BIOLOGICAL TREATMENT OF SOURCE SEPARATED URINE IN A SEQUENCING BATCH REACTOR

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Thesis presented in partial fulfilment of the requirements for the degree Masters of Engineering (Research) in the Faculty of Engineering at Stellenbosch University

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December 2014

DECLARATION

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December 2014

Synopsis

Urine contains up to 80% of nitrogen, 50 % of phosphates and 90 % of potassium of the total load in domestic wastewater but makes up less than 1% of the total volume (Larsen et al., 1996). The source separation and separate treatment of this concentrated waste stream can have various downstream advantages on wastewater infrastructure and treated effluent quality. The handling of undiluted source separated urine however poses various challenges from the origin onward. The urine has to be transported to a point of discharge and ultimately has to be treated in order to remove the high loads of organics and nutrients. Wilsenach (2006) proposed onsite treatment of source separated urine in a sequencing batch reactor before discharging it into the sewer system.

This study focused on the treatment of urine in a sequencing batch reactor (SBR) primarily for removal of nitrogen through biological nitrification-denitrification. The aim of the study was to determine nitrification and denitrification kinetics of undiluted urine as well as quantification of the stoichiometric reactions. A further objective was to develop a mathematical model for nitrification and denitrification of urine using experimental data from the SBR.

The SBR was operated in 24 hour cycles consisting of an anoxic denitrification phase and an aerobic nitrification phase. The sludge age and hydraulic retention time was maintained at 20 days. pH was controlled through influent urine during volume exchanges. Undiluted urine for the study was obtained from a source separation system at an office at the CSIR campus in Stellenbosch. Conditions in the reactor were monitored by online temperature, pH and ORP probes. The OUR of the system was also measured online.

One of the main challenges in the biological treatment of undiluted urine was the inhibiting effect thereof on nitrification rate. The anoxic mass fraction was therefore limited to 17 % in order to allow longer aerobic phases and compensate for the slow nitrification rates. Volume exchanges were also limited to 5% of the reactor volume in order to maintain pH within optimal range.

Samples from the reactor were analysed for TKN, FSA-N, nitrite-N, nitrate-N and COD. From the analytical results it was concluded that ammonia oxidising organisms and nitrite oxidising organism were inhibited as significant concentrations of ammonia-N and nitrite-N were present in the effluent. It was also concluded that nitrite oxidising organisms were more severely inhibited than ammonia oxidising organisms as nitrate-N was present in very low concentrations in the effluent and in some instances not present at all.

Ultimately the experimental system was capable of converting 66% of FSA-N to nitrite-N/nitrate-N of which 44% was converted to nitrogen gas. On average 48% of COD was removed.

A mathematical model was developed in spreadsheet form using a time step integration method. The model was calibrated with measured online data from the SBR and evaluated by comparing the output with analytical results. Biomass in the model was devised into three groups, namely heterotrophic organisms, autotrophic ammonia oxidisers (AAO) and autotrophic nitrite oxidisers (ANO). It was found that biomass fractionation into these three groups of 40% heterotrophs, 30% AAO and 30% ANO produced best results.

The model was capable of reproducing the general trends of changes in substrate for the various organism groups as well as OUR. The accuracy of the results however varies and near-exact results were not always achievable. The model has some imperfections and limitations but provides a basis for future work.

Acknowledgements

I would like to express my deepest gratitude to my study leaders, Prof. J.A. Du Plessis and Dr. J.A. Wilsenach, for their guidance and patience during the long time it took to complete this thesis.

I would also like to thank Jason Germanis for his support and effort.

Furthermore I would like to thank Prof. G.A. Ekama from UCT for making available his wastewater laboratory as well as for his willingness to share his extensive knowledge.

This study for this thesis was funded by the Water Research Commission of South Africa and conducted at the Council for Scientific and Industrial Research of South Africa who also provided student funding for me. I would like to thank both organisations for their generous support.

Finally, I would like to thank my family and friends for their support.

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Abbreviations

AAO	–	autotrophic ammonia oxidiser
ANO	–	autotrophic nitrite oxidiser
BNR	–	biological nitrogen removal
COD	–	chemical oxygen demand
DO	–	dissolved oxygen
FSA	–	free and saline ammonia
HRT	–	hydraulic retention time
ISS	–	inert suspended solids
OP	–	ortho-phosphates
OUR	–	oxygen utilisation rate
ROP/ORP	–	reduction-oxidation potential
SBR	–	sequencing batch reactor
SRT	–	sludge retention time
SVI	–	sludge volume index
T	–	temperature
TDS	–	total dissolved salts
TKN	–	total Kjeldhal nitrogen
TP	–	total phosphorus
TSS	–	total suspended solids
VSS	–	volatile suspended solids
WWTW	–	wastewater treatment works

Chapter 1

Introduction

1.1 THE SOUTH AFRICAN WATER SITUATION

The geographic location and climate of South Africa renders the country a water scarce region. With an average rainfall of approximately 450 mm/a South Africa falls well below the world rainfall average of 860mm/a (NWRS, 2004). This situation is further accentuated by poor spatial distribution of rainfall (Figure 1.1), seasonality of rainfall and comparatively high evaporation. The total annual runoff of the region is estimated to be 49 000 million m^3/a of which approximately 66% can be captured by current impoundments, bringing the total water storage capacity of South Africa to 32 400 million m^3/a.

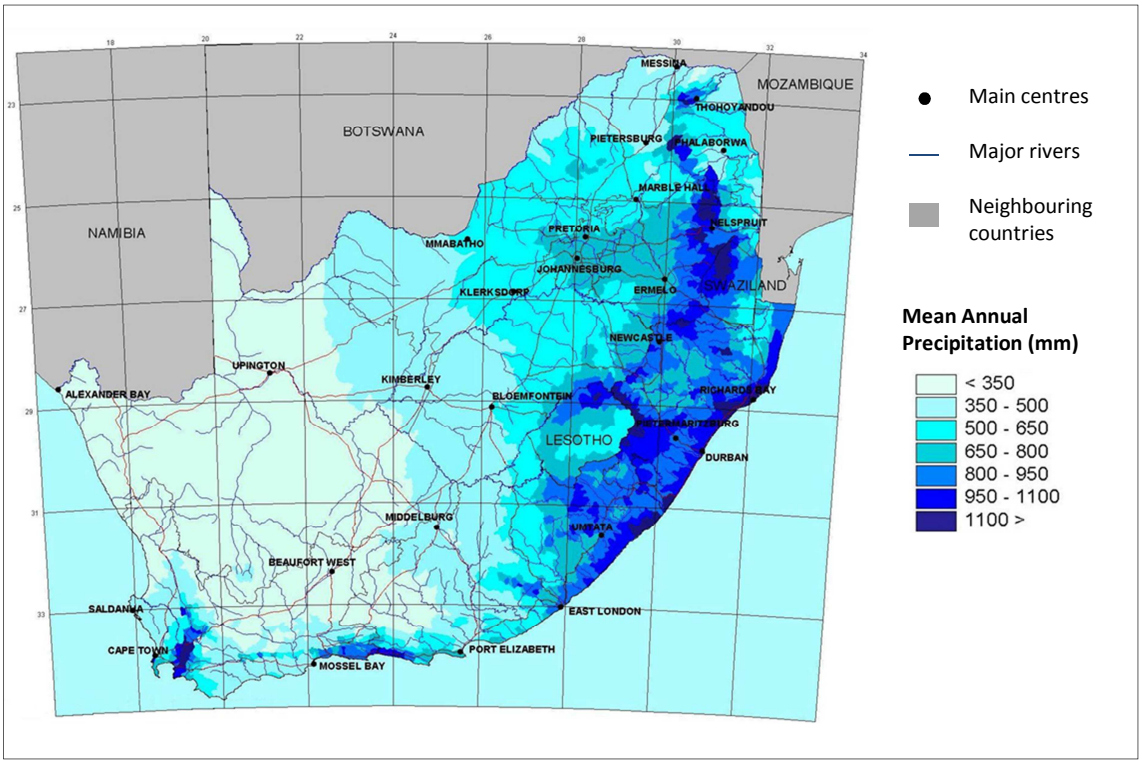


Figure 1.1: Rainfall distribution of South-Africa (Midgley et al. 1994)

The country depends mainly on surface water resources with ground water being limited due to the geology of the region. Ground water is however of strategic importance in rural and arid areas where suitable surface water resources lack or are distant. Industry, urban areas and irrigational use form the bulk of the water requirements in South Africa as reflected in Figure 1.2.

