observed in the operation of this FBBR (day 200 – 300), where the pH dropped to 6.5 – 6.7 due to nitritation. With pH control and under anaerobic conditions, the N removal rate of the FBBR as a whole was measured after a nitrite spike. Figure 12 shows the rates at which nitrite decreases in the FBBR, without any influent, for three different constant pH values, i.e. 6.5, 6.7 and 7. The N removal rates for these batch tests were 1 800, 2 200 and 2 500 mgN/l_{react}.d respectively.

FIGURE 12 RESULTS FROM BATCH TESTS TO INVESTIGATE THE INFLUENCE OF PH ON ANAMMOX ACTIVITY (NITRITE REMOVAL RATE INDICATED BY THE SLOPES)



Changes in ammonium and nitrate concentrations during these experiments could not be measured accurately, since both the ammonium and nitrate concentrations were around 300 mg/l, and the change would be within 10% of these values. The removal rate was based on nitrite removal and normal anammox stoichiometry. Nitrite concentrations decreased almost linearly, except at lower concentrations (15 mgN/l) below which the removal rate decreased at constant pH. Although the activity decreased significantly at lower pH, the N removal rate was still relatively high.

At day 530, the pH of the feed mixture was only increased to pH 6.0 (the pH of previous feed mixtures were increased to around 7 by bicarbonate addition). An immediate decrease in removal rate was observed, from operating continuously with pH 7.9 at 2 200 mgN/l_{react}.d, the N removal rate dropped to 1 400 mgN/l_{react}.d at a pH of 6.7 (day 551, figure 10). The FBBR was then operated continuously at 1 500 mgN/l_{react}.d at a pH of 6.45 – 6.50 (day 566 onwards). During this operation, the nitrite concentration in the bulk liquid was around 30 mgN/l (influent 1660 mgN/l). The removal rate at pH 6.5 was almost 25% lower than at pH 7. This is similar to the drop in removal rate observed in the experiments on the effect of pH (figure 12).

In general, a slight increase in pH due to anammox activity was observed. While the influent had a pH of 6.0 with hydraulic retention time of 2 days, the pH in the reactor at pseudo steady state remained between 6.45 and 6.50 during this period (day 566 - 600).

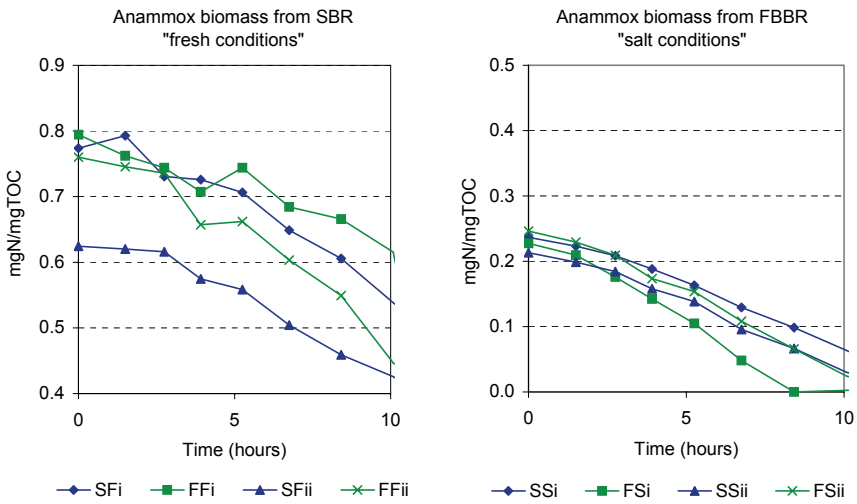
3.3.3 BATCH TESTS TO DETERMINE INFLUENCE OF VARYING SALT CONCENTRATIONS ON ANAMMOX BACTERIA

Figure 13 shows results from batch tests with anammox sludge from different origins: the FBBR from this study (bacteria grown in synthetic urine mixture referred to here as “salt bacteria”) and an older SBR (bacteria grown in normal fresh conditions referred to as “fresh bacteria”) under different conditions. The activity is expressed as N removed per total organic carbon (TOC). The sludge from the FBBR was taken from the bottom of the glass column where sloughed material built up. The FBBR biomass therefore contained a large fraction of inert material, which explains the general lower activity of the FBBR bacteria compared to SBR bacteria.

In the batches with fresh biomass, the difference between activity under salt and fresh water conditions are not too clear. Activity at salt conditions was slightly lower than activity of the same bacteria under fresh conditions.

In batches with salt biomass, a clear difference was seen between activity under salt conditions and fresh conditions. The slopes of the lines FSi and FSii (indicating fresh conditions/salt biomass) are steeper than that of SSi and SSii (indicating salt conditions/salt biomass). There seems to be a 30% increase in the N removal rate for bacteria grown in the FBBR in fresh water conditions compared to the salt conditions (urine). No grounds for the assumption that these bacteria grew accustomed to the salt concentration in their environment could be found. Bacteria that normally grow normally under fresh water conditions performed equally well under salt water conditions in comparison with their salt water counterparts. The bacteria in the FBBR are the same as those found in fresh water reactors, and simply have a 30% reduction in activity under the salt conditions of undiluted urine.

FIGURE 13 RESULTS FROM BATCH TESTS TO DETERMINE THE EFFECTS OF SALT CONCENTRATION ON ANAMMOX ACTIVITY (SALT-BIOMASS & FRESH-CONDITIONS, FRESH-BIOMASS & FRESH-CONDITIONS, ETC.)



3.3.4 INHIBITION OF ANAMMOX ACTIVITY DUE TO HIGH NITRITE CONCENTRATIONS

Although not planned, incidents of nitrite inhibition occurred and were documented. With sudden increases in salt concentration during start-up, nitrite accumulated in the reactor before the feed was stopped. In two cases (day 126 and 154, in figure 10), the nitrite increased to 120 and 200 mgN/l respectively. When the feed mixture was stopped, the nitrite decreased to zero within 24 hours. Apparently, a concentration gradient exists over the biofilm, where bacteria on the inside of the biofilm are exposed to lower nitrite concentrations and continue their activity.

During the period in which the reactor was aerated, the nitrite concentration increased to 250 mgN/l (after day 450). It is not clear why the nitrite concentration increased, but it could have been due to high oxygen concentration (inhibiting anammox N-removal). In this case, the influent also contained a fraction of nitrite, which accumulated in the reactor after anammox activity ceased. The nitrite concentration remained at around 250 mgN/l for two weeks, while influent continued. After influent was stopped, the nitrite concentration slowly returned to zero. Hereafter the reactor was operated anaerobically again, and high removal rates were achieved immediately (day 500 onwards).

Extreme nitrite concentrations occurred during a period where the reactor was stressed for high performance at low pH (on day 558 and 581 in figure 14). With 1660 mg NO_2^--N/l in the influent, the FBBR was overloaded and the nitrite concentration in the reactor increased to 1000 mg NO_2^--N/l over a weekend. The feed was stopped, but no decrease in nitrite concentration could be seen over two days. All liquid was drained from the reactor and kept separate. The reactor was flushed with tap water and then filled. The drained liquid was used as feed mix and relatively high N removal rates, around 1500 mgN/l_{react}.d, were reached again almost immediately (just before day 600).

3.3.5 REMOVAL EFFICIENCY OF THE FBBR

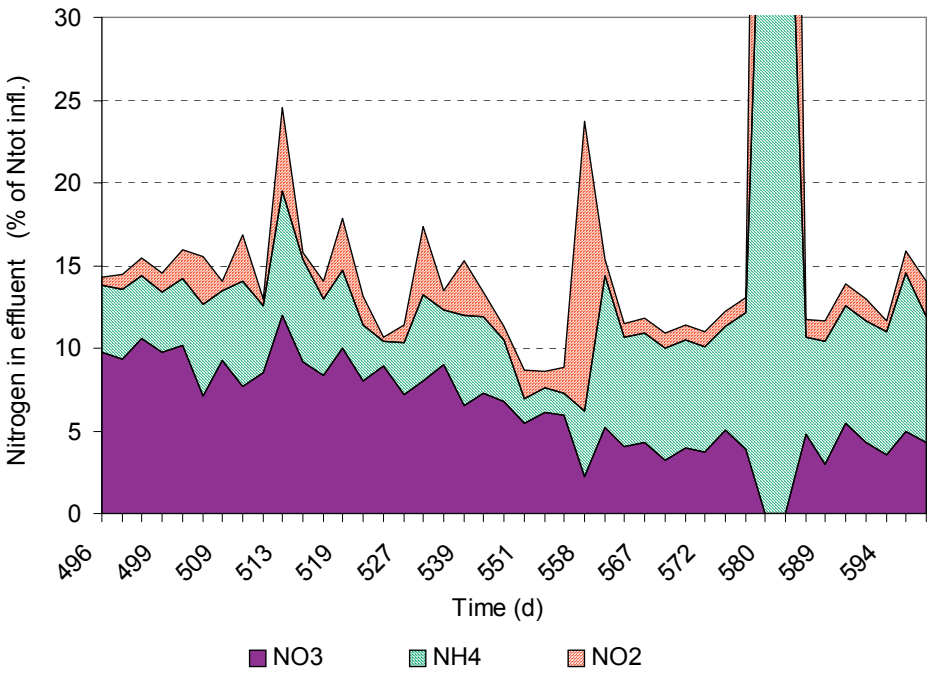
In the period from day 500 to 558, the influent to the FBBR was changed from the normal 1:1 ammonium-nitrite mixture to 1:1.2. During this period, very little nitrite and ammonium remained in the effluent, and effluent nitrate consisted mainly of nitrate (figure 14, from day 496 to 558). Over this period the N removal rate was gradually increased from 500 mgN/l_{react}.

d to 2000 mgN/l_{react}.d, but the effluent composition remained virtually unchanged (except for slowly decreasing nitrate concentration, discussed in the next section). For most of this period, the total N removal efficiency was above 85%.

Just before day 558, ammonium became the limiting substrate, leading to an accumulation of nitrite and process failure (NO_2^- = 450 mg/l). After this incident, 1:1 ammonium-nitrite was again fed to the FBBR. The relatively high ammonium fraction in the effluent was the direct result of this change of influent composition (day 560 –600 figure 14). Nitrite was then almost completely removed. Nitrate in the effluent was much lower than that expected from normal stoichiometry.

While the reactor was stressed for improved removal rates, nitrite became too high and process failure occurred after day 580. In this case the influent pump was not stopped and nitrite accumulated to 1,000 mgNO_2^--N/l over a weekend. When the influent was stopped, the nitrite concentration remained constant for 2 – 3 days. Only when the reactor was drained and filled with fresh water did activity return to normal after one week.

FIGURE 14 **REMOVAL EFFICIENCY OF FIXED BED BIOFILM ANAMMOX REACTOR, SHOWING EFFLUENT AMMONIUM, NITRATE AND NITRITE AS CUMULATIVE PERCENTAGES OF TOTAL INFLUENT NITROGEN**