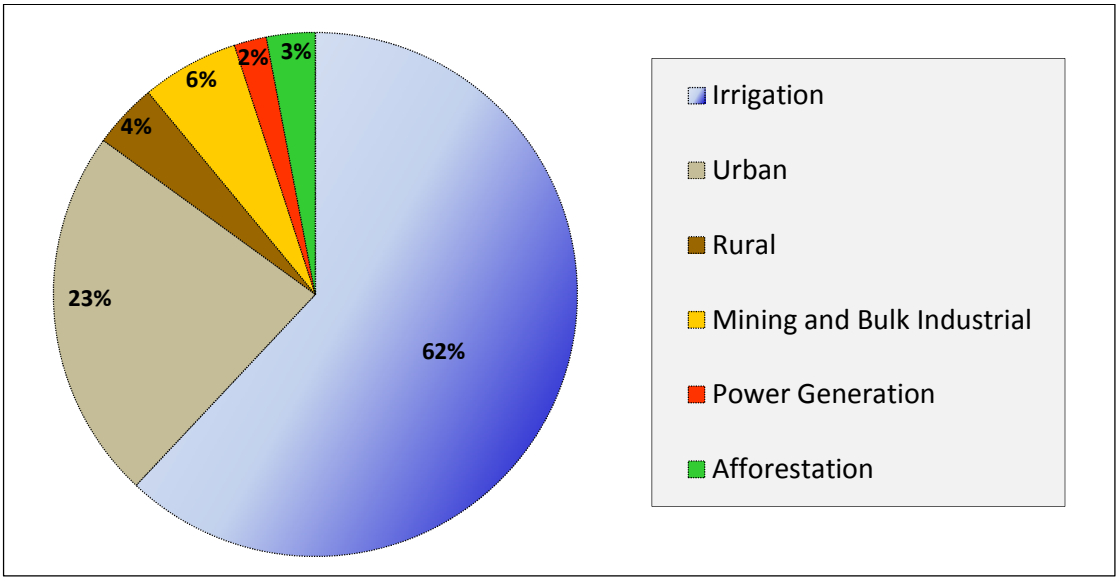


Figure 1.2: Distribution of water requirements of South Africa in 2000 (DWAF, 2004).

The natural ecology is also considered a "water user" as recent legislative changes with respect to water laws acknowledge the water needs of the environment. Therefore a component of the total water reserve is allocated to the biophysical environment in amounts sufficient to maintain a healthy ecology.

Water requirements not only refer to the amount of water required but also the quality of the water. Deteriorating water quality, resulting from pollution, is one of the major threats to surface water resources in South Africa. Pollution of surface water derives from, among others, poor quality wastewater effluents (DWAF, 2004) and includes substances such as salts, nutrients, bacterial/microbial contamination, pharmaceuticals and hormones. Furthermore the effects of pollutants on aquatic ecosystems can be detrimental and in some cases irreversible.

Population growth, economic development and climate change translates into mounting pressure on the presently available water resources of South Africa and a growing future need. Water is the centre of life and human activity and as an extremely limited resource in this country, it is vital that it be well managed and protected from pollution to ensure that there is enough for future needs.

1.2 CURRENT WASTEWATER SYSTEMS AND THE NEED FOR CHANGE IN MANAGEMENT METHODS

In a context of modern day sanitation the disposal of human waste plays a central role. Human waste has to be disposed of in a manner which is safe so as to prevent danger to human and environmental health (SIWI, 2004). Safe disposal of human waste implies that it should not contaminate drinking water and pollute natural water systems which people rely upon or use (Davis and Masten, 2004).

In urban areas the common way of disposing human waste is by discharging it with water as flushing medium, into a public sewer system (where accessible) where it is transported away by the rest of the wastewater flow. From a sanitary point of view this is a conceptually perfect system. However, from a water quality point of view this is somewhat of a paradox as the mixing of water with human waste results in the contamination thereof. Therefore wastewater has to be transmitted to wastewater treatment plants where it is processed to remove the contaminants before being discharged back into natural aquatic systems and so prevent water pollution and sanitary dangers for users downstream.

Treatment of urban wastewater involves the removal of nutrients such as nitrogen, phosphates and carbonaceous materials which form the bulk of pollutants in wastewater. Current wastewater treatment works (WWTW) rely to a great extent on biological treatment processes which require adequate mass of micro-organisms (bacteria) within the treatment system to effectively remove the nutrients entering the system. The mass of nutrients entering the system, determines the size of the system therefore the greater volume of wastewater or the higher the load of nutrients in the wastewater, the larger the WWTW needs to be. If the daily volume of wastewater or concentration of nutrients in the wastewater increases beyond the capacity of the plant, it becomes incapable of sufficiently removing nutrients. In South-Africa this problem is exacerbated by the fact that many wastewater facilities are in a dilapidated state due to inadequate management and poor maintenance (SAICE, 2006). These WWTW have trouble treating normal loads and flows of wastewater let alone increased volumes and so produce bad quality effluent that still contain high concentrations of nutrients. Bad quality effluent results in eutrophication and

pollution of receiving aquatic systems to which this effluent is discharged as illustrated in Table 1.1.

Table 1.1: Trophic status of monitored impoundments in South Africa, October2002 to November 2003 (National Eutrophication Monitoring Programme, DWAF)

Dam Name	TotalP*	Status	Dam Name	TotalP*	Status	Dam Name	TotalP*	Status
-	mgP/l	-	-	mgP/l	-	-	mgP/l	-
Albasini	0.014	Oligotrophic	Klipfontein	0.117	Eutrophic	Nzhelele	0.015	1
Albert Falls	0.03	Oligotrophic	Klipvoor	0.777	Hypertrophic	Olifantsnek	0.057	3
Allemanskraal	0.083	Oligotrophic	Knellpoort	0.032	Oligotrophic	Orange River[1]	0.06	Mesotrophic
Bloemhof	0.114	Hypertrophic	Koppies	0.1	Oligotrophic	Rietvlei	0.38	Hypertrophic
Boegoeberg	0.216	Oligotrophic	Kosterrivier	0.059	Mesotrophic	Roodekopjes	0.059	Mesotrophic
Bon Accord	0.63	Hypertrophic	Krugersdrift	0.135	4	Roodeplaat	0.194	Hypertrophic
Boskop	0.048	Oligotrophic	Laing	0.485	Oligotrophic	Roodepoort	0.165	Mesotrophic
Bospoort	0.791	Hypertrophic	Lindleyspoort	0.041	Oligotrophic	Shongweni	0.059	Eutrophic
Bronkhorstspruit	0.074	Hypertrophic	Loskop	0.027	Oligotrophic	Spitskop	0.092	Eutrophic
Buffelspoort	0.028	Oligotrophic	Lotlamoneng	0.207	Oligotrophic	Sterkfontein	0.026	Oligotrophic
Cooks Lake	0.345	Eutrophic	Luphephe	0.028	2	Taung	0.033	Oligotrophic
Disaneng	0.044	Oligotrophic	Magoebaskloof	0.043	Oligotrophic	Tzaneen	-	Oligotrophic
Douglas Barrage	0.051	Oligotrophic	Maguga	0.022	Oligotrophic	Umtata	0.078	Oligotrophic
Driekloof	0.043	2	Middelburg	0.031	Oligotrophic	Umzinto	0.035	Mesotrophic
Driekoppies	-	Oligotrophic	Middle Letaba	0.021	Oligotrophic	Vaal Barrage	0.069	Oligotrophic
EJ Smith	0.041	Mesotrophic	Midmar	0.066	Oligotrophic	Vaaldam	0.077	Mesotrophic
Erfenis	0.289	Oligotrophic	Misverstand	0.098	Eutrophic	Vaalkop	0.114	3
Gariep	0.049	Oligotrophic	Modimola	0.142	Mesotrophic	Vanderkloof	0.039	2
Grootdraai	0.063	Oligotrophic	Mutshedzi	0.023	Oligotrophic	Voelvlei	0.046	Oligotrophic
Gubu	0.02	2	Nagle	0.027	Oligotrophic	Vondo	0.022	Oligotrophic
Hartbeespoort	0.254	Hypertrophic	Nahoon	0.099	Oligotrophic	Vygeboom	0.012	1
Hazelmere	0.033	Oligotrophic	Neusberg Noord	0.057	Eutrophic	Welbedacht	0.076	Mesotrophic
Henkries	0.038	Mesotrophic	Nooitgedacht	0.035	2	Witbank	0.04	Mesotrophic
Henley	0.004	Oligotrophic	Nsami	0.035	Mesotrophic	Wriggleswade	0.039	2
Inanda	0.024	Oligotrophic	Nungwane	0.018	Oligotrophic			
Kalkfontein	0.059	3	Nwanedzi	0.03	Oligotrophic			

1 - Negligible potential for algal productivity: 0 < chlorophyll ug/l <= 10
2 - Moderate potential for algal productivity: 10 < chlorophyll ug/l <= 20
3 - Significant potential for algal productivity: 20 < chlorophyll ug/l <= 30
4 - Serious potential for algal productivity: 30 < chlorophyll ug/l

* Mean annual values

[1] at Uppington

Once surface water has been polluted with nutrients, removing it and remediating the aquatic system can be a difficult and long process. One such example is the Hartebeespoort dam which has been in a eutrophic state for decades. The pollutants entering the dam derive mainly from the various WWTWs situated in the catchment (Table 1.2) and it is estimated that more than 170 tonnes of phosphorus is discharged into the dam annually (North West Provincial Government, 2005).

Table 1.2: Phosphorus discharge from various sewage treatment works in the Hartebeespoort dam catchment area (North West Provincial Government, 2005).

Sewage Treatment Plant	Median phosphorous in effluent	Phophorus load
-	mgP/l	tonsP/annum
Percy Stewart	6.1	30.5
Randfontein	5.0	12.5
Hartbeesfontein	0.8	10.5
Olifantsfontein	0.5	8.2
Centurion	*No data provided*	*No data provided*
Johannesburg N	0.6	66.0
Esther Park	1.4	0.2
Schoemansville	5.0	3.3
Background	-	42.0
TOTAL	**-**	**173.0**

The biophysical factors of the dam such as the water temperature, depth and flow combined with the high nutrient load leads to large algal blooms and cyanobacteria growth as shown in Figure 1.3. This situation has prevailed in the Hartebeespoort dam since the early 1970's and has had a severe impact on the usability of the water.

Figure 1.3: Algal bloom in the Hartebeespoort dam

Over the years the Hartebeespoort dam has been the topic of various studies and investigations. This included a 10 year study between 1975 and 1985 (documented by Ashton et al.) which was the most comprehensive study of the water quality in a reservoir in the country. Despite all the research done and rehabilitation possibilities (focusing on point source control of nutrients) the condition of the reservoir deteriorated (North West Provincial Government, 2005). Even if all the WWTWs in the catchment (Table 1.2) comply with the special phosphate standard of 1 mgP/l, the amount of nutrients that would enter the Hartebeespoort dam would still be significant (in excess of 90 tons per annum, excluding Centurion). Perhaps this indicates that national limit values for nutrients in wastewater effluent are still too high.

The size of WWTWs have to increase with the growing size of urban areas that it serves in order to accommodate the loads and volumes of wastewater it generates. Subsequently the amount of nutrients discharged into surface waters also increases with an increase in effluent volumes. The question can be asked: To what extent can conventional methods of wastewater treatment still be used before it becomes unsustainable and insufficient? Can larger and more complex WWTWs continued to be built to handle the large volumes and high amounts of pollutants in wastewater and is this viable?

1.3 Wastewater Quality and Associated Implications

A possible alternative to overloaded wastewater system or expanding and building new more complex WWTWs might be found by looking at the source of the problem; the origin of the wastewater. The quality of wastewater (and subsequently the effluent quality) can be improved by reducing the amount of nutrients that enter the sewer system and which have to be removed at the treatment works.

The reduction of nutrient loads would ultimately translate into enhanced capacity of existing WWTWs that are overloaded as well as an extension of their lifetime without the need for alterations. As a result the need for new wastewater treatment works could also be delayed, which will result in capital costs savings. Energy consumption associated with the treatment processes of wastewater would also be reduced. A number of options to reduce the amount

of nutrients that enter the sewer system are available of which one is the source separation of urine.

1.4 Source Separation of Urine

The majority of nutrients in urban wastewater originate from urine. Urine contains up to 80 % of nitrogen, 50% of phosphate and 90% of potassium of the total load in wastewater while making up less than 1 % of the total volume (Larsen et al., 1996). The source separation and treatment of urine could therefore improve on the overall quality of wastewater entering the system.

The idea to separate urine at the source originated in Europe during the 1990's when various researchers such as Kirchman and Petterson (1995), Larsen and Gujer (1996) and Hellström (1998) investigated the concept as a nutrient recovery method and a solution to better wastewater management. By keeping urine separate from other waste streams it is possible to prevent the high concentration of nutrients in urine from being diluted with less concentrated waste streams in the sewer system. In doing so the nutrient load of domestic wastewater can be reduced and the high nutrient load in source separated urine can be handled in a concentrated form. This implies that domestic wastewater can be treated more effectively to obtain a better quality effluent while reducing resource consumption associated with wastewater treatment.

Ecosan (ecological sanitation) initiatives aim at nutrient recovery and reuse by source separation. In Germany such Ecosan projects implement vacuum toilets at office and apartment blocks to separately collect urine and feaces while saving water (Werner, 2006; Winblad et al. 2006). Wastewater collected from this system is then treated onsite by means of a compact activated sludge reactor combined with membrane filtration.

Sweden has mandated that 60% of phosphorous must be recovered from wastewater by 2015 so that it can be reused for agricultural purposes (Swedish Environmental Objectives Council, 2007; Cordell et al., 2008). To achieve the objective, municipalities such as the Tanum municipality in Sweden has implemented a urine diversion policy which encourages

the installation of urine separation systems at new and rehabilitated houses (Cordell et al., 2008; Kvarnstrom et al., 2006. The municipality collects the urine by means of a separate pipe system or from onsite storage containers.

1.5 Handling of Source Separated Urine

The source separation of urine is a promising concept as it holds many advantages. The separated urine however, has to be dealt with and this creates some quandary around the handling of the substance from point of origin onward. One question that arises is how best to transport the source separated urine. This might be done by storing the substance locally in containers and carting it away regularly by truck. Alternatively source separated urine can be diverted to a separate pipe system. Both these options have practical and cost implications. Ultimately the urine has to be treated and this leads to questions surrounding the selection of an appropriate treatment method. The answer can probably be found in determining what the main objective is with the treatment of the urine. These objectives can include stabilisation, nutrient recovery and the removal of excess nutrients to mention only a few.

Wilsenach (2006) proposed the onsite treatment of source separated urine using a sequencing batch reactor in order to, primarily, remove nitrogen and, possibly as a later step, the excess phosphorous. Once the urine has been treated it can then be released back into the sewers as an effluent with a reduced nutrient load resulting in overall improved wastewater quality. It is this suggestion which forms the basis of the work done in this study.

1.6 Scope

This aim of this study is to investigate the treatment of source separated urine in a sequencing batch reactor (SBR) and evaluate the effectiveness and viability of the concept of onsite urine treatment as a method to improve the overall waste water system, including sewers. This study therefore focuses on the biological removal of nitrogen from urine using a sequencing batch reactor.

As biological nitrogen removal is a two-stage process, the SBR will function in two phases. The first phase is aerobic to allow for nitrification of the urine, followed secondly by an anoxic phase in which the nitrified urine is denitrified. Various factors such as substrate inhibition, alkalinity, pH, availability of organic carbon etc. that influence the kinetics of these two phases will form the core of this study.

1.7 OBJECTIVES

The main objectives of this study are to:

- Implement a sequencing batch reactor and produce sludge which is capable of nitrifying and denitrifying source separated urine.
- Ascertain the kinetics for the nitrification and denitrification of urine.
- Quantify the stoichiometric reactions that occur during the hydrolysis, nitrification and denitrification of source separated urine.
- Establish a mathematical model based on the kinetics.
- Prepare design parameters for the onsite treatment of source separated urine in a bio-reactor.

The success of this study relied on the close monitoring of the biological processes in order to determine what the optimal operating conditions were for the nitrification and denitrification of urine. The ultimate outcome is the definition of the biological system in terms of a mathematical model which can be used to design a bio-reactor for onsite treatment of source separated urine. The most important aspect will be to determine what effluent can be produced, starting with a given urine composition.

Chapter 2

Literature Review

Treatment of wastewater is an extensively researched topic and much information is available on the biological and chemical processes involved. Insight can also be gained by investigating different types of wastewater and the associated implications in the treatment thereof.

Biological nitrogen removal is a well established process within the realm of wastewater treatment and this chapter commences with a study on relevant literature relating to nitrification and denitrification. The focus falls mainly on the various factors that influence the bacteria facilitated processes. It is followed by an inquiry into ammonia-rich waste streams and biological treatment thereof. The chapter concludes with an overview of urine, its composition and possible treatment methods.