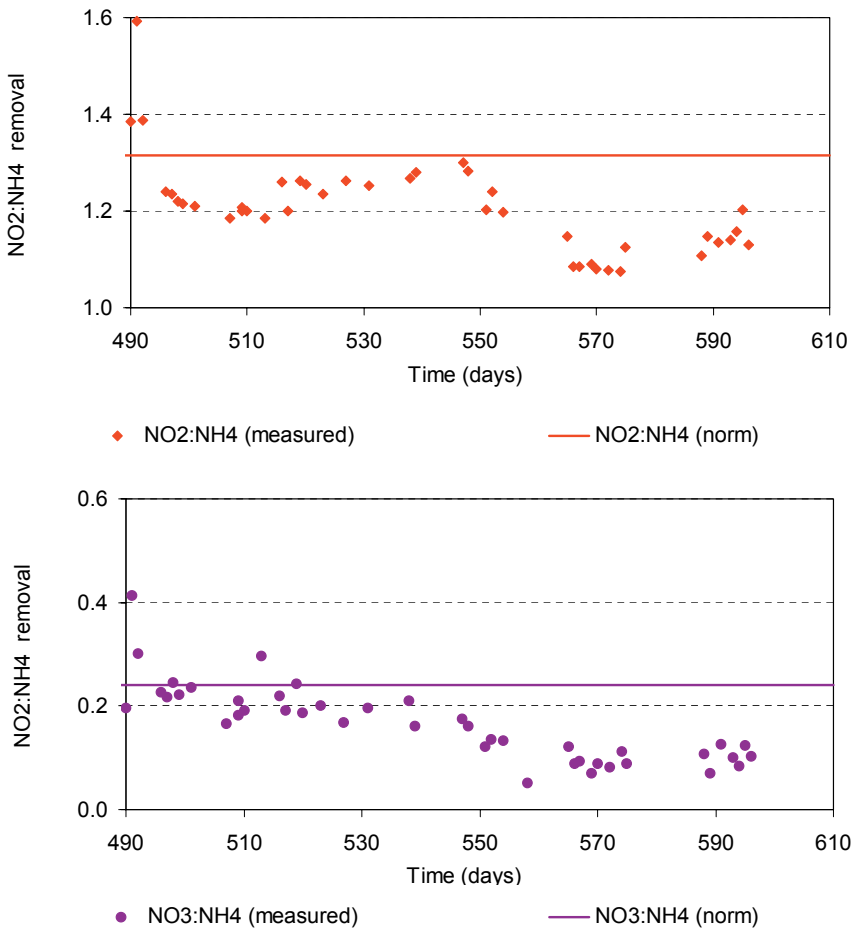


3.3.6 NITROGEN REMOVAL OTHER THAN ANAMMOX ACTIVITY UNDER EXTREME OXYGEN LIMITATION

During the anaerobic operation of the FBBR (days 300 – 400) an average NO_2^-:NH_4^+ removal ratio of 1.26:1 was maintained. Over the same period, the average ratio of nitrate production to ammonium removal was 0.2. These values correspond well with the normal annamox stoichiometry (see equation 3). However, figure 14 shows that the nitrate percentage in the effluent decreased from around day 530 onward. Figure 15 shows exact ratios of NO_2^-:NH_4^+ removal and NO_3^-:NH_4^+ production from day 490 to 600. The horizontal lines show the expected ratios, with the actual measurements plotted. There is a gradual decrease in the amount of nitrate produced (this was also seen in figure 14). The nitrate production decreased until

it was only 10% of the removed NH_4^+. The influent was stopped twice (to rule out the effect of effluent dilution), but the decrease in nitrate continued at a rate of 50 $mgN/l_{react}.d$. This was most likely due to some heterotrophic denitrification. At this stage of operation, the sludge age must have been in excess of 500 days and endogenous respiration would supply organic carbon for denitrification. However, this phenomenon alone could not completely account for the decrease in nitrate production. A decrease in growth rate could also have led to less nitrate production. This would also seem more likely at the lower operating pH of 6.5. Furthermore, the onset of the lower nitrate production coincides with the change in influent, which lowered the pH in the reactor (from day 530 onwards).

FIGURE 15 CHANGES IN PROCESS STOICHIOMETRY, SUGGESTING NORMAL DENITRIFICATION AND SOME OXYGEN LIMITED NITRIFICATION



Over the same period, there was also more ammonium removal than expected, relative to nitrite removal. Two explanations could be offered for this observation: First, some nitritation could occur, as the reactor was always exposed directly to atmosphere. This hypothesis was tested by stopping influent and measuring ammonium decrease over a period of one day. However, oxygen concentration during this period was extremely low, around 1% in the bulk liquid. Very little ammonium removal was measured (only 10 – 15 $mgN/l_{react}.d$), which was certainly not enough to account for the change in removal ratio shown in figure 15. This supports the hypothesis above that the growth rate had decreased, converting less nitrite to nitrate. Lower growth rate leads to relatively more ammonium removal and less nitrate production. We believe this second explanation is most likely correct.

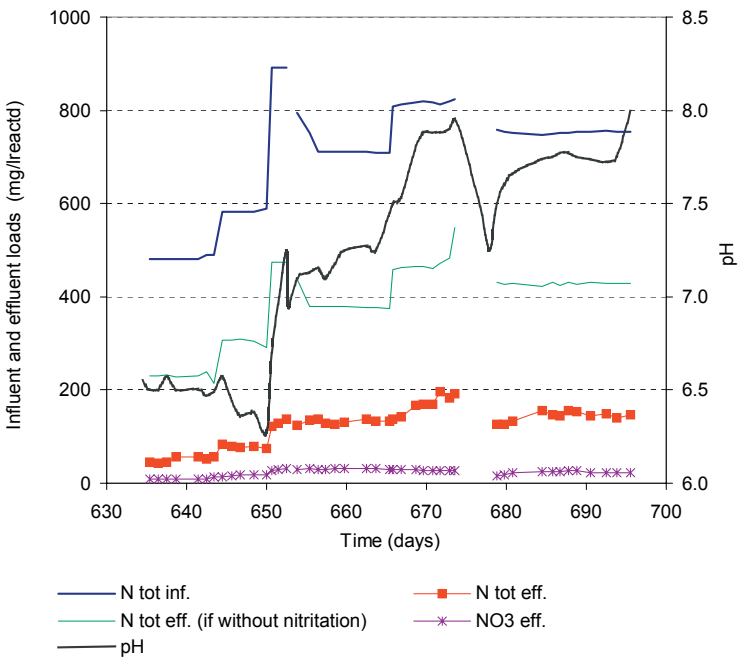
3.3.7 NITROGEN REMOVAL FROM URINE IN A SHARON/CANON REACTOR CONFIGURATION

Combined effluent from SBR batches, which contained 5 gNH_4^+-H/l and 2 gNO_2^--N/l, was fed continuously into the FBBR at around 0.5 l/d. Figure 16 shows results of N-removal in the FBBR. The total nitrogen influent load is expressed as $mgN/l_{react}.d$. Based on the influent composition and load (shown in figure 16) and assuming only the anammox N-removal activity (based on normal stoichiometry), an effluent concentration could be predicted, and is shown in figure 16 (Ntot eff. (if without nitritation), following the profile of the influent load. However, as was observed, the actual nitrogen concentration in the effluent was much lower under conditions with limited aeration (i.e. nitritation occurred). Nitrate concentrations were low throughout the experiment.

The pH reflects the removal of nitrogen from this reactor. Over the first few days of operation in this mode, the pH was constant, as was the total N in the effluent (until day 645). When the influent load was increased, the recycle rate was also increased to 900 l/d for additional aeration. The pH dropped to 6.25 on day 650, where the influent load was increased a second time, to 900 $mgN/l_{react}.d$. This was too high for the nitritation capacity, resulting in an immediate pH increase. When the influent flow was stopped (gap in influent load, figure 16), but aeration via recirculation was maintained, the pH dropped again, to 6.9 on day 653, concurrently with a small decrease in the total nitrogen concentration. The load rate was then maintained at around 700 $mgN/l_{react}.d$ and during this period the effluent total nitrogen concentration also remained constant. However, despite increases in recycle rate, the pH increased steadily and no additional nitritation occurred (nitrite concentrations remained below 10 mgN/l during this period).

When the pH reached 8 (day 672) the influent was stopped again, while recirculation was maintained. The pH then dropped to 7.3 over 4 days, again concurrently with a decrease in total nitrogen concentration. This decrease was only around 200 $mgN/l_{react}.d$. When influent flow was started again, a steady pH was maintained for a while, before the experiment was stopped after a sudden increase in pH and nitrite.

FIGURE 16 NITROGEN REMOVAL FROM FBBR DURING AEROBIC OPERATION (MECHANISM AS SHOWN IN FIGURE 5B) TREATING EFFLUENT FROM SEQUENCING BATCH REACTOR WITH $NO_{2\ IN}$ = 2G/L AND $NH_{4\ IN}$ = 5 G/L.



Oxygen was never limiting in the bulk liquid during this experiment. Although DO measurements were taken, probes were quickly covered in biomass, giving dubious results. The measurements were therefore more quantitative than qualitative. A drop in DO from top to bottom of the reactor was still evident. DO measurements, directly after the biomass was removed from probes, showed that oxygen concentrations of around 0.8 mgO_2/l at the top and 0.25 mgO_2/l at the bottom of the reactor (return line) were maintained. Overall, a nitrogen removal rate of around 600 $mgN/l_{react}.d$ was maintained for around 40 days.

3.3.8 SCALING INSIDE REACTOR WALLS

Upon decommissioning the FBBR, the walls were inspected and samples of scales found investigated under a microscope. None of the typical needle-like crystals associated with struvite were observed. Struvite normally forms at pH 9, but this reactor was operated in the range $6.5 < pH < 8$.

FIGURE 17 **SCALING ON THE INSIDE OF THE REACTOR WALL (LEFT), AND DETAIL OF SCALING (RIGHT)**

The scales were analysed with X-ray diffraction, but only amorphous states could be detected and no clear phases. Salts were most probably $CaCl_2$ or $CaCO_3$. In this case, with no evidence of struvite scaling inside the reactor, struvite could best be recovered as potassium struvite after biological treatment.

3.3.9 BIOFILM GROWTH AND SLUDGE DISTRIBUTION

FIGURE 18 **BIOMASS DISTRIBUTION ON CARRIER MATERIAL, WITH DETAIL (LEFT) AND BIOFILM GROWTH ON REACTOR WALLS VIEWED FROM OUTSIDE (RIGHT)**

The biomass distribution was also evaluated when the FBBR was decommissioned. Carrier material with biomass was removed layer-by-layer, from top to bottom, but no obvious differences in biomass distribution could be seen. The growth of biomass towards the centre of the column was also not obviously different from the growth towards the outside edge. Furthermore, it would not really be appropriate to speak of biofilm, as biomass accumulated in lumps within the carrier material's grooves (see detail in the left of figure 18). The reactor wall was completely covered in a thick biofilm of 0.5 to 1 mm (see right hand side of figure 18). This occurrence of biomass further indicates the effectiveness of biofilm as a kind of filter where individual organisms are protected in adverse environmental conditions, specifically high nitrite and dissolved oxygen concentrations.

4

DISCUSSION

4.1 GENERAL: EFFICIENT BIOLOGICAL N-REMOVAL

The efficiency of biological N-removal processes should not only be expressed in terms of effluent products (removal efficiency), but also with regard to conversion rate and resource utilisation. Table 2 compares results from this study with recent developments in nitrogen conversion and removal. All these processes are superior to conventional technology (e.g. modified UCT-system, van Loosdrecht *et al.*, 1998).

NITRITATION

Nitritation processes without pH control normally produces a solution with a NH_4^+:NO_2^- ratio close to one. The nitritation process produces two moles of H^+ for each mole of NH_4^+ oxidised (reaction 1). Therefore, all alkalinity is consumed when 50% ammonium is oxidised, and when the pH drops below 7 the biological process stops. Still, this makes a reasonably good influent for anaerobic ammonium oxidation (anammox), or even conventional denitrification. If the pH is controlled, relatively more nitrite can be produced, which would be an ideal influent for the anammox process (Fux *et al.*, 2002). The best overall removal efficiency for nitritation and anammox reactors was therefore also reported by Fux *et al.* (2002). In this study, nitritation in the SBR was rather poor, with a final NH_4^+:NO_2^- ratio of 70:30. Although the NH_4^+:NO_2^- ratio was always close to one at the end of each batch, not all urea was hydrolysed and the urealysis continued inside the effluent collection vessel. On the other hand, urine with completely hydrolysed urea can be nitritised to produce an NH_4^+:NO_2^- effluent ratio of one (Udert *et al.*, 2003), either in a SBR or in a CSTR.

TABLE 2 **OVERVIEW OF N-CONVERSION/REMOVAL IN VARIOUS REACTOR CONFIGURATIONS**

Process	Reactor type; Size (litres)	Temp (°C)	Effluent products (% of influent N_{tot}) NH_4^+; NO_2^-; NO_3^-; N_2	Conversion/ removal rate ($gN/m^3_{react}.d$)	Reference
Advanced BNR	UCT; $8x10^6$	12-15	2; 0; 18; 80	40	Loosdrecht, 1998
Nitritation	CSTR; $2x10^3$	30	42; 58; 0; 0	350	Fux, 2002 (1)
	CSTR; 2.8	30	49; 51; 0; 0	790	Udert, 2003
	SBR; 7.5	24-25	49; 51; 0; 0	280	Udert, 2003 (2)
	SBR; 10	18-19	70; 30; 0; 0	190	This study (3)
Nitritation/	SBR; $1.8x10^6$	35	10; 0; 0; 90	300	Kempen, 2001
Denitritation (4)	SBRs;	21	40; 0; 0; 60	320	Jenicek, 2004
(SHARON)	CSTRs;1.5+2	23-24	37; 33; 0; 30	1,000	This study
Anammox	FluidBR;		5; 0; 10; 85	4,800	Graaf, 1996
	Gaslift; 1.8	30-33	10; 0; 7; 83	8,900	Sliekers, 2003
	SBR; $1,6x10^3$	30	0; 0; 11; 89	600	Fux, 2002 (5)
	FixBR; 3.5	26-27	10; 0; 10; 80	3,500	Fux, 2004
	FixBR; 5.8	23-24	6; 1; 7; 86	2,200	This study
CANON	Gaslift; 1.8	30-33	58; 0; 3; 39	1,500	Sliekers, 2003
	FixBR; 5.8	23-24	14; 0; 3; 83	520	This study (6)

BNR = Biological nutrient removal, UCT = modified UCT-process, excluding clarifier volume in conversion rate, CSTR = Continuous stirred tank reactor, SBR = Sequencing batch reactor, FluidBR = Fluidised bed reactor, FixBR = Fixed bed reactor.