2.1 BIOLOGICAL NITRIFICATION AND DENITRIFICATION

2.1.1 Nitrification

Nitrification is an oxidation reaction whereby ammonium is converted to nitrate by bacterial action. Nitrification can be split into two subsequent reactions, illustrated in Figure 2.1, that occur under aerobic conditions. In the first step of nitrification, displayed in Equation 2.1, ammonium is oxidised to nitrite (nitritation) by bacterial species such as Nitrosomonad spp. The second step of nitrification is shown in Equation 2.2 and involves oxidation of nitrite to nitrate (nitratation) by bacterial species such as Nitrobacter spp. Once this step is completed full nitrification is achieved.

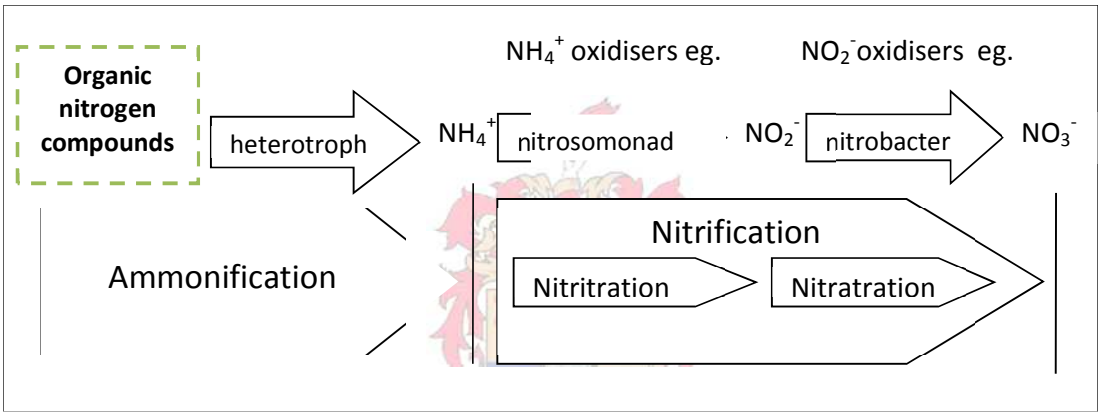


Figure 2.1: Conversion of organic nitrogen to nitrate (Anthonisen et al. 1976)

Catabolic (energy deriving) process of nitrification:

$$NH_4^+ + {}^3/_2O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (2.1)$$

$$NO_2^- + {}^1/_2O_2 \rightarrow NO_3^- \quad (2.2)$$

$$NH_4^+ + O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (2.3)$$

The complete metabolic process looks very similar, since the anabolic process is autotrophic, and no organic carbon is involved as carbon source.

The biological nitrification of urine requires that the oxidation rate of nitrite to occur at the same rate as that of ammonia oxidation in order to ensure steady nitrate production (Udert

et al., 2003). There are however various factors that can influence the nitrification process and therefore ultimately determine the rate.

2.1.1.1 Oxygen

Nitrification is an aerobic process which requires sufficient dissolved oxygen to maintain nitrifying bacteria populations and oxidise ammonium and nitrite. The accepted minimum oxygen concentration for aerobic activated sludge systems is 2 mgO/L but 4-5 mgO/L seems to be an ideal and more optimal range to sustain healthy populations of bacteria. Very high concentrations of dissolved oxygen do not appear to affect nitrification rate (Ekama and Marais, 1984). Nitrite oxidisers however have a lower affinity for oxygen than ammonia oxidisers (Udert et al., 2003a). The half saturation constants for ammonia oxidisers range from 0.5 – 1.0 mgO_2/L and for nitrite oxidisers, 0.5 – 1.5 mgO_2/L.

2.1.1.2 pH and Alkalinity

One of the main considerations during nitrification is pH as it determines the acid-base equilibriums of ammonium, nitrite and hydroxylamine. The ammonia and nitrous acid equilibriums are illustrated in Figure 2.2.

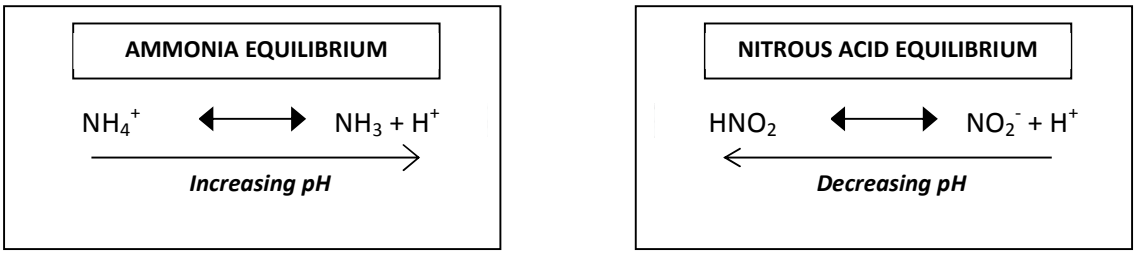


Figure 2.2: pH dependency of ammonia- and nitrous acid equilibrium

The proton concentration also directly influences the metabolism of ammonia and nitrite oxidisers (Udert et al., 2003a). When pH reaches a level of approximately 6, nitritation stops as nitrite oxidisers are strongly inhibited at this pH level by its substrate (nitrous oxide). Conversely this same inhibition effect does not occur at higher pH levels. If pH levels drop below 6, no ammonia oxidation occurs altogether. However if pH levels are restored the nitrification can recover immediately.

Alkalinity which serves as a buffer against strong pH changes can also affect ammonia oxidation. During ammonia oxidation protons are produced which consumes alkalinity and leads to a decrease in pH. Therefore the alkalinity of the solution can determine the amount of ammonia oxidation that occurs (Udert et al., 2003a). In order to prevent strong pH fluctuation during the treatment of urine, pH control can be done through the controlling of the inflow conditions (Udert et al.,2003a).

2.1.1.3 Temperature

Nitrification is a temperature dependant process which increases in rate from 0 to 32°C where after the rate remains constant to approximately 40°C. From 40°C upward the nitrification rate decreases rapidly until the process ceases at approximately 45°C (Henze et al., 1997). Udert et al. (2003a) adds that the growth rate of nitrite oxidisers increases slower than the growth rate of ammonia oxidisers with an increase in temperature.

2.1.1.4 Inhibitors

The inhibition of nitrification can be caused by many substances which affect ammonia oxidisers or nitrite oxidisers or both. During nitrification of ammonia-rich solutions, ammonia oxidisers can be inhibited by their own substrate as well as its product i.e. nitrous acid which is in turn the substrate for nitrite oxidisers (Udert et al., 2003).

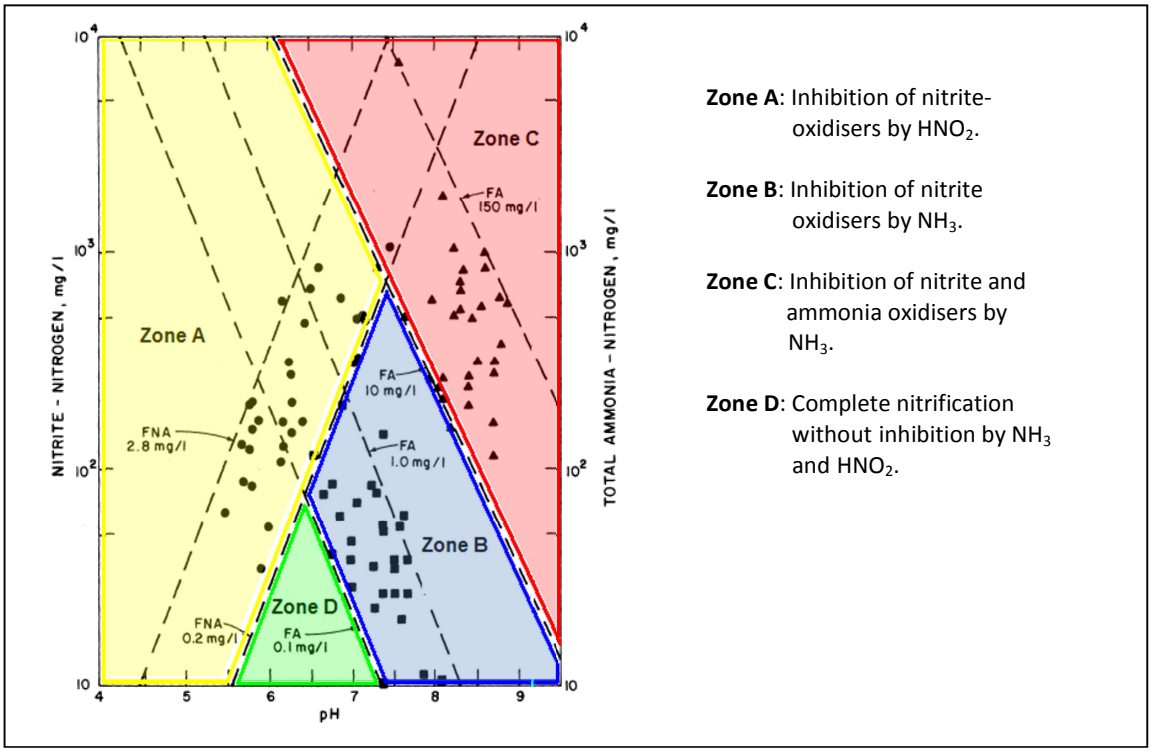


Figure 2.3: Boundary conditions of zones of nitrification (Anthonisen et al. 1976)

Inhibition of nitrite oxidisers by its product is claimed (Udert et al., 2003) to be negligible however, they strongly inhibited by hydroxylamine (NH_2OH) which is an intermediate of ammonia oxidation. Antonissen et al. (1976) determined the boundary conditions of nitrification zones related to pH, free nitrous acid and free ammonia concentrations as illustrated in Figure 2.3.

In activated sludge systems metals can cause inhibition and organic materials such as sulphur components, aniline components, phenols and cyanide have a particular strong inhibition effect (Henze, 1997).

2.1.2 Denitrification

Knowles (1982) describes denitrification as process in which ionic (aq) nitrogen oxides are reduced to gaseous oxides (NO and N_2O) and di-nitrogen (N_2) by reductases, which are enzymes produced by denitrifying bacteria. During denitrification, the nitrogen oxides act as terminal electron acceptors in the absence of dissolved oxygen and the process is therefore anoxic. Organic compounds (substrate) are oxidised and release electrons which are

accepted by the nitrate (and intermediates) until fully reduced to nitrogen gas. Denitrification generally proceeds through some combination of the following intermediate forms:

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (2.4)

The overall catabolic process, with acetate as energy source, can be described as follows:

$NO_3^- + 0.375\ H^+ + 0.625\ CH_3COO^- \rightarrow 0.5N_2 + 0.5H_2O + 1.25\ HCO_3^-$ (2.5)

With the same carbohydrate as carbon source, the overall metabolism could be described as:

$$0.933NO_3^- + 0.2NH_4^+ + 0.625H^+ + 1.108CH_3COO^- \rightarrow$$
$$CH_{1.8}O_{0.5}N_{0.2}\ (\text{biomass}) + 1.216HCO_3^- + 0.866H_2O + 0.466N_2 \quad (2.6)$$

The various steps of nitrification are brought about by different reductase enzymes and are described by Knowles (1982) as follows:

The *nitrate reductase enzyme* (NaR) reduces nitrate (NO_3^-) to nitrite (NO_2^-). These enzymes contain elements such as iron, labile sulphide and molybdenum. Azide is considered as being an inducer of nitrate reduction resulting in 3 to 4 times the activity of NaR.

Nitrite reductase (NiR) is the enzyme which catalyzes the reduction of nitrite (NO_2^-) to N_2O and N_2 and in some cases NO.

Nitric oxide reductase (NOR)and *nitrous oxide reductase* (N_2OR) catalyzes the reduction of NO to N_2O and N_2O to N_2 respectively. Nitrous oxide (N_2O) appears to be a free obligatory intermediate which forms before the final reduction to di-nitrogen (N_2). Acetylene (C_2H_2) and sulfide are two known inhibitants of N_2OR.

According to Henze (1997) the intermediates of denitrification i.e. NO_2, NO and N_2O, are all adverse substances as nitrite inhibits micro-organisms, nitric oxide turns toxic when converted to nitrogen dioxide in the atmosphere and N_2O is a greenhouse gas. The amount intermediates produced and released during denitrification increases if the process is hampered by factors such as limited organic substrate or environmental influences. The best description of factors influencing denitrification was found in the work of Knowles (1982) and is described in section 2.2.2.1 to 2.2.2.5.

2.1.2.1 Oxygen

The presence of excess oxygen in a system represses reductases as it competes for electrons during reduction of nitrogen oxides. Reductases can take place in a semi-anaerobic environment or when O_2 is gradually depleted as the synthesis of at least NaR can then still take place. A rapid shift to anaerobiosis (anaerobic conditions) however does not have the same result. Not all the oxygen has to be removed from a system in order for denitrification to take place and it has been found that bacterium from activated sludge had NaR 20% derepressed with oxygen levels of 15mg/l still present.

The earlier reductases in the dentrification sequence are apparently less sensitive to O_2 presence than the later reductases. This is probably the result of earlier nitrogen oxide being stronger electron acceptors than later nitrogen oxide (i.e NO_3^- stronger e - acceptor than NO_2^- etc.). Nitrite reductase also requires a longer time to derepress than NaR.

2.1.2.2 Organic Carbon

Organic carbon is the source of electrons during the denitrifcation process and the availability of organic carbon is one of the most important controlling factors that influence the activity of denitrifying bacteria. Henze (1997) also mentions that the type of carbon available influences the rate of denitrification. It is believed that the rate of denitrification is not however, affected by an abundance of organic carbon.

2.1.2.3 pH

The rate of denitrification is strongly related to pH as the optimal pH level can be found to be in the range of 7 to 8. Denitrifcation may occur at pH levels of up to 11 however, at lower than optimum levels nitrogen oxide reductases are progressively inhibited especially that which reduces N_2O. The rate of denitrification decreases but mole fraction of N_2O increases and at pH 4, N_2O is the major product. Thus increasing O_2 and decreasing pH result in a decreasing denitrification rate with the proportion N_2O in the evolving products increasing.

2.1.2.4 Temperature

The rate of denitrification is a temperature dependent process. As observed in activated sludge systems, denitrification rate decrease with an increase in temperature up to about 60-75°C where after there is a sharp decline in rate. Temperature appears to have a specific effect on N_2O as the mole fraction of this substance in products can be very high at elevated temperatures.

2.1.2.5 Inhibitors

There are various inhibitors that can be involved in denitrification but inhibition appears to be more of a problem during nitrification.

2.2 AMMONIA-RICH WASTEWATER

2.2.1 Origin and Characteristics

Wastewater derived from activities such as petrochemical, fertilizer and food industries, landfill leachates, sludge reject water (e.g. supernatant) and pig farms is similar to source separated urine in that both contain high loads of ammonia (Table 2.1). It is this very similarity that makes these substances and handling thereof different from domestic wastewater. The biological nitrogen removal (BNR) from ammonia-rich wastewater can be problematic as high ammonia and nitrite concentrations result in inhibition of nitrification and denitrification which form the basis of biological nitrogen removal (Anthonisen et al., 1976). A different approach is therefore required in the biological treatment methods of these substances.

Table 2.1: COD, Nitrogen and Phosphorous concentrations of domestic- and high ammonia load wastewaters

Source of Wastewater		Strong Domestic Wastewater	Strong Septage	Strong Anaerobic Digester Supernatent	Strong Municipal Landfill Leachate	Source Separated Urine
Reference Literature		1	1	1	2, 3, 4	5
COD	(g/m^3)	1000	703000	14650	99000	10000
N_{tot}	(g/m^3)	85	1060	1044	1416	9200
TKN ($NH_3 + N_{tot}$)	(g/m^3)	85	1060	1044	-	-
N_{org}	(g/m^3)	35	940	560	-	-
NH_4^+ / NH_3	(g/m^3)	50	116	480	-	8100
NO_2^-	(g/m^3)	#	#	#	-	0
NO_3^-	(g/m^3)	#	#	#	-	0
P_{tot}	(g/m^3)	15	760	83[a]	-	540
Alkalinity	($g\ CaCO_3/m^3$)	200	4200	1392[a]	730 - 15050	490

1: www.earthwise.dep.state.pa.us
2: Canter et al. (1988)
3: McGinley and Kmet (1984)
4: Lee and Jones (1991)
5: Udert et al. (2006)

\- Data not available
\# Value insignificantly low
[a] Mean value only

2.2.2 Biological Nitrogen Removal from Ammonia-Rich Wastewater

Treatment of wastewater for the removal of nitrogen by means of biological nitrification and denitrification is one of the most widely used methods of treating waste streams such as domestic wastewater which has low concentrations of NH_4^+-N (<500 mg/l) (Gali et al., 2008; Carrera et al., 2003). A well operated wastewater treatment plant can maintain the process well enough to convert the majority of ammonia to nitrate and subsequently nitrogen gas.

Biological nitrogen removal is not however a common treatment method for ammonia-rich (> 500 mg/l) wastewater as the presence of high concentrations of ammonia and nitrous acid severely inhibits biological nitrification resulting in the breakdown of the nitrogen removal process (Anthonisen et al., 1976). This has led to the implementation of other means of treatment for the handling of ammonia-rich wastewater such as physical-chemical systems like ammonia stripping (Carrera et al., 2003).