1) Conversion rate was limited by loading rate
2) Average conversion rate for complete batch. Maximum conversion rate during aerobic period up to 1,300 $gN/m^3_{react}.d$.
3) Average conversion rate for complete batch. Maximum conversion rate during aerobic period up to 340 $gN/m^3_{react}.d$.
4) For the three cases, nitritation rate is based on the aerobic retention time.
5) Average N-removal rate for complete batch. Maximum N-removal rate during nitrite-containing periods was up to 2,400 $gN/m^3_{react}.d$.
6) Influent contained 5,780 gNH_4^+-N/m^3 and 2,440 gNO_2^--N/m^3 (effluent from nitritation SBR - this study). N-removal rate was only around 300 $gN/m^3_{react}.d$ without any influent nitrite.

NITRITATION/DENITRIFICATION

Denitrification with nitrite as electron acceptor justifies the use of external carbon sources, such as methanol. However, the primary reason for denitrification in the SHARON process was pH correction. Up to 90% of NH_4^+ can be oxidised with denitrification (methanol dosing) as a means of pH correction (Van Kempen *et al*., 2001). Primary settled sludge was adequate for some denitrification, but the efficiency is lower than with methanol (Jenicek *et al*., 2004). If up to 90% of NH_4^+ had to be oxidised, the process was slowed down considerably while utilizing the fraction of slowly degradable organics in primary sludge. In this study, treatment of 50% diluted and completely urealysed urine in a CSTR gave superior results compared to the SBR. Around 30% of the total nitrogen in synthetic urine was removed in the anoxic compartment, with recirculation from the aerobic compartment, and with $COD:N_{tot}$ = 1 in the influent urine. In this way, the pH was corrected somewhat (to around 6.8 in the aerobic zone) and relatively more ammonia was oxidised (63% at 24°C) than in the case of a single CSTR for urine treatment (51% at 30°C, Udert et al., 2003). However, because of denitrification the effluent $NO_2^-:NH_4^+$ ratio remained less than ideal (on average the $NO_2^-:NH_4^+$ ratio was 0.9). Although the ideal ammonium nitrite mixture ($NO_2^-:NH_4^+$ = 1.2 – 1.3) could not be produced in this experiment, it would be less important considering the substantial amount of nitrogen already removal in this process. Moreover, a very high conversion rate of 1,000 $gN/m^3_{react}.d$ was achieved.

ANAMMOX

The fixed bed reactor in this study proved to be an excellent system for almost complete sludge retention at low temperature (24ºC), high salt concentrations (ionic strength = 0.28) and without any control mechanisms. With nitrogen removal rates of up to 2,200 mgN/l_{react}. d, this reactor compares well with available literature on anammox reactors at temperatures of 30ºC, without any salt stress and with pH control (table 2). The effects of pH and temperature on anammox were documented by Strous *et al.* (1999), suggesting a reduction in activity of more than 50% between optimal temperature (30-35ºC) and 24ºC. Even so, and without the ideal influent solution, high nitrogen removal rates as well as high nitrogen removal efficiencies (around 85%) were achieved in this experiment over long periods under adverse conditions. Long operation in the biofilm reactor (more than one year) resulted in endogenous decay of autotrophic biomass, which led to some conventional heterotrophic denitrification of the nitrate produced in the anammox metabolism (around 5% of total removal and included in the overall removal efficiency mentioned above).

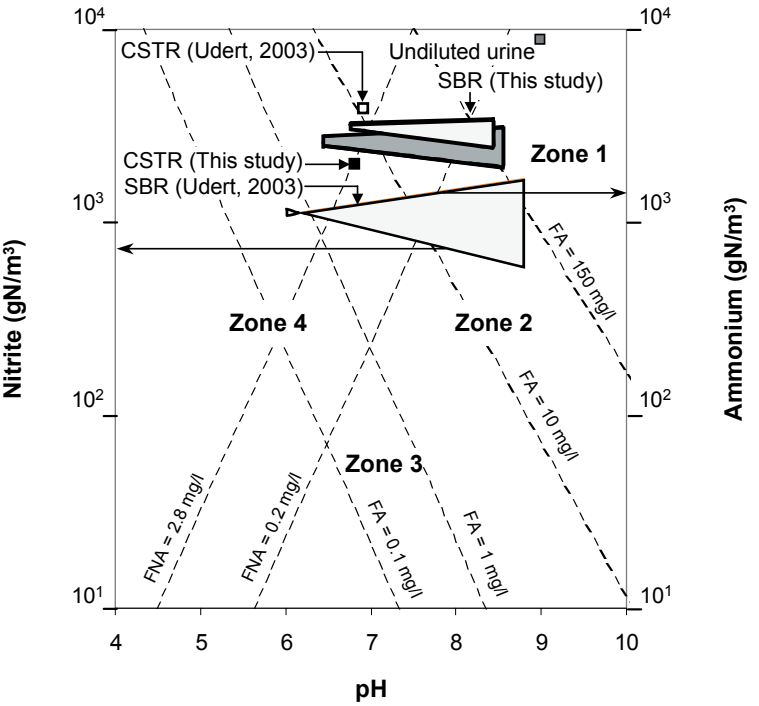
CANON

Although the CANON process is hailed for its potential as a highly efficient single reactor, no convincing evidence supports the claims yet. As was done in Sliekers *et al.* (2003), the same reactor was operated here as an anaerobic reactor (Anammox) or aerobic reactor (CANON). In both cases the nitrogen removal rate under anaerobic conditions was four to five times higher than under aerobic conditions. This is hardly surprising, because the dissolved oxygen concentration, which inhibits anammox organisms, must be limited in the CANON process, but at the same time, this would limit the nitritation process. In both CANON studies, nitrite was therefore always the limiting substance, resulting in removal rate well under the anammox capacity.

4.2 INHIBITION OF AMMONIUM AND NITRITE OXIDISING ORGANISMS

Nitritation of supernatant can only be obtained at a high temperature (30ºC) and short sludge age to ensure continual wash out of nitrite oxidisers (e.g. Fux *et al.*, 2002). This study, however, has confirmed the findings of Udert et al. (2003) and shown that even with long solids retention times, virtually no nitrate was produced in a SBR. Inhibition of nitrifiers by free ammonia (FA) and free nitrous acid (FNA) explains this fact. Figure 19 shows the operational range of urine treatment reactors of this study and Udert et al (2003) superimposed on the inhibition chart first introduced by Anthonisen *et al*. (1976).

FIGURE 19 **OPERATIONAL RANGE OF REACTORS FOR NITRIFICATION OF URINE, SUPERIMPOSED ON THE NITRIFICATION INHIBITION CHART PUT FORWARD BY ANTHONISEN ET AL. (1976): ZONE 1, NITRIFICATION INHIBITED BY FREE AMMONIA (FA); ZONE 2, ONLY NITRITE OXIDISERS INHIBITED BY FA; ZONE 3, COMPLETE NITRIFICATION; ZONE 4, NITRIFICATION INHIBITED BY FREE NITROUS ACID (FNA)**



Complete nitrification can be expected in zone 3 of the inhibition chart, where neither inhibition due to high FA or FNA, nor limitation of these substrates occurs. The normal SHARON reactor has a total nitrogen concentration around 100 gN/m^3 at pH 6.9-7.0 (e.g. Van Kempen *et al*. 2001) and is therefore positioned in zone 3. The elimination of nitrite oxidisers consequently relies fully on short sludge ages. In zone 2, inhibition of ammonium oxidisers starts from NH_3 = 10 g/m^3 upwards, while in zone 4 inhibition starts from HNO_2 = 0.2 g/m^3 upwards (indicated by diagonal lines). Different nitritation reactors, where the production of ammonium-nitrite for a subsequent anammox reactor is desired, have NH_4^+ and NO_2^- concentrations both around 500 gN/m^3 (e.g. Fux *et al*., 2002). These reactors are positioned above zone 3 at neutral pH, and between zones 2 and 4, in a critical position on the graph where inhibition will not completely prevent nitrite oxidation. Nitrite oxidisers must therefore still be washed out at short sludge ages.

Results from the SBR by Udert *et al*. (2003), with SRT > 40 days, are plotted in figure 19 for NO_2^- (read to the left) and NH_4^+ (read to the right) over pH. The batch starts with high NH_4^+ and low NO_2^- concentrations at pH 9 and proceeds through oxidation to equal concentrations of NH_4^+ and low NO_2^- at pH 6. Because NH_4^+ is only converted to NO_2^- the lines are mirrored around the horizontal. The interesting point is that the batch that starts with NH_3 > 150 mg/l, which is in zone 1 where nitrification is inhibited by FA. The batch then ends with HNO_2 > 2.8 mg/l, which is in zone 4, where nitrification is inhibited by FNA. Between these extremes, the batch process continues through zone 2, where only nitrite oxidisers are inhibited by FA. In other words: if nitrite oxidisers are not inhibited by FA at high pH, they are inhibited by FNA at low pH. Results from the SBR in this study further support this explanation. These batches were done with less dilute urine, but with smaller exchange volumes. Consequently, higher NH_4^+ and NO_2^- concentrations occurred, with higher FA and FNA concentrations throughout the batch, but with slightly lower initial pH. In this case, the NH_4^+ and NO_2^- lines were not

mirrored around the horizontal, as some urea was always being hydrolysed. Higher FA and FNA concentrations were maintained throughout the batch and could partly explain the much slower conversion rate of this study, compared to Udert *et al.* (2003) as shown in table 2. Nonetheless, the extreme FA and FNA concentrations at the beginning an end of each batch were not significantly different from that of Udert *et al.* (2003), suggesting that the principle put forward by Anthonisen *et al.* (1976) is valid beyond the scope of their experiments. When more concentrated urine was used (or higher exchange volumes), the nitrification process failed completely. The chart shows the position of undiluted and hydrolysed urine at pH 9. Under these conditions, the NH_3 concentration approached 1,000 mg/l and nitritation was completely inhibited.

The CSTR in this study had a better NH_4^+ oxidation rate at 24ºC (1,000 $gN/m^3_{react}.d$) than that of Udert *et al*. (2003) at 30ºC (790 $gN/m^3_{react}.d$). Both reactors had NH_4^+:NO_2^- ratios close to one and are shown as squares in figure 19. Urine was roughly 50% diluted in both cases and effects of different ionic strengths can be ruled out. The explanation for the improved conversion rate of this study is probably a combination of both the lower FA and the FNA concentrations, because of denitrification via nitrite. This set-up is promising given the high ammonia conversion rate and the stability of the process. Since the SBR results showed no nitrate accumulation at long sludge ages, a CSTR could also be designed with some form of sludge retention to maintain sludge ages of 20-30 days, which would result in even more stable processes.

4.3 INHIBITION AND NON-INHIBITION OF ANAMMOX IN A FIXED BED REACTOR

The effect of salt concentration on anammox bacteria have not yet been thoroughly studied. However, anammox exists even in sea water and have been found to play an important role in the N cycle in oceans (Thamdrup and Dalsgaard, 2002 and Dalsgaard and Thamdrup, 2002). As results in this study have shown, a higher salt concentration would indeed inhibit the activity of anammox organisms: around 30% with ionic strength of 0.28 (equivalent of undiluted urine). This is analogous with results from research on effects of salt on nitrifying bacteria (Moussa, 2004). Although no grounds were found to belief that the organisms adapted to the salt environment in this study, it was still possible to start and operate the process with high salt concentrations.

The fixed bed anammox reactor not only showed that N can be removed from urine, but also led to macro-observations that differed considerably from previous studies on anammox. After an anammox population was cultured as biofilm under adverse conditions, it survived several incidents normally thought to be fatal. In general, biofilms forming on fixed beds create heterogeneous environments where local conditions differ from that in the bulk liquid and life becomes possible under conditions normally believed to inhibit or kill specific organisms. It would be the physical/chemical phenomena that occur due to the fixed bed and biofilm structure (influencing mass transfers, concentration gradients, etc.) rather than microbial differences (e.g. special adaptation via special enzymes), which enable operation in a hostile macro-environment. This hypothesis offers an explanation for some of the observations made in this study that are not consistent with the available literature.