Biological treatment of wastewater is relatively inexpensive, produces little to no unwanted side-products (Rostron et al., 2000) and is an environmentally friendlier way of dealing with nitrogen in water. Much research has been done on the nitrification-denitrification of ammonia-rich wastewater, producing various ways of overcoming the inhibition problems.

Inhibition can be counteracted by methods such as ammonia loading-rate control as done in a two-sludge system (Carrera et al., 2003). Alternatively retention times of slow growing nitrifiers can be increased in order to produce higher concentrations of biomass of the ammonia tolerant organisms by means of immobilising media to which the organisms can attach and so prevent washing out (Rostron et al., 2000). When inhibition is overcome full nitrification and denitrification can be achieved.

One of the most important issues that arise in the biological nitrification of high ammonia wastewater is the availability of alkalinity. When high amounts of ammonia have to be nitrified it can stoichiometricly be found that there is not enough alkalinity available to complete the process. Although some alkalinity can be recovered from denitrification, it will still be required to add an external source of alkalinity for a complete process.

There are two other factors that have to be considered when treating ammonia-rich wastewater as well:

- Large amounts of ammonia have to be oxidised and therefore high aeration rates are required.
- Large amounts of nitrate, resulting from ammonia oxidation, have to be reduced and therefore an adequate amount of organic carbon is required.

Effects that these two factors might have on the treatment of ammonia-rich wastewater can however be counteracted by applying new biotechnology such as the SHARON-Anamox process (Van Dongen et al. 2001) which involves only partial nitrification and anaerobic ammonium oxidation. This implies a reduction in oxygen and COD requirements during treatment. Ammonia oxidising bacteria use 1.5 mol of O_2 and nitrite oxidising bacteria use 0.5 mol of O_2 to convert 1 mol of NH_4^+ to NO_3^- during full nitrification. However during

partial nitrification only ammonia is oxidised resulting in a 25% reduction of oxygen requirement. Subsequently the denitrification of nitrite instead of nitrate also reduces the demand for organic carbon (Ruiz et al., 2002).

Biological wastewater treatment is a very realistic and promising way of removing nitrogen from ammonia-rich wastewater. Any difficulties associated with it can be overcome and new innovating technology can simplify processes and reduce resource requirements.

2.3 Urine As an Ammonia-Rich Waste Stream

2.3.1 Composition of urine

The composition of urine is reflective of human dietary consumption and therefore the main constituents of urine are N, P, K, S, Ca, Cl and Mg as well as trace elements such as B, Cu, Zn, Mo, Fe, Co and Mn (Kirchmann and Pettersson, 1995; Udert et al., 2006; Maurer et al., 2006; Fenget al., 2007). Though the heavy metal content of human urine is relatively low, the concentration of elements such as copper, mercury, nickel and zinc are still 10 – 500 times higher than in surface waters (Kirchmann and Pettersson, 1995). Urine also contains high loads of pharmaceuticals and hormones excreted by the human body and may be toxic to receiving aquatic systems (Maurer et al., 2006).

The nature of urine collection systems influences the composition of urine as the ratios of the constituents varies according to contributing user groups and can differ over time (Maurer et al., 2006). The composition of fresh urine (i.e. urine immediately after leaving the body) also differs from that of stored urine in collection systems as certain chemical alterations occur due to bacteria and dilution with water. It is therefore difficult to establish the exact formula for the composition of urine.

2.3.2 Chemical alteration of urine

2.3.2.1 Microbial urea hydrolysis

When urine is exposed to a non-sterile environment, the enzyme urease (from ubiquitous bacteria), catalyses the hydrolyses of urea in urine to bicarbonate and ammonia (Udert et al., 2003; Maurer et al., 2006) as shown in Equation 2.7.

$$NH_2(CO)NH_2 + 3H_2O + CO_2 \rightarrow 2NH_4^+ + 2HCO_3 \quad (2.7)$$

This reaction leads to an increase in the pH of the urine solution from 6 to a level of approximately 9. Udert et al. (2003b) found that urease-active bacteria, responsible for urea hydrolysis, grow mainly in the pipes of a collection system and get washed into the storage containers where the urea is then completely hydrolysed within only a few days. Udert also estimates that complete urea hydrolysis can occur in the pipes of a collection system under full flow conditions, thus resulting in a hydrolysis time of only a few minutes.

2.3.2.2 Mineral precipitation

The hydrolysis of urea is associated with a sharp increase in pH and together with the formation of ammonia and bicarbonate triggers the precipitation of mineral compounds such as struvite ($MgNH_4PO_4 \bullet 6H_2O$), hydroxyapatite ($Ca(PO4)_6(OH)_2$) and, if urine is diluted with water, calcite ($CaCO_3$) (Udert et al., 2003b&c). Struvite and hydroxyapatite are both phosphate minerals and after precipitation has commenced it can be found that 30% of phosphate in undiluted urine is in the form of precipitates (Udert et al., 2006).

Udert et al. (2006) found that only small amounts of urea (11-24%) have to be hydrolysed in order for a significant quantity of precipitation (87-97%) to occur. Calcium and magnesium is the stoichiometric limiting factor complete precipitation. Therefor addition of calcium and magnesium to urine can enhance precipitation processes as well.

2.3.2.3 Ammonia volatilisation

After hydrolysis occurs, stored urine contains high concentrations of ammonia (Table 2.1). Ammonia is a volatile substance which results in urine in collection systems being an

unstable solution of which any agitation can lead to the volatilisation of ammonia (Udert et al., 2006; Hellstrom and Johansson, 1999).

Despite the fact that NH_3 is highly soluble in water, minor losses of ammonia-N can occur in urine storage systems that are not closed or properly sealed. This can lead to odour problems and negatively affect human health and the environment (Galloway and Cowling, 2002; Udert et al., 2006). Up to 33% of the ammonia in urine is volatile ammonia and volatilisation does become a bigger problem during transport or handling of urine as much greater ammonia losses and odour problems can occur than during storage (Udert et al. 2006). Ammonia volatilisation might be a possible characteristic to take into consideration during treatment of urine such as when the urine solution is aerated or stirred.

2.3.3 Major compounds

2.3.3.1 Nitrogen

Nitrogen is the most abundant of all the elements in urine and can be found in different forms. Before urea hydrolysis of fresh urine, 85% of total nitrogen is present as urea and 5% as total ammonia. After the process of hydrolysis, 90% of nitrogen is present as total ammonia (Udert et al., 2006). Stored urine also contains very small fractions of nitrite/nitrate-N.

2.3.3.2 Phosphate

Dissolved phosphate makes up for 95 - 100% of the total phosphorous in urine however during storage of urine this figure is influenced by precipitation as large amounts of phosphorous can be fixed in precipitates (Ciba-Geigy, 1977; Udert et al., 2003c).

2.3.3.3 Potassium

Potassium is the third major nutrient in urine of which the concentration is not really affected by chemical alteration processes of urine. Potassium is known to be included in certain precipitates that form in stored urine but this is not always common or only consumes a small fraction of potassium when it occurs (Udert et al., 2006).

2.3.3.4 Magnesium and calcium

Magnesium and calcium is present at a relatively low concentrations in fresh urine (Table 2.1) however, the dilution of urine with water can add additional amounts of these two elements (Maurer et al., 2006).In stored urine the majority of magnesium and calcium can be present in the form of precipitates (Udert et al., 2006).

2.3.3.5 Sulphur

Sulphate contains 90% of the total sulphur content of urine with compounds such as sulphuric acid esters and neutral sulphur compounds accounting for the rest of the sulphur content (Udert et al., 2006; Ciba-Geigy, 1977). In stored urine, where there is an absence of oxygen, nitrate or nitrite, sulphate is prone to reduction by microbial activity as it becomes the most favourable electron acceptor (Udert et al., 2006).