High concentrations of nitrite were maintained during continuous operation and a few incidents of extreme nitrite concentration were recorded. When the anammox reactor was operated for a period of 30 days with pH = 6.5, nitrite concentrations of 15 – 30 gNO_2^-N/m^3

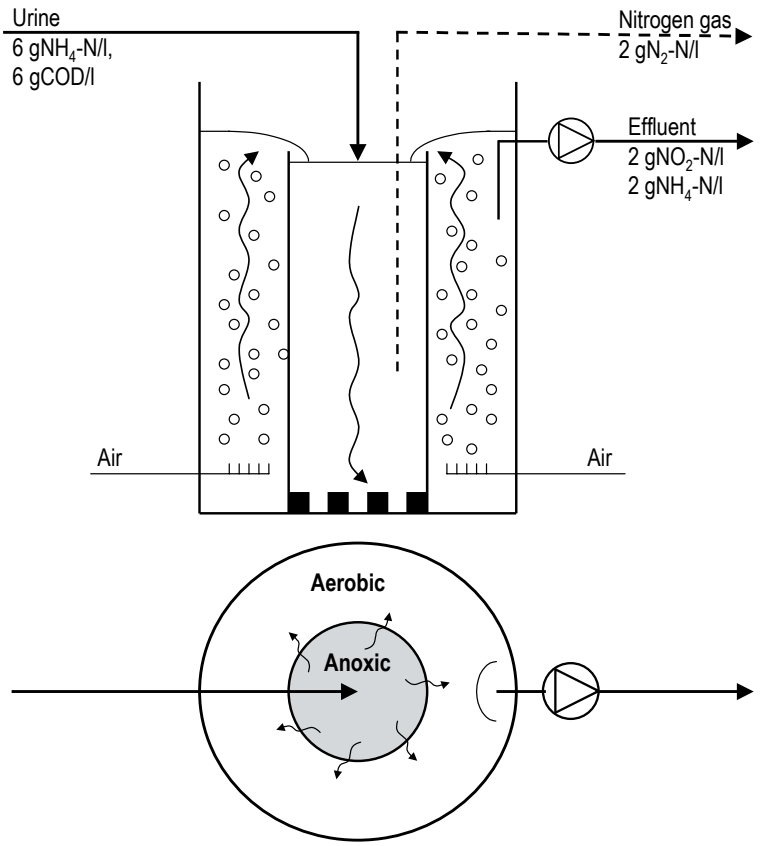
was sustained with little problems. As with nitrifiers, one would expect free nitrous acid and not nitrite to be the inhibiting substance. Figure 19 made the relationship between HNO_2, NO_2^- and the pH clear. The fixed bed reactor of this study was successfully operated with a bulk liquid having 0.04-0.08 mgHNO_2/l. Fux *et al.* (2002) reported inhibition at 60 gNO_2^--N/m^3 with pH 7.5 (i.e. 0.015 mgHNO_2/l), after which the reactor's removal rate was 50% lower for two weeks. The fixed bed reactor in this study could still be operated without a decrease in removal rate at nitrite concentrations of 60 – 70 gNO_2^--N/m^3. This can also be seen from figure 12 for a pH of 6.5. Normally, nitrite inhibition is expected to be complete and irreversible at around 100 gN/m^3 (Strous *et al.* 1999). In this study, several incidents of nitrite accumulation above this limit were recorded (including cases of 200 and 450 gNO_2^--N/m^3). In these cases, the reactor was self-regulating in the sense that the nitrite concentration slowly decreased to zero when the influent was stopped. It also seems as if an anammox biofilm (or at least some organism inside the biofilm) is resistant to extreme nitrite concentrations. In one incident, a nitrite concentration of 1,000 gNO_2^--N/m^3 accumulated in the bulk liquid. In this case, the concentration remained this high for 2 days, i.e. no more activity. Still, when the reactor was emptied completely and filled with clean water, the removal rate recorded before the incident was achieved again after one week.

During the anaerobic operation of the reactor, no attempts were made to prevent oxygen from entering the reactor (e.g. covering the reactor, or bubbling with N_2/CO_2 gas). We can confirm the results of Fux *et al.* (2002) that such measures are unnecessary, because a diverse population (e.g. ammonium oxidisers) are always likely to be present and will deplete available oxygen. During the aerobic periods, oxygen concentrations in the bulk liquid were maintained far in excess of the inhibitory concentrations, which is around 0.1% of oxygen saturation. An oxygen gradient from top (aerated area) to bottom of the reactor was observed, but even at the bottom, concentrations were always around 1-5%. The biofilm in this study probably enabled higher dissolved oxygen concentrations, but simultaneous nitritation was still limiting the overall process rate severely. Some clogging inside the fixed bed structure and the resulting poor mixing probably limits the oxygen transfer (air was never introduced directly into the reactor, but liquid was aerated with the recycle flow), which would also explain the growth and survival of anammox organisms under extreme oxygen and nitrite conditions in the bulk liquid. Although growth of anammox continued, this was at a much lower rate, based on NO_3^- production.

4.4 IMPLEMENTATION OF URINE TREATMENT AND WASTEWATER INTEGRATION

Biological treatment of undiluted urine in an SBR was not possible in this study. This has been explained within the framework of free ammonia (FA) and free nitrous acid (FNA) inhibition on ammonia and nitrite oxidisers. It should be possible to treat undiluted urine in a CSTR set-up as described here, where 30% N is removed. However, such a system could be expected to be severely rate limited. Salt stress also plays an inhibiting role in the treatment of undiluted urine. A decrease of between 20-30% in activity of both ammonium and nitrite oxidisers could be expected with undiluted urine (Moussa, 2004).

FIGURE 20 **PROPOSED BIOLOGICAL REACTOR CONFIGURATION FOR NITRITATION AND DENITRIFICATION OF URINE, WITH ANOXIC COMPARTMENT IN CENTRAL COLUMN (DOWN FLOW) AND AEROBIC COLUMN IN OUTER COLUMN (UP FLOW WITH AIR)**



If urine were diluted by 50% (e.g. some toilet flush water), all biological treatment techniques would be improved, and the inhibition due to FA and FNA would affect only nitrite oxidisers. The use of some flush water would therefore improve biological N-removal on a local scale. Still, undiluted urine could also be mixed with supernatant from anaerobic digestion. This strategy has the double advantage of treating a bigger waste stream with more efficient technology. In such a case, urine should be collected undiluted, for transport and process efficiency. With longer storage, urea hydrolysis (which limited the reaction rates in some of the experiments from this study) could also be expected to be complete.

The system of choice would then be a nitritation/denitrification reactor (e.g. with airlift for internal recirculation, as shown in figure 20), followed with a fixed bed anammox reactor. Despite its conceptual interest, the fixed bed reactor operated as CANON in this study performed worse than the two-reactor system (SHARON/Anammox). The control of a CANON system requires intensive supervision. Operation of anammox in a fixed bed under anaerobic conditions (this study) was more robust, required almost no control and in the end was more efficient. Our results suggest that an overall removal rate for the combined SHARON/Anammox process of between 900 - 1000 $gN/m_{react}.d$ (based on 85% N_2 removal in the anammox process) is possible.

5

PRELIMINARY DESIGN CONSIDERATIONS AND PARAMETERS

The combination of anoxic and aerobic zones for treatment of urine could be combined in a column reactor where upward flow is generated through aeration and downward flow through influent urine, as illustrated in figure 20.

Nitritation requires 0.8 litres of aerobic reactor volume for each gram of ammonium per day (or 1.25 $gN/l_{reactr}.d$) to be oxidised to nitrite (with hydraulic retention time of 4 days). This relates to 10 litres per person per day, where all urine is collected separately.

The anammox process, in a fixed bed biofilm reactor, requires 0.5 – 0.7 litres of reactor volume per gram nitrogen gas to be removed per day (or 1.5 – 2 $gN/l_{reactr}.d$). This relates to 6 – 8 litres per person per day, where all urine is collected separately. This volume would be less if nitrogen were removed in a denitrification step with the nitritation, but the volume saved in the anammox process would be required in denitrification.

In total, 16 – 20 litres reactor volume per person would be required for biological nitrogen removal from urine (if all urine were collected separately). This compares very well with a conventional wastewater treatment plant, where 200 - 300 litres per person are required.

Care should be taken to design nitritation reactors with material resistant to the severely corrosive environment of aerated urine.

Odour problems are unlikely in functional reactors. When urine was aerated, it had smelled similar to humus, while even the synthetic urine had a foul smell after urealysis and degradation of organic material.

Biomass clogging was not a serious problem in this study, as shown with the equal distribution of biomass after the decommissioning of the fixed bed reactor. Even though small carrier balls (17 mm diameter) were used, one could opt to use larger carrier material (e.g. 50mm) to be on the safe side when scaling up the process.

Formation of salts and scales were also not a serious problem and no evidence of struvite was found in the fixed bed reactor. Furthermore, the synthetic urine used in this study had a low pH and not much precipitation occurred in the feed vessel, but some occurred in the fixed bed reactor where the pH was elevated. In normal urine collection systems, one could expect a greater proportion of the scaling to occur in the collection and storage system. Controlled struvite crystallization after biological N-removal would enable recovery of potassium.

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CHAPTER 4

INTEGRATION OF PROCESSES FOR THE TREATMENT OF WASTEWATER AND SOURCE SEPARATED URINE

CONTENTS

1

INTRODUCTION

The traditional concept of sewer networks and central treatment plants is increasingly being criticised. The criticism is normally based on the concept "sustainability". Sustainability is an umbrella term that includes various problems such as effluent quality, resource consumption, operation and capital costs, land area required and nutrient losses. However, suspicions arise when "superior" alternatives are proposed without any quantitative comparison between the alternative and conventional systems. A problem with most discussions on sustainable wastewater treatment is the lack of transparent and quantitative data.

The amounts of total nitrogen (N_{tot}) and total phosphorus (P_{tot}) in municipal wastewater are normally much higher than required for cell synthesis of the bacteria in activated sludge. Only around 20% of the influent nutrient loads (N_{tot} and P_{tot}) are removed through cell synthesis and excess sludge removal (Tchobanoglous and Burton, 1991, Henze et al., 2002). Effective nutrient removal therefore requires more complex treatment processes. Nitrogen is traditionally removed by nitrification and denitrification steps, requiring oxygen and an organic energy source respectively. Phosphate is removed either through chemical precipitation or through biological excess phosphate removal. Up to 80% of the N_{tot} load and around 45% of the P_{tot} load in municipal wastewater, originate from urine (Larsen and Gujer 1996; Hanæus et al. 1997). Separate collection of urine therefore presents interesting alternatives to nutrient removal (Larsen and Gujer 1996; Otterpohl et al. 1999; Larsen et al. 2001).

Effects of separate urine collection on an optimised biological N and P removal process have been discussed previously (Wilsenach and Van Loosdrecht 2004). It was found that in current wastewater treatment plants the N_{tot} effluent concentration would decrease to between 2 – 3 gN/m^3, if 50% of all urine were collected separately. At urine separation efficiencies above 50%, the effluent concentration would not improve much more, while the relative contribution of denitrification to nitrogen removal was found to decrease drastically. On the other hand, if some urine were collected separately, the removal of organic material through primary sedimentation would not restrict the denitrification capacity.

The goal of this study is to further evaluate the improvement of central wastewater treatment plants through separate urine collection. This is done by a comparison of new treatment options with more conventional technology. In the previous evaluation (Wilsenach and Van Loosdrecht 2004), neither the treatment of the separated urine, nor sludge treatment was investigated. Here we propose a process configuration for the central treatment of wastewater, excess sludge, supernatant and separately collected urine. The proposed system will be referred to as the IntWUT process (Integrated Wastewater and Urine Treatment) and will be described in the following section.

A reference scenario for this evaluation is defined by the Biological/Chemical Phosphate and Nitrogen removal, or BCFS process (Van Loosdrecht et al. 1998; Wilsenach and Van Loosdrecht

2004), which is here supplemented with the treatment of excess sludge and supernatant. The reference scenario is illustrated by the combination of figure 1 and figure 2a. No urine is collected separately in the reference scenario. Methanol is dosed to the wastewater treatment plant for increased denitrification, to ensure effluent quality of 2-3 g N_{tot}/m^3. This value is often indicated as future effluent standard for the Netherlands. The effluent soluble phosphate in the BCFS process is normally below 0.2 gP/m^3.

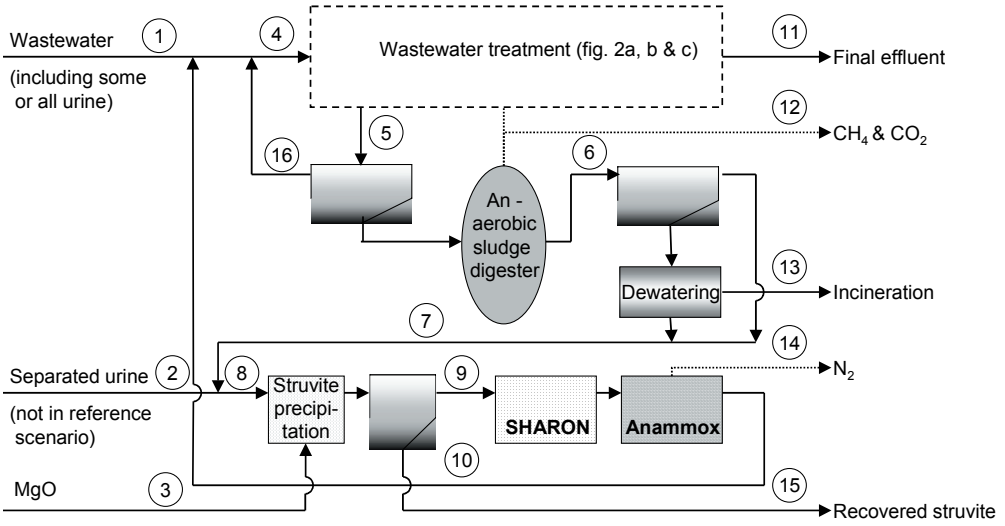
Recovery of ammonia from urine, or the direct use of urine as a fertiliser, has been suggested as more sustainable alternatives for conventional wastewater management (Van Loosdrecht, 2003). These options are not considered in this study for a number of reasons. Firstly, the Netherlands is currently a net importer of nitrogen. Nitrogen is imported either directly as industrial fertiliser (which is produced from atmospheric nitrogen in a relatively inexpensive process) or indirectly in the form of animal fodder (which further contributes to the waste load). Although this may change someday, one may safely assume that ammonia recovered from urine has no potential market now or in the near future. For economic reasons, nitrogen removal would by far be the best option. Secondly, apart from the economic benefit, the difference in energy consumption between direct ammonia recovery and biological N removal combined with industrial ammonia production is relatively small (Maurer et al. 2003; Wilsenach et al. 2003). Some processes for ammonia recovery (e.g. stripping) require even more energy than the combined amount for ammonia production and nitrogen removal via SHARON/Anammox (Maurer et al. 2003). If large transport distances from cities to farmlands are involved, the argument for ammonia recovery weakens even further. These issues must be further addressed as part of a life cycle analysis, which is not the purpose of this study. Lastly, one has to accept that the main interest of water boards is to maintain (or improve) wastewater effluent quality as efficiently as possible, rather than to improve the sustainability of society as a whole. In this study, we therefore choose to focus only on the direct impact of urine separation on wastewater treatment.

2

INTEGRATED WASTEWATER AND URINE TREATMENT PROCESS

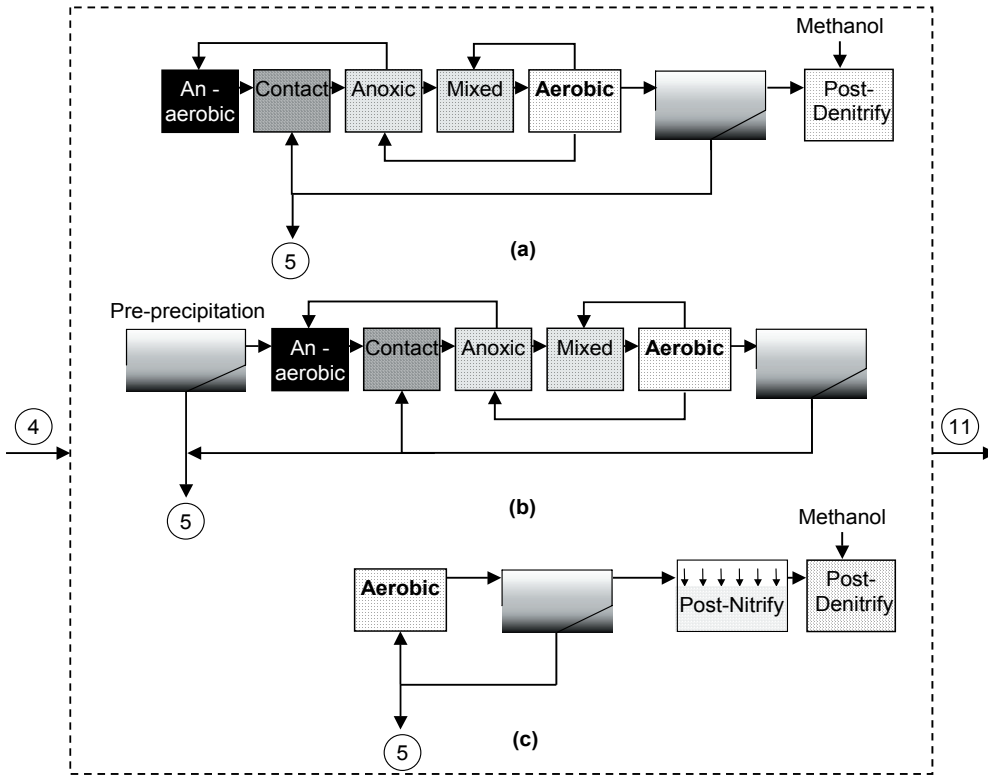
The combination of existing and well-described process that constitutes the IntWUT process is described below. Figure 1 shows the IntWUT process flow diagram.

FIGURE 1 **PROCESS FLOW DIAGRAM OF THE REFERENCE SCENARIO AND INTEGRATED WASTEWATER AND URINE TREATMENT (INTWUT) PROCESS (FLOW NUMBERS REFER TO THE NUMBERS IN TABLE 2 AND THE SUBSCRIPTS IN THE TEXT, Q_1, Q_2, Q_3, ETC.**



Two variations of the IntWUT process are compared to the reference scenario, detailed in figure 2a. The two variations differ from each other only in the treatment of the main wastewater stream, which still includes a portion of the urine. Figure 2b shows the first variation, where the BCFS process is employed for wastewater treatment after pre-precipitation and 50% urine separation (IntWUT-BCFS). Figure 2c shows the second variation, where only an aerobic reactor is employed for nutrient removal through excess sludge production (IntWUT-A). Larsen and Gujer (1996) already pointed out that separate urine collection would change the composition of wastewater to such an extent that bacterial growth would be limited by COD, N and P simultaneously. We investigate the hypothesis that if more than 50% of all urine were collected separately, excess sludge production would be sufficient for complete N and P removal in the IntWUT-A process. This reactor would be high loaded with a short solids retention time (1 day), similar to the first stage (A) of a two-sludge process, e.g. the "Absorption/ Belebungsverfahren" or A/B process (Böhnke, 1976). Because nitrification is impossible in this type of reactor, post-nitrification is needed (e.g. with trickling filter). The IntWUT-A process is investigated for different urine separation efficiencies from 50% upward.

FIGURE 2 THREE PROCESS VARIATIONS FOR WASTEWATER TREATMENT:
(A) BCFS, WITHOUT ANY URINE SEPARATION (REFERENCE)
(B) INTWUT-BCFS, FOLLOWING PRE-PRECIPITATION AND 50% URINE SEPARATION
(C) INTWUT-A, FOR DIFFERENT PERCENTAGES OF URINE SEPARATION, FOLLOWED BY POST TREATMENT (IF NECESSARY).



Sludge handling consists of the same unit operations for all options: Excess sludge is treated in an anaerobic digester to produce methane. In the IntWUT-BCFS process, primary sludge goes to the anaerobic digester with a smaller amount of excess sludge. We assumed de-watering by means of centrifugation. De-watered sludge is then incinerated. Liquid from the sludge dewatering normally has high ammonium and phosphate concentrations and is here mixed with urine and treated together.

Soluble phosphate is be recovered as struvite in a precipitation reactor. Struvite precipitation is a simple process with low capital investment, low operational cost and low energy requirement.

Ammonium is then removed (as N_2) in a complete autotrophic combined SHARON/Anammox process (Van Dongen et al. 2001a, 2001b). The two processes are described by the following simplified reactions:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+ \quad (1)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \quad (2)$$

In this way, only 40% of the oxygen demand of traditional nitrification is required, while no organic carbon is needed for denitrification. A prerequisite for this combined process is a high ammonium influent concentration, typically 1 gN/m^3.

Effluent from the Anammox reactor is returned to the influent wastewater upstream of the wastewater treatment process. In the case of the IntWUT-A process, some form of final effluent polishing might still be necessary after this integrated treatment.

Where these processes (IntWUT-BCFS and IntWUT-A) produce the same effluent quality as the reference scenario, the difference in primary energy consumption could be used as measure for the relative sustainability. Although this study is not a life cycle analysis, the results could be used to such an end. Ultimately, investment in separate urine collection, storage, transport, etc. should of course not exceed the benefits of separate treatment.

3

METHOD

3.1 INFLUENT CHARACTERISTICS

A total wastewater flow rate of 15 250 m^3/d was assumed for comparison with previous research (Wilsenach and Van Loosdrecht 2004). This flow rate includes domestic effluent, rainwater runoff and some industrial effluent, and represents the wastewater production of just over 50 000 people, with daily flow of 300 l/p. Average Dutch wastewater concentrations were assumed (537 $gCOD_{tot}/m^3$, 50 gN_{tot}/m^3, 40 gNH_4-N/m^3 and 8 gP_{tot}/m^3). Daily COD, nitrogen and phosphate loads are then 161 gCOD/p.d, 15 gN/p.d and 2.4 gP/p.d.
The organic and nutrient loads in urine were assumed 12 gCOD/p.d, 12 gN/p.d and 1 gP/p.d (Ciba Geigy 1997, STOWA 2001-39, Udert et al. 2003, Wilsenach and Van Loosdrecht 2004). Complete urea hydrolysis usually occurs within a few days in urine collection systems (Udert et al. 2003). For purposes of the processes described here, the nitrogen load from urine was assumed to consist of ammonium only. Modern no-mix toilets use only small amounts of water to flush urine and some urinals operate waterless (e.g. http://www.waterless.com or Larsen et al. 2001). The volume of urine produced (including flush water) was assumed 2 l/p.d.

Effluent from the sludge and urine treatment processes was combined with influent wastewater, as shown in figure 1. The influent flow rate and concentrations (Q_3) were influenced by the wastewater (Q_1), the pre-thickener overflow (Q_4) and effluent from the Sharon/Anammox process (Q_{10}). This combination led to a different wastewater composition, which influences the activated sludge performance. The process units were integrated and masses were balanced by iteration, using a spreadsheet.

3.2 MODELLING OF THE BCFS REFERENCE PROCESS

The BCFS process has previously been modelled and calibrated by Meijer et al. (2001). Effects of urine separation on the BCFS process at Hardenberg wastewater treatment plant were described earlier (Wilsenach and Van Loosdrecht 2004). This model was based on the COD and N removal modules of the activated sludge model ASM2d (Henze et al. 1998) combined with metabolically structured bio-P removal model (Murnleitner et al. 1997). Fractionisation of COD in influent wastewater was done for X_S, X_I, S_A, S_F and S_I, as defined in ASM2d, according to the guidelines of Roeleveld and Van Loosdrecht (2002).

We used the computer software package AQUASIM 2.0 (Reichert 1998) to implement the dynamic simulation of the aerobic activated sludge process. The process simulation was done for 12°C. The process had a total volume of 10,000 m^3, with clarifiers volume of 2,800 m^3.

Excess sludge removal is incorporated in the model. The excess sludge flow rate (taken from the sludge compartment of the clarifier) was defined in terms of the solids retention time, as formulated in equation 3:

$$Q_{exc} = Q_{rec}.V/|(Q_{in} + Q_{rec}).SRT - V| \quad (3)$$

Where Q_{exc} = excess sludge flow rate, Q_{rec} = sludge return flow rate, V = reactor volume, Q_{in} = inflow rate (Q_3) and SRT = solids retention time. The simulation results included excess sludge flow rate and composition, which were used as such for the anaerobic digester load.

Post-denitrification was incorporated as a single anoxic reactor with clarifier and sludge return. A small but fixed excess sludge flow rate to the BCFS process controlled the mixed liquor suspended solids. Methanol was added directly to the anoxic reactor.

3.3 MODELLING OF THE INTWUT-BCFS PROCESS

Wastewater treatment with the BCFS process, following pre-precipitation and integrated with 50% urine treatment, was simulated as described for the reference scenario (above). It was assumed that 80% of particulate influent COD is removed through addition of organic cationic polymers (Mels et al. 2001). Pre-precipitation was modelled by multiplying particulate influent COD fractions by a factor of 0.1. Nitrogen and phosphate removal through pre-precipitation is incorporated in the treatment plant model.