Table 2.2: Composition of urine from different sources of collection

Source		Fresh Urine	School	Household		Workplace		
Reference Literature		1	2	2	3	4	5	6
Dilution[a]	(-)	1	0.33	0.33	0.75	0.26	#	1
pH	(-)	6.2	8.9	9.0	9.1	9.0	9.0	9.1
N_{tot}	(g/m^3)	8830	2610	1795	3631	1793	-	9200
$NH_4^+ + NH_3$	(g/m^3)	463	2499	1691	3676	1720	4347	8100
$NO_3^- + NO_2^-$	(g/m^3)	-	0.07	0.06	<0.1	-	-	0
P_{tot}	(g/m^3)	800 - 2000	200	210	313	76	154	540
COD	(g/m^3)	-	-	-	-	1650	6000	10000
K	(g/m^3)	2737	1150	875	1000	770	3284	2200
S	(g/m^3)	1315	175	225	331	98	273[b]	505[b]
Na	(g/m^3)	3450	938	982	1210	837	1495	2600
Cl	(g/m^3)	4970	2235	2500	1768	1400	2112	3800
Ca	(g/m^3)	233	13.34	15.75	18	28	-	0
Mg	(g/m^3)	119	1.5	1.63	11.1	1	-	0
Mn	(g/m^3)	0.019	0	0	0.037	-	-	-
B	(g/m^3)	0.97	0.44	0.435	-	-	-	-

1: Ciba-Geigy (1977)
2: Kirchmann & Pettersson (1995)
3: Jonsson et al. (1997)
4: Udert et al. (2003b)
5: Ronteltap et al (2003)
6: Udert et al. (2006)

[a] Dilution factor as obtained from related reference literature by Maurer et al. (2006)

Dilution factor defined as $V_{urine}/[V_{urine} + V_{water}]$

[b] Sulfate-S (SO_4^{2-}-S) value only

The Council for Scientific and Industrial Research (CSIR, South Africa) conducted a study on the composition of urine generated by one of the office blocks at the CSIR Stellenbosch campus over a period of 7 months (Anderson, 2009). The male and female restrooms in this

building were fitted with source separating (no-mix) toilets of which the waste streams were diverted to separate onsite storage containers, one for brown water from ladies and gents toilets, one for male urine and one for female urine. The male urinals were also retrofitted so that urine was diverted to a fourth onsite container. The urine from the three containers were analysed individually over the period of a few months and the results are summarised in Table 2.3.

Table 2.3: Average composition of urine collected from office block at CSIR

Source		Male No-Mix Toilets	Female No-Mix Toilets	Urinals
Samples	(-)	8	8	46
K	(mg/l)	545.6	431.9	1866.8
Na	(mg/l)	619.0	524.4	2141.7
Ca	(mg/l)	22.6	20.4	30.3
Mg	(mg/l)	0.8	1.9	3.0
NH_4^+	(mg/l)	1402.5	978.8	3705.5
OrthoP	(mg/l)	93.0	62.6	249.0
Total P	(mg/l)	121.7 [1]	79.3 [1]	-
SO_4^-	(mg/l)	575.8	336.5	1284.2
Cl	(mg/l)	1111.5	704.4	4098.0
COD	(mg/l)	1890.6	1271.5	7719.9
TKN	(mg/l)	2113.2	1273.8	6603.5
TDS	(mg/l)	3865.0	2837.1	14161.5
Alkalinity	(mg $CaCO_3$/l)	5375.3	3688.3	18172.6
EC	(mS/m)	1273.8	903.1	3414.4
pH	(-)	9.1	8.9	9.1
DOC	(mg/l)	459.0	240.1	2587.9
DOC	(mgCOD/l)	1224.0	715.8	6901.1

[1] Only 6 samples tested

The urine from the urinals contains higher concentrations of the various constituents than urine from the no mix toilets. This is as a result of the dilution of urine that occurs in the male and female no-mix toilets when flush water spills into the urine separating compartment of the toilet during flushing. The flush mechanisms of the male urinals were however disconnected so as to prevent urine diluted with water. A total of 50 samples from the urinal system were analysed of which the first four were discarded as hydrolyses had not yet set in.

2.4 TREATMENT OF SOURCE SEPARATED URINE

The treatment of source separated urine has been the topic of a number of studies since the concept of urine separation took root in the engineering community. The treatment methods used for urine treatment are determined by the objective of urine treatment. As this study involves nitrogen removal from urine, the emphasis was on nitrification and denitrification as treatment method of urine. Therefore research literature relating mainly to this form of urine treatment was pursued.

2.4.1 Basis for urine treatment

Maurer et al. (2006) investigated several treatment methods based on different reasons for urine treatment namely hygienisation, volume reduction, stabilisation, nutrient recovery and removal of micro-pollutants (Table 2.4). The work was based on treatment techniques that have been tested at least in a laboratory however, treatment technologies applied to other waste streams could be adapted to urine treatment and would almost certainly be effective because of the unique chemical properties of urine (Maurer et al., 2006). Although Maurer does not specifically look at the nitrification and denitrification of urine, some insight can be gained from this study on urine treatment.

Table 2.4: Treatment methods for various purposes of urine treatment as investigated by Maurer et al. (2006)

Purpose	Treatment
Hygienisation	Storage
Volume reduction	Evaporation Freeze-thaw Reverse osmosis
Stabilisation	Acidification Partial nitrificaion
Phosphorous recovery	Struvite precipitation
Nitrogen recovery	Ion-exchange Ammonia stripping Isobutylaldehyde-diurea precipitation
Nitrogen removal	Anammox process
Micropollutants removal	Electrodialysis Nanofiltration Ozonation and advanced oxidation

2.4.2 Biological Nitrification and Denitrification of Urine: Trialled methods

Explicit information on the complete nitrification and denitrification of urine is vague as the available research either refers to one or the other or just partial nitrification. The available information on urine composition and urine treatment has to be combined with literature on ammonia-rich wastewater treatment and conventional biological nitrogen removal theory to gain insight on nitrification and denitrification of urine.

Work done by Udert et al. (2003a) relates to the nitrification and denitrification of urine for the purpose of stabilisation. The main goal of his study was to produce an ammonium nitrate solution and therefore nitrification of only a fraction of the ammonia in urine was required. In his study Udert et al**.** (2003a) confirmed that without pH control during nitrification of urine, only 50% of total ammonia can be oxidised to nitrite/nitrate resulting in a solution with a 1:1 ammonia to nitrite/nitrate ratio.

As a secondary part of the study, Udert looked at the denitrification of urine using anaerobic ammonium oxidation (ANAMMOX) which only requires partial nitrification i.e. ammonium oxidation to nitrite. This suits the treatment of urine well as urine has the characteristic of inhibition of the conversion of nitrite to nitrate during nitrification (Maurer et al., 2006). A possible cause of this inhibition could be low pH which inhibits nitrite oxidisers when high nitrite concentrations are present as well (Maurer et al., 2006).

The various treatment units that were used by Udert (2003a) during this study was a moving bed biofilm reactor for nitrate production, a continuous flow stirred reactor for nitrite production, a sequencing batch reactor and a batch reactor also for nitrite production and a batch reactor for anaerobic ammonium oxidation.

Feng et al. (2008) investigated the complete nitrification of urine as a means to stabilise it and recover nutrients using Spirulina platensis culture. For this purpose Feng made use of a packed-bed bio reactor. The reactor was initially run using diluted synthetic human urine until nitrifying bacteria were established. Thereafter the synthetic human urine was switched with diluted real human urine. It was observed that nitrifying bacteria could adapt

rapidly to the change. Throughout the experiment the temperature was maintained at 27°C so as to attain favourable climatic environment for nitrification. The pH was also adjusted daily to 8.0 in order to counter the decline in pH during nitrification and sustain optimal conditions for nitrification.

2.5 Sequencing Batch Reactor (SBR) as Proposed Treatment Unit

The onsite treatment of source separated urine may be spatially limited and therefore have constraints on the unit in which the processes must occur. A sequencing batch reactor suits the purpose of onsite treatment very well as the unit can incorporate the processes of nitrification and denitrification in the same vessel making it compact and a practical device.

2.5.1 SBR Background

Sequencing batch reactors have been in use since the 1920's and are growing in popularity in Europe, China and the USA (Al Rekabi et al., 2007). The increasing interest in the application of SBR technology can be attributed to the cost efficiency thereof in combination with its flexibility and efficiency in the treatment of a variety of industrial and municipal wastewaters, especially where waste streams are produced in varying flow patterns.

SBR's where originally used to treat wastewater for COD removal (Kargi et al., 2002). Since Irvin and Davies's (1971) explanation of SBR's, the technology has received much attention and has become subjected to extensive research (Al Rekabi et al., 2007; Artan et al., 2001). This has led to the development and wider application SBR's as a treatment unit capable of removing COD, nutrients and particulates from wastewater to produce effluents which meet high standards (Al Rekabi et al., 2007).

2.5.2 SBR Description

A sequencing batch reactor can be described as an activated sludge wastewater treatment unit which functions in time rather than space (EPA, 1999). A SBR consists of a single basin which operates in temporal sequences on a withdraw-and-fill basis. The basin serves as equaliser, clarifier and reactor which can accommodate various biological processes

depending on how the SBR is operated. Multiple basins can be combined to form a system of SBR's which function in parallel (Irvine et al., 1977; Artan et al., 2001).