3.4 SENSITIVITY ANALYSIS FOR INWUT-A PROCESS

The same basic model, described for the reference scenario, was used for the simulation of wastewater treatment with a single aerobic reactor, with different urine separation efficiencies. The aerobic reactor was modelled as a plug flow reactor by using five compartments (each with a volume of 200m^3) in series. While model parameters are well calibrated for normal operating conditions, results for typical conditions as expected for the IntWUT-A would be less reliable. Sensitivity analyses were done to investigate the effects of different temperatures, different solids retention times and different nutrient contents in particulate material.

Effects of solids retention time on nutrient removal through sludge production were considered for sludge ages from 0.3 - 8.0 days, with 85% urine separation and constant temperature of 12°C. Default values for nutrient fractions, as shown in table 1, were used.

Effects of temperature on nutrient removal through sludge production were investigated between 8°C and 26°C, with 85% urine separation and constant solids retention time of 0.8 d. Default values for nutrient fractions, as shown in table 1, were used.

TABLE 1 **DEFAULTS VALUES AND RANGE OF NITROGEN AND PHOSPHATE CONTENTS OF DIFFERENT SLUDGE COMPONENTS (INERT, SLOWLY BIODEGRADABLE AND BIOMASS)**

	N – content, Default (range)	P – content, Default (range)
Inert particulate, (X_I)	0.02 (0.015 – 0.060)	0.01 (0.007 – 0.015)
Degradable particulate, (X_S)	0.04 (0.020 – 0.080)	0.01 (0.007 – 0.015)
Biomass (X_H, X_Aut)	0.07 (0.055 – 0.080)	0.015 (0.007 – 0.020)

Effects of different nutrient contents in particulate material nutrient effluent concentrations were investigated for urine separation efficiencies from 50% upward. Temperature and SRT were maintained constant at 12ºC and 0.8d respectively. The N and P content of different influent COD fractions (S_F, S_I, X_I and X_S) as well as activated sludge are variable within a range of values that depend on environmental conditions and sludge age. The sensitivity of the IntWUT-A process to different nutrient contents in particulate material was investigated in two scenarios; one with high sludge nutrient content and one with low sludge nutrient content, based on the normal range found in literature and shown in table 1 (Grady and Lim 1980; Tchobanoglous and Burton 1991; Henze et al. 1999: Henze et al. 2000).

3.5 INTEGRATION OF DIFFERENT PROCESS UNITS

Excess sludge is taken from the sludge return line and thickened (gravity) up to a suspended solids concentration of 25 kg/m^3 (Tchobanoglous and Burton 1991). Overflow from the pre-thickener (Q_4) containing dilute ammonium and phosphate is returned to the aerobic reactor. We assume excess sludge treatment in a completely mixed anaerobic digester under mesophilic conditions, with a solids retention time of 15 days (Tchobanoglous and Burton 1991; Malina and Pohland 1992). The digester volume was determined from a hydraulic retention time of 15 days, based on excess sludge flow rate (Q_5). Digested sludge (Q_6) was assumed to be thickened (80 kg/m^3) and dewatered (200 kg/m^3) before incineration.

The composition of excess sludge from the process simulation was used to determine the amount that could be transformed into biogas in the digester. We assumed that inert COD does not lead to any gas production, while 90% of the COD of biomass (X_AUT, X_H, X_PAO, X_PHB and X_GLY) and 100% of biodegradable COD (X_S) could be transformed into biogas (Siegrist et al. 1993). The CH_4:CO_2 ratio in the biogas was assumed 65:35 (Tchobanoglous and Burton 1991; Malina and Pohland 1992).

It was assumed that no gaseous nitrogen escapes the digester and that at steady state, all nitrogen entering the digester leaves as either NH_4^+, or nitrogen in dewatered sludge (Q_{13}). The P-content in excess sludge differs considerably between the BCFS process (including phosphate storage products) and the reactor in the IntWUT-A process (phosphate only in cell composition). All excess phosphate is released under anaerobic conditions. Even though phosphate precipitation normally occurs in anaerobic digesters and downstream pipelines (Williams 1999), it was further assumed that all phosphate entering the digester leaves the digester either as soluble phosphate, or as part of bacterial cell composition in the dewatered sludge. Implications of this assumption are discussed in Results.

With the assumptions stated above, separately collected urine contains 6000 gNH_4^+-N/m^3 and 500 gP/ m^3. Supernatant and centrate (Q_7) were combined and mixed with the separately collected urine (Q_2).

Controlled struvite precipitation from urine has been done successfully on laboratory scale (Lind et al. 2000 and chapter 3 of this report). Struvite has also been successfully precipitated from calf urine in a full-scale process (Schuiling and Anrade 1999), as well as from wastewater side streams (Battistoni et al. 2000; Ueno and Fujii 2001). Addition of MgO to the combined stream (Q_8) in a ratio Mg:P = 1, is sufficient to increase pH to 9 and precipitate phosphate as struvite, which can be removed from the liquid (Q_{15}). The effluent from the struvite precipitation and settling was assumed to yield a constant effluent concentration of 18 gP/m^3

(Schuiling and Anrade 1999). Ammonium removed with struvite precipitation was included in calculations.

The SHARON process takes place in a completely mixed chemostat reactor with temperature of 30°C and hydraulic retention time of around one day. Slightly more than half of the ammonium is oxidised to ensure complete downstream ammonium removal in the Anammox process, which can be operated either as a granular sludge or bio-film reactor. Various studies have shown that 85 - 95% of the influent ammonium is removed as nitrogen gas (Q_{14}) (Fux et al. 2002, Van Dongen et al. 2001b and Chapter 3 of this report). We assumed 90% N removal, with the equal amounts of ammonium and nitrate in the effluent from the Anammox process. This effluent is returned to the main stream (Q_{10}).

3.6 ASSESSMENT OF ENERGY DEMAND FOR DIFFERENT SCENARIOS

The net primary energy consumption of the IntWUT-BCFS and IntWUT-A processes were compared to the reference process. The comparison is based on an effluent quality of 1 gNH_4^+-N/m^3 and 2.5 gN_{tot}-N/m^3 for each process. We made use of the theoretical energy calculation described by Van Loosdrecht et al. (1997), which is based on four aspects of wastewater treatment, i.e. aeration (E_{aer}), sludge dewatering (E_{dew}), sludge incineration (E_{inci}) and methane gas from anaerobic sludge digestion (E_{CH_4}). Additionally, we included energy demands for pumping (E_{pump}), mixing of tank reactors (E_{mix}), heating the digester and the SHARON/Anammox process (E_{heat}) and the transport of separately collected urine by truck (E_{truck}). We also included the use of methanol in post-denitrification as an energy demand. All energy values are expressed as in terms of primary energy sources. Electrical output is roughly one third of the primary energy input (based on the heat value of coal fired power stations). We multiplied electrical energy (aeration, mixing, pumping) by a factor 3. Total net primary energy requirement (E_{net}) is here defined in equation 4:

$$E_{net} = E_{aer} + E_{MeOH} + E_{mix} + E_{pump} + E_{dew} + E_{incin} + E_{heat} + E_{truck} - E_{CH_4} \quad (4)$$

Aeration energy includes the oxygen demand for the activated sludge process, the SHARON process and post-nitrification. The oxygen requirement for the aerobic reactor was obtained from the process simulation. The total oxygen requirement for the SHARON/Anammox process is 1.82 gO_2/gNH_4-N influent, based on the assumption that 53% of the influent NH_4-N is oxidised to nitrite (Van Dongen et al 2001a,b). Because no nitrification takes place in the IntWUT-A process, post-nitrification to limit the ammonium effluent concentration to 1 gNH_4^+-N/m^3 requires 4.57 gO_2/gNH_4^+-N. An average aerator efficiency of 2.4 MJ/kgO_2 was assumed after correction for “clean water performance” (Tchobanoglous and Burton 1991).

Methanol consumed in post-denitrification of the reference process can be expressed in terms of energy. We assumed 30 MJ/kg CH_3OH, based on heat value of natural gas in the modern methanol production, i.e. low pressure gas refraction. This value approaches the thermodynamic limit. It is therefore unlikely to change much in future, even within power co-generation processes (Gao *et al*., 2004).

The power requirement of mixing was based on an average figure of 10 W/m^3 mixed volume (Grady and Lim 1980). Mixing energy was calculated for reactor zones, based on this continuous power requirement.

Energy required for pumping was based on average daily flow rates and the power requirement is expressed in equation 5:

$$P = \rho.Q.g.h/\eta \quad (5)$$

Where ρ = density of liquid (1000 kg/m^3), Q = flow rate (m^3/s), g = gravity constant (9.81 m/s^2), η = combined pump and motor efficiency (usually 0.75x0.9) and h = pump head (m), which is the sum of static and dynamic head. Static heads were based on the actual reference process (0.1m for internal flows, 0.85m for return activated sludge and 8m for thickened excess sludge to anaerobic digester). The dynamic head loss was determined theoretically.

The suspended solids concentration of post-thickened digested sludge was assumed 80 kg/m^3 (Tchobanoglous and Burton 1991). 15 MJ/kg was used as energy for centrifugation (Koot 1980). The temperature of dewatered sludge entering the incinerator was assumed 20^{o}C and the sludge, water (or steam) and air was heated to 250^{o}C. Energy demand for heating of reactors (anaerobic digester and SHARON) was calculated on the same basis. Temperature of urine was assumed 12^{o}C and the heat production of nitrification 18.25 MJ/kg NH_4^+-N (Davido *et al.*,2003). The temperature increase is determined with the heat capacity of water.

Energy required for transport of urine by truck was compared to the total energy consumption. We assumed primary energy consumption of 4.8 MJ/ton.km (empty going forth, full on return) for ordinary trucks after the ORWARE model (Dalemo et al. 1997). A distance of 10 km from collection point to treatment plant was assumed, which is typical for the Netherlands. The effect of urine separation on energy consumption in wastewater collection (sewerage) is immaterial and not included in the comparison.

The energy value obtained through anaerobic digestion is expressed by equation 6:

$$E_{CH_4} = [\phi_{gas}.(1- f_{CO_2})M_{CH_4}/V_{gas(35\,^oC)}].\Delta H_{CH_4} \quad (6)$$

Where ϕ_{gas} = volume of digester gas, f_{CO_2} = CO_2 fraction by volume in the produced digester gas (0.35), M_{CH_4} = molecular weight of methane (16 g/mol), $V_{gas(35\,^oC)}$ = volume of methane at 35^{o}C (25.3 l/mol CH_4), and ΔH_{CH_4} = heat value of methane (50 MJ/kg).

4

RESULTS AND DISCUSSION

4.1 EFFLUENT CONCENTRATIONS OF THE REFERENCE - AND THE INTWUT-BCFS PROCESS

According to the model simulation, the reference process with post-denitrification produces high quality effluent; 1 gNH_4^+-N/m^3, 2.5 gN_{tot}/m^3 and 0.3 gP/m^3. In the case of the IntWUT-BCFS process, the same effluent quality could be achieved with 50% separate urine collection, but without the need for post-denitrification. The only difference in effluent quality is a lower ammonium concentration (0.7 gNH_4^+-N/m^3). This is due to improved nitrification with longer sludge age, which is possible after primary sedimentation. There is little difference in phosphate effluent concentrations between the reference (0.3 gP_{tot}/m^3) and the IntWUT-BCFS process (0.4 gP_{tot}/m^3). Biological phosphate removal is efficient in both cases, the only difference being the higher sludge age in the case of the IntWUT-BCFS, hence the slight increase in effluent concentration.

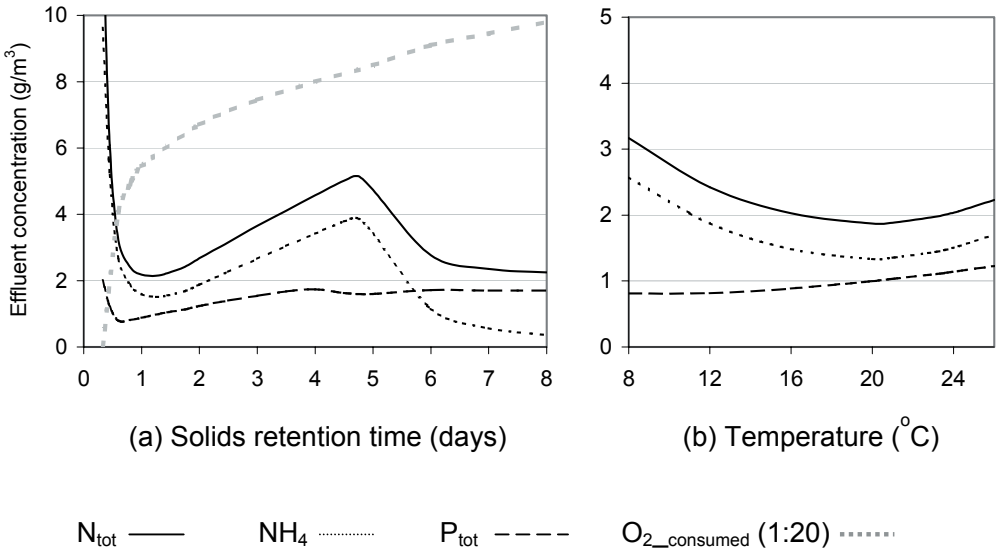
4.2 EFFECTS OF SLUDGE AGE AND TEMPERATURE ON EFFLUENT CONCENTRATIONS; INTWUT-A PROCESS

The effects of different solids retention times (SRT) and temperatures on effluent concentrations were investigated for the IntWUT-A process, upstream of the tertiary treatment (i.e. excluding post-nitrification and denitrification). Figure 3(a) shows the relation between SRT in the aerobic reactor (IntWUT-A process), and nutrient effluent concentrations, for wastewater with a urine separation efficiency of 85% and default values for the nutrient contents in activated sludge.

Generally, a lower SRT leads to an increase in excess sludge production, with an increase in overall nutrient uptake. Lower effluent concentrations can be expected, provided the maximum growth rate of organisms does not limit sludge production. The model predicts washout of bacteria at SRT < 0.5 day, which is clear from figure 3(a). The oxygen consumption also indicates the sludge activity. A drastic decrease in oxygen consumption can be seen at SRT < 0.7 day, indicating that not all biodegradable COD is removed. Higher SRT (> 2 days) also results in higher effluent nutrient concentrations. Nitrification starts at SRT ≅ 5 d, leading to lower ammonium effluent concentrations. Some denitrification could then occur in the clarifier's sludge blanket, leading to lower nitrate and total nitrogen effluent concentrations. However, higher SRT also require more reactor volume. All further calculations were done with SRT = 0.8 d, where the lowest overall nutrient effluent concentration is achieved. This is slightly higher than the normal operating range of the A-stage in an A/B process (Böhnke 1976).

Wastewater temperature also determines the rate of bacterial growth and sludge production. Figure 3(b) shows the change in nutrient effluent concentrations at different temperatures. Temperature variations don't seem to be very important at SRT = 0.8d. Temperature is normally most important for nitrification, which is irrelevant in this case.

FIGURE 3 **EFFECTS OF (A) SOLIDS RETENTION TIME, WITH T = 12°C, AND (B) TEMPERATURE, WITH SRT = 0.8 D, ON EFFLUENT CONCENTRATIONS OF THE INTWUT-A PROCESS, AT 85% URINE SEPARATION EFFICIENCY**



The slight increase in the nutrient effluent concentrations at temperatures above 20°C is partly due to the increased sludge hydrolysis rate. At temperatures higher than 20°C, the amount of particulate slowly biodegradable COD (X_S) in the aerobic reactor is much less than at lower temperatures under the same process conditions. According to the model simulation, the decrease in X_S removed with excess sludge at higher temperatures is not balanced with an increase in X_I and X_H. That part of the nutrients normally removed at lower temperatures with the un-hydrolysed slowly degradable particulates, would now be released into the effluent. In such a case, shorter SRT would be possible (at higher temperature) for an increased sludge production and therefore better nutrient removal

4.3 EFFECTS OF DIFFERENT NUTRIENT CONTENTS ON THE EFFLUENT CONCENTRATION; INTWUT-A PROCESS

The activated sludge model (ASM2d) makes no distinction between particulate COD in the wastewater influent and in the reactor (Henze et al. 1995). In reality, these are different substances. The nutrient content of particulate COD in the influent is largely determined by faeces and undigested foods. The nutrient content of activated sludge is determined by microbial metabolism and decay. This inconsistency is normally of no consequence, because the model is used for simulating processes not relying on excess sludge production for nutrient removal. However, in this case the model simulation shows that some slowly degradable particulates are not oxidised, but removed with the settled sludge. Modelling the nutrient removal efficiency of the IntWUT-A process can therefore not only be based on the familiar activated sludge characteristics.

The effects of different nutrient contents (N and P) in activated sludge model parameters (*X_S*, *X_I* and *X_H*) on effluent concentrations of the IntWUT-A process were evaluated, while keeping temperature and sludge age constant (T=12°C and SRT=0.8d). Figure 4 shows the effluent concentrations and nutrient removal efficiencies of the IntWUT-A process, upstream of tertiary treatment, for urine separation form 50% to 95%.

Figure 4a shows there is virtually no difference between NH_4^+ and N_{tot} in the effluent, which is expected as no nitrification occurs. A steep decrease in effluent concentration is seen with increasing urine separation. Based on the default nutrient contents, all the ammonium is consumed for biological growth and no ammonium remain in the final effluent with urine separation efficiencies of around 85% and upward (figure 4a). The low ammonium load actually limits growth and leads to insufficient sludge production. The effluent phosphate therefore increases with urine separation efficiencies above 85% (figure 4b).

FIGURE 4 **EFFLUENT CONCENTRATIONS AND REMOVAL EFFICIENCIES OF THE INTWUT-A PROCESS, UPSTREAM OF TERTIARY TREATMENT, FOR (A) NITROGEN AND (B) PHOSPHATE, FOR DIFFERENT N AND P CONTENTS OF COD FRACTIONS IN ACTIVATED SLUDGE; WITH T = 12°C AND SRT = 0.8 D.**

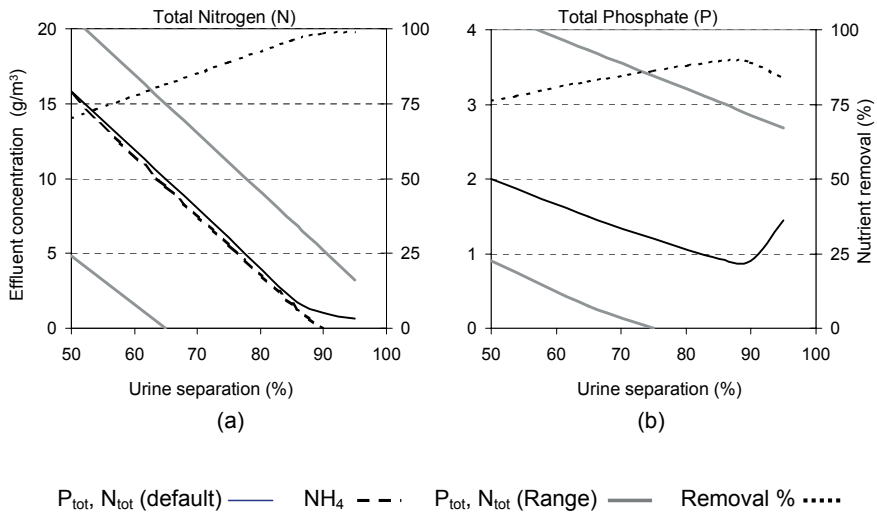


Figure 4a and 4b show that the range of nutrient contents (given in table 1) greatly determines the nutrient removal capacity of the IntWUT-A process. For a total nitrogen effluent concentration of, e.g., 5 gN_{tot}/m^3, 50% urine separation would be sufficient based in case of a high nitrogen content, while 90% urine separation would be required in case of a low nitrogen content. The uncertainty with phosphate is even greater. While the high nutrient content scenario is more like normal activated sludge, the low nutrient content is more towards nutrient removal through primary sedimentation. The default values used perhaps give an unoptimistic view of the amountof urine to be collected separately for this process to be condisered seriously, this would have to be established more experimentally.

4.4 MASS BALANCES AND EFFLUENT NUTRIENT CONCENTRATIONS

Table 2 shows the mass fluxes of N, P and COD in the reference process and IntWUT variations in flow lines as defined in figure 1. In the case of the IntWUT-A process, the default nutrient content of particulate material was used (table 1). If $M_{1, 2, etc}$ are masses of N, P or COD, corresponding to the flows $Q_{1,2, etc}$, the mass balances can be formulated by equation 7.

$$\Sigma |M_1, M_2| = \Sigma |M_{11}, M_{12}, M_{13}, M_{14}, M_{15}| \quad (7)$$

With the default values used in this study, excess sludge had a lower than expected nutrient content. From the values in table 2 it is clear that $i\_N_{sludge} = 0.02$ and $i\_P_{sludge} = 0.01$ (Q_{13}). This is on the low end of the values presented in table 1. Assuming higher values for the nutrient content of excess sludge, the removal efficiency increases dramatically (as seen in figure 4).

TABLE 2 INFLUENT AND EFFLUENT MASS BALANCE FOR NITROGEN (N), PHOSPHATE (P) AND CHEMICAL OXYGEN DEMAND (COD), FOR THE REFERENCE PROCESS, INTWUT-BCFS AND INTWUT-A PROCESS WITH 75, 85 AND 95% URINE SEPARATION

Flow numbers (Figure 1)		Mineral loads (kg/d) for different urine separation efficiencies						
		Reference	IntWUT process variations					
		0%	BCFS-50%	A-50%	A-65%	A-75%	A-85%	A-95%
Q_1	**N**	**763**	**458**	**458**	**366**	**305**	**244**	**183**
(Wastewater)	P	122	97	97	89	84	79	74
	COD	*8189*	*8189*	*8189*	*8189*	*8189*	*8189*	*8189*
Q_2	**N**	**0**	**305**	**305**	**397**	**458**	**519**	**580**
(Urine)	P	0	25	25	33	38	43	48
Q_{11}	**N**	**38**	**35**	**229**	**143**	**85**	**28**	**9**
(Final effluent)	P	4	6	29	21	18	13	20
	COD	*671*	*637*	*637*	*627*	*620*	*620*	*1379*
Q_{12}								
- Aerobic oxidation	*COD*	*3266*	*2190*	*1602*	*1630*	*1637*	*1637*	*1199*
- Anaerobic digestion	*COD*	*1758*	*2976*	*3482*	*3471*	*3470*	*3473*	*3198*
Q_{13}	**N**	**46**	**50**	**53**	**53**	**53**	**53**	**49**
(Incineration ash)	P	22	19	22	22	22	22	21
	COD	*2494*	*2387*	*2468*	*2460*	*2461*	*2459*	*2413*
Q_{14} (Nitrogen gas - N_2)	**N**	**632**	**655**	**442**	**525**	**579**	**635**	**665**
Q_{15}	**N**	**44**	**45**	**33**	**36**	**38**	**40**	**39**
(Struvite crystals)	P	98	99	73	80	85	89	85

The digested sludge mass (Q_{13}) from the reference process is practically equal to that of both the IntWUT process variations. However, in both IntWUT process variations, much higher amounts of primary and secondary sludge were produced and entered into the digester (data not shown). Then again, the sludge composition also varied considerably between the different cases. For the reference process (with SRT = 12 days) the fraction of particulate inert material (X_I) in the excess sludge was 55%, while it was only 35% in the IntWUT-A process. Furthermore, almost no biodegradable substrate (X_S) occurred in excess sludge form the reference process, while 25% of the IntWUT-A excess sludge consisted of X_S. This difference also explains differences in the amounts of biogas produced (Q_{12}). Table 2 shows that double the amount of biogas was produced in the IntWUT-A process compared to the reference process. The amount of X_I in the IntWUT-BCFS process excess sludge was similar to the reference process, but combined with the primary sludge only around 40% of the sludge. Due to primary sedimentation, biogas production in the IntWUT-BCFS process is somewhat better than the reference, but not as good as the IntWUT-A, where soluble COD converted into biomass is also digested. In the reference and IntWUT-BCFS process, soluble COD is oxidised mostly to CO_2.

It was assumed that no precipitation occurs in the anaerobic digester, which meant high supernatant phosphate concentrations could be expected. The amount of recovered struvite (Q_{15}) is therefore the maximum potential, and would be lower in practice. It is seen that more struvite is removed from the reference and IntWUT-BCFS process than from the IntWUT-A process, mostly due to poor effluent quality in the IntWUT-A process (Q_{11}). The biological phosphate removal is far superior to improving effluent quality through urine separation. In the reference process, potentially 80% of the phosphate could be recovered. The poor effluent quality, and phosphate recovery, in the IntWUT-A process is due to the rather low overall phosphorus content of 0.01 in the dewatered sludge (Q_{13}). If the phosphate content in dewatered sludge were in fact higher, it would improve the effluent quality of the IntWUT-A process, but not necessarily phosphate recovery efficiency.

The reference process and the IntWUT-BCFS process have the same nutrient removal efficiencies, which were around 95% for N_{tot} as well as P_{tot}, as seen from the values for Q_{11}.

The IntWUT-A process in general had lower nutrient (N and P) removal efficiencies, without any tertiary treatment between 50% and 75% urine separation. With increasing urine separation, the shift in ammonium load from the wastewater influent to the SHARON/Anammox reactor leads to an increased nitrogen gas production (Q_{14}). At 85% urine separation, nitrogen is the lowest of all processes, but phosphate still more than the reference or IntWUT-BCFS processes. The lower nitrogen gas production at low urine separation efficiencies is directly correlated to higher effluent concentrations, and necessitates tertiary treatment if even systems are to be compared.

4.5 ENERGY BALANCE

Table 2 was used as basis to determine the necessary tertiary treatment to ensure equal effluent nitrogen concentrations of 1 gNH_4^+-N/m^3 and 2.5 gN_{tot}-N/m^3 from the IntWUT-A process. Table 3 gives a summary of energy requirements of the different treatment options. The first column shows the energy account of the reference system (BCFS process followed by post-denitrification). The second column shows the energy account of the IntWUT-BCFS process, with 50% urine separation and pre-precipitation of wastewater. The remaining four columns show the energy accounts of the IntWUT-A process for increasing urine separation efficiencies, with varying degrees of post-nitrification and –denitrification. Relative contributions energy components are shown as percentages of the total primary energy requirement, for each specific case. It is clear that the energy demands of a few components are relatively unimportant, regardless of the different cases. Dewatering and pumping seem to be insignificant in comparison to the total demand. Sludge incineration is also relatively unimportant, especially since equal amounts of dewatered sludge was produced in the different scenarios. Although a noticeable percentage in all the scenarios, the amount of energy is almost equal regardless of process choice. A substantial amount of heat is also produced in the incineration process. This cancels some of energy required for heating and evaporation of water, stressing the importance of sludge thickening and drying before incineration.

TABLE 3 SUMMARY OF ENERGY REQUIREMENTS FOR DIFFERENT WASTEWATER TREATMENT SCENARIOS WITH SEPARATE URINE COLLECTION (CONTRIBUTORS TO ENERGY REQUIREMENT ARE SHOWN AS % OF THE PRIMARY ENERGY REQUIREMENT)

	Reference	IntWUT-BCFS	IntWUT-A process					
Urine separation	**0**	**50**	**50**	**65**	**75**	**85**	**95**	**%**
Separately collected urine	0	50833	50833	66083	76250	86417	96583	kg/d
Net primary energy	**43964**	**9869**	**13939**	**2906**	**-4507**	**-11114**	**-9678**	**MJ/d**
Aeration	44	32	29	30	32	34	30	%
$E_{aeration}$	34981	22633	24129	22270	21157	19989	16510	MJ/d
Methanol (post denitrification)	8	0	28	18	9	0	0	%
E_{MeOH}	6500	0	23465	13024	6083	0	0	MJ/d
Mixing	17	22	8	9	11	12	12	%
E_{mix}	13190	15161	6889	6949	6961	6992	6644	MJ/d
Pumping	3.4	3.5	1	1	1	1	1	%
E_{pump}	2692	2425	695	687	680	674	662	MJ/d
Dewatering	1	1	1	1	1	1	1	%
E_{dew}	688	644	666	664	665	664	652	MJ/d
Incineration	9	10	8	10	11	12	13	%
E_{inci}	7363	6901	7136	7113	7116	7110	6978	MJ/d
$E_{Heat\ and\ evaporation}$	32462	30427	31464	31361	31373	31348	30765	MJ/d
$E_{Heat\ produced\ by\ incineration}$	-25100	-23526	-24328	-24248	-24258	-24238	-23787	MJ/d
Heat	18	28	23	26	30	33	35	%
$E_{Anaerobic\ digester}$	10469	13870	13911	13913	13862	13848	13103	MJ/d
E_{SHARON}	3704	6073	5139	5441	5615	5808	5917	MJ/d
Transport	0	3	3	4	6	7	8	%
E_{truck}	0	2440	2440	3172	3660	4148	4636	MJ/d
Methane (as heat)	-45	-86	-83	-96	-107	-119	-118	%
E_{CH4}	-35622	-60279	-70531	-70326	-70306	-70347	-64780	MJ/d

The aeration requirement is the main component governing the energy balance. In the reference process, the longer sludge age leads to a higher O_2 consumption. Furthermore, almost all ammonium is nitrified. Almost 50% of the primary energy demand is needed for by aeration, which is consistent with most advanced nutrient removal plants. The aeration demand of the IntWUT-BCFS process is reduced considerably as results of both pre-precipitation and 50% urine separation. In the IntWUT-A process, the aeration demand is even less, and only half of the reference process. Due to the short SRT, less organic material is oxidised, but some ammonium is still nitrified in the post-nitrification unit. The requirement for post-nitrification fades out differences in aeration demand between various process options, except that with urine separation, and more nitrogen removal through SHARON/Anammox, aeration demand is only around 60% of the reference.

Methanol dosing for post-denitrification in the reference process could be seen more as effluent polishing (the reference process already had an effluent quality around 6 gN_{tot}/m^3, upstream of the post-denitrification). The relative energy value of methanol is therefore rather low. However, in the IntWUT-A process with only 50% urine separation (and still assuming default nutrient sludge content), much more denitrification is required, hence the higher methanol demand. This is also the most important factor in placing the IntWUT-A (50%) process behind the IntWUT-BCFS (50%) in terms of net primary energy.

Mixing requires a relatively large amount of (electrical) energy when primary sources are considered. The energy requirement in the IntWUT-A process is here only half of the reference or IntWUT-BCFS processes, mostly due to the considerable decrease in reactor volume. The energy requirement for mixing of the anaerobic digester remain considerable in relation to the whole and does not change much between the different cases (not shown).

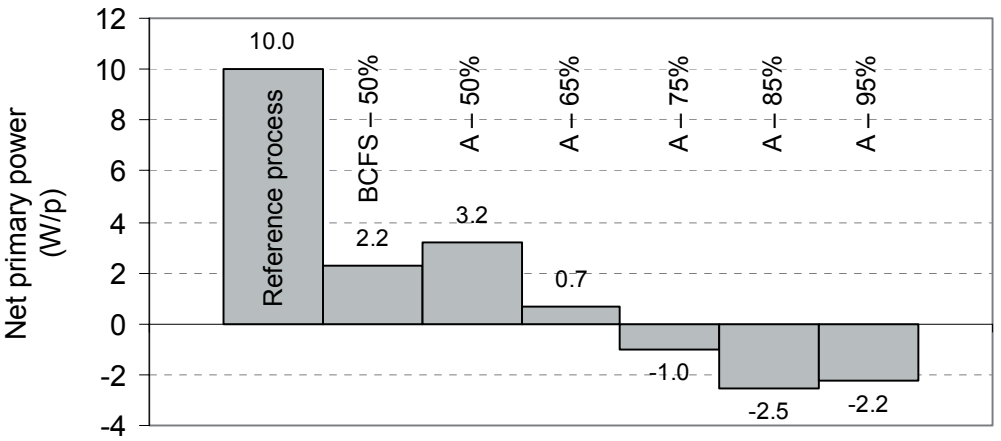
Heating is important for operation of both the anaerobic digester and SHARON process. It seems be important in the energy balance too, making up 20% - 30% of the total primary energy requirement. More sludge is digested and more supernatant and urine jointly treated in the IntWUT processes. The heat requirement is directly related to the volume of water in the treatment process, and therefore increases somewhat from the reference to the IntWUT processes. These values have to be qualified though, being dependant on many assumptions, such as thermal insulation of process units, heat loss between process units, dimensions of process units, ambient temperature, etc. Nevertheless, the heat requirement for anaerobic digesting is more or less equal in different treatment options. Heat generation in the SHARON reactor due to ammonium oxidation limits the heat requirement in urine separation systems. Heating and heat management regarding the anaerobic digester and SHARON processes should be thoroughly considered in a process design.

Energy required for transport of separately collected urine is also relatively unimportant (4-6% of the total primary energy demand). It is however crucial that urine is collected without much dilution. If more flush water were included and 10 l/p.d had to be transported (instead of 2 l/p.d assumed here), the situation would change completely, with transport then making up 25% of the total primary energy requirement. This will greatly reduce the benefit of separate urine collection and treatment.

Production of methane (expressing energy as heat) is crucial in this comparison. Although 45% of the energy required in the reference process can be obtained from methane, this is even higher in the other options. Pre-precipitation greatly improves methane production

in the IntWUT-BCFS process, while short SRT further improves methane production in the IntWUT-A processes. In this way, net primary energy production is possible where a sufficient amount of urine is collected separately.

FIGURE 5 **NET PRIMARY POWER REQUIREMENT(+)/PRODUCTION(-) OF ALL TREATMENT OPTIONS INVESTIGATED, EXPRESSED AS WATT/PERSON**



This study predicts an average continuous power demand of 10 watt/person (W/p) in the reference process. In the IntWUT-BCFS process the net continuous power *requirement* is only 2.2 W/p, a saving of almost 80%. This is clearly due to lower aeration and higher methane production. The same holds for the IntWUT-A process, where even more methane is produced with still lower aeration demand at high urine separation efficiency. Continuous power *generation* between 1 and 2.5 W/p seems possible (energy savings of around 120%). Nutrient fractions play an important role in aeration demand of the IntWUT-A process. If more nutrients were removed with digested sludge, then less ammonium would have to nitrified and denitrified in tertiary treatment, saving on oxygen and methanol. If in fact, the default values used in this study for nutrient content in sludge is too low, the effect would be that the net power generation shown here possible at 75% and 85% would be possible at 50% or 65% urine separation.

4.6 AREA REQUIREMENT AND LAND USE

The reference process had a biological reactor of 10,000 m^3 while the aerobic reactor in the proposed process was evaluated based on only 1,000 m^3. The volume of the anaerobic sludge digester and SHARON/Anammox process would be around 1,750 m^3 for the reference process and around 2,250 m^3 for the separate urine treatment, based on hydraulic retention time. The various scenarios predict equal amounts of digested sludge, so that the size of sludge handling facilities would be equal for all practical purposes. The volume of the secondary settling tank in the IntWUT-BCFS process would be around 3,000 m^3 and would be equal in the simple aerobic reactor, assuming equal total suspended solids concentrations and sludge volume indexes. Based on hydraulic retention times for all other sludge treatment facilities, the IntWUT-A process requires only around 50% of the volume of the reference process, including all sludge treatment units.

4.7 IMPLEMENTATION OF NEW TECHNOLOGY

The IntWUT process described could be implemented in future. It was however shown that in the case of the IntWUT-A process, too high ammonium and phosphate concentrations could occur at urine separation efficiencies up to 65%. Uncertainties in terms of final effluent quality are due to different possible sludge nutrient fractions. The values used in this study are towards the lower end of the possible nutrient sludge content, and better nutrient removal could be expected for the IntWUT-A process, as shown in figure 4. Furthermore, the relatively high ammonium effluent load can be addressed by effluent polishing techniques (e.g. trickling filter for post-nitrification). Figure 2 c shows such a process as an optional extension to the IntWUT-A process. With this additional step, the total N would consist mostly of nitrate, instead of mostly ammonium.

Phosphate in the effluent of the IntWUT-A process (between 1.5 and 2 gP/m^3) could be removed by metal salt or polymer addition. This holds for the case of a low sludge phosphate content (the default values used in this study). Excess biological phosphate removal could also be possible at higher sludge ages. At higher actual sludge nutrient contents, all phosphate in wastewater would be removed through cell synthesis.

The BCFS process and the aerobic reactor of the IntWUT-A process represent two extremes in terms of wastewater treatment complexity. Still, many other existing processes are neither as complex as the BCFS process, nor as simple as the single aerobic reactor. These processes could all be upgraded (treating higher loads) or improved (producing better effluent quality) according to the principles of the IntWUT process described here.

5 CONCLUSION

This model study demonstrated that if 50% or more of urine were collected separately, wastewater treatment performance could be greatly improved. More compact and energy efficient processes for integrated treatment of urine and wastewater are feasible.

The main advantage of urine separation is not the production of better effluent quality, for there are processes capable of producing very good effluent quality. The main advantage of integrated wastewater and urine treatment is the production of very good effluent quality with a substantial saving in resources and even net production of primary energy.

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