2.5.3 Operation

The SBR system is operated in cycles that incorporate sequencing steps in which volume exchange and treatment processes are facilitated. The steps are defined in cyclical order shown in Figure 2.4 as (Artan et al., 2001; Al Rekabi et al., 2007; Akin et al.,2005; EPA, 1999):

1 – Idle

2 – Fill

3 – React

4 – Settle

5 – Draw

The total cycle time is a function of the combined duration of these steps which in turn depends the type of wastewater and the treatment strategy (Artan et al., 2001; EPA, 1999).

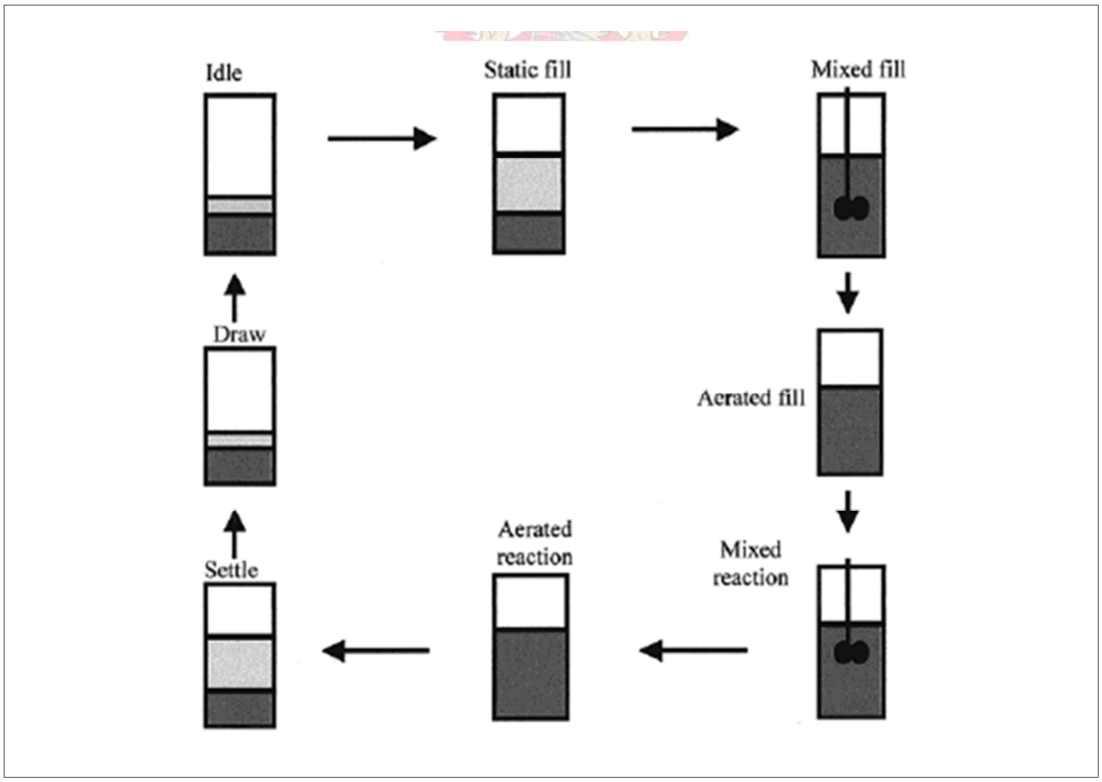


Figure 2.4: Schematic cyclical operation of a SBR (Mace et al., 2002).

2.5.3.1 Idle

The idle step occurs in a period between the draw and fill step. This stage in a cycle can be implement to waste sludge and/or serve as stabilisation period when the basin is filling with effluent (Al-Rekabi et al.,2007; EPA, 1999). Stabilisation enables the system to cope with peak flows and peak loads in the influent. The system can be mixed during the idle step to condition the biomass and to assist sludge wasting. It is common practise to waste sludge on a regular basis but in some cases it is done as infrequently as once every two to three months (Al-Rekabi et al., 2007)

2.5.3.2 Fill

The fill step involves the inflow of wastewater into the system which may be raw or settled. The fill procedure can be characterised into three regimes which are static fill, mixed fill and aerated fill. An EPA (U.S.) report on SBR's (1999) best explains the characteristics of the fill procedures:

The static fill occurs with no aeration or mixing in the system. This results in a high substrate concentration when mixing commences which produces favourable conditions for floc forming organisms that are associated with improvement of the ability of sludge to settle.

The mixed fill is facilitated by mixing the wastewater and biomass as inflow occur which initiates immediate biological action. Organisms, that utilise organics, rapidly deplete available oxygen in the system and then proceed to use nitrate or sulphate as electron acceptor. This type of fill regime is typically associated with nutrient removal systems.

An aerated fill regime takes place by aerating the system while influent is added. This initiates aerobic processes which are to be implemented in the following "react" step and may reduce the total aeration time required.

2.5.3.3 React

The react step is the phase during which bacterial action is induced (or resumed from mixed/aerated fill) by creating favourable conditions for the desired bioprocesses. This is achieved by operating the system in a mixed react and/or aerated react mode. Aerated react

mode creates aerobic conditions for organics removal and nitrification Mixed react mode facilitate anoxic conditions for denitrification or anaerobic conditions for sulphate reduction. Nutrient removal in a SBR is achieved by altering the react phase to include a number of aerobic, anaerobic and anoxic periods in various sequences and duration, based the wastewater characteristics and required treatment strategy (Kargi et al., 2002).

2.5.3.4 Settle

The completion of the react step is follow by the phase during which solids are separated from the bulk liquid and is defined as the settle step. Conditions during settling are normally quiescent during which no inflow or outflow takes place (Al-Rekabi et al., 2007). The initial stages of settling can be assisted by gentle mixing which may produce clearer effluent and denser settled sludge (EPA, 1999).

2.5.3.5 Withdraw

The withdrawal of treated effluent from the SBR is aided by a decanting mechanism. The decanter can be of a floating kind which maintains the inlet orifice just below the liquid surface and in doing so, assists in preventing solids from leaving with the effluent (EPA, 1999). Alternatively decanters can be of a fixed type which is fitted to the basin wall at a predetermined level. The flow rate from the reactor can be regulated by means of a valve, pump or adjustable weir (Al-Rekabi et al., 2007).

2.5.4 Application and Performance

The scale of implementation for SBR's is extensive and includes laboratory, pilot and full scale applications. Mace et al. (2002) completed an extensive review on the application of SBR's in which the treatment of various types of wastewater and the performance of the systems are discussed. In this review Mace refers to SBR systems that treat the following types of wastewater:

- Municipal sewage
- Sludge reject water
- Winery and brewery wastewater
- Landfill leachate

- Paper industry effluents
- Food industry and dairy wastewater
- Piggery wastewater

The outcome of the review by Mace et al. (2002) and similar work by others (Altaf et al., 2010; Al-Rekabi et al., 2007; Suresh et al., 2011; Gali et al.,2008 etc.) manifests the efficiency of SBR's in the treatment of an array of wastewaters, removing nutrients, organics, particulates and other pollutants to high standards.

2.7 SUMMARY

From wastewater literature and past studies on urine presented in this chapter, a general idea was compiled of the experimental system and how it should progress given the nature of the organisms involved, the characteristics of urine and the treatment system constraints. Information collected in the literature review will be implemented in the approach and execution of experimental work to follow.

The study will commence by setting up an experimental system which is able to accommodate the organisms that facilitate nitrification and denitrification. It will also be necessary to evaluate the progress of the processes by monitoring environmental conditions and changes in the system. The will be discussed in the following chapter.

Chapter 3

Materials and Methods

This chapter provides an overview of the experimental work and procedures during the study. It comprises a description of the experimental setup and operation as well as the analytical methods used.

3.1 EXPERIMENTAL SETUP

The main experimental setup used for this study consisted of a laboratory scale sequencing batch reactor (SBR) system. This system was operated continuously for the duration of the study. A set of smaller batch reactors were implemented as well in order to do additional experiments for shorter periods of time without affecting the main system.

3.1.1 Sequencing Batch Reactor

3.1.1.1 Reactor Vessel

The reactor vessel and fixtures is illustrated in Figure 3.1. The reactor vessel consisted of a vertical perspex tube with 153 mm inside diameter, 1020 mm high and 20.0 l operating volume. The reactor height was later extended by 300 mm allowing for headroom and preventing spillage during operation. The reactor was fitted with 3 ports/valves, one at the top, one at the base and one in the middle. Two probe ports were inserted at mid-level, one on either side of the mid-level valve.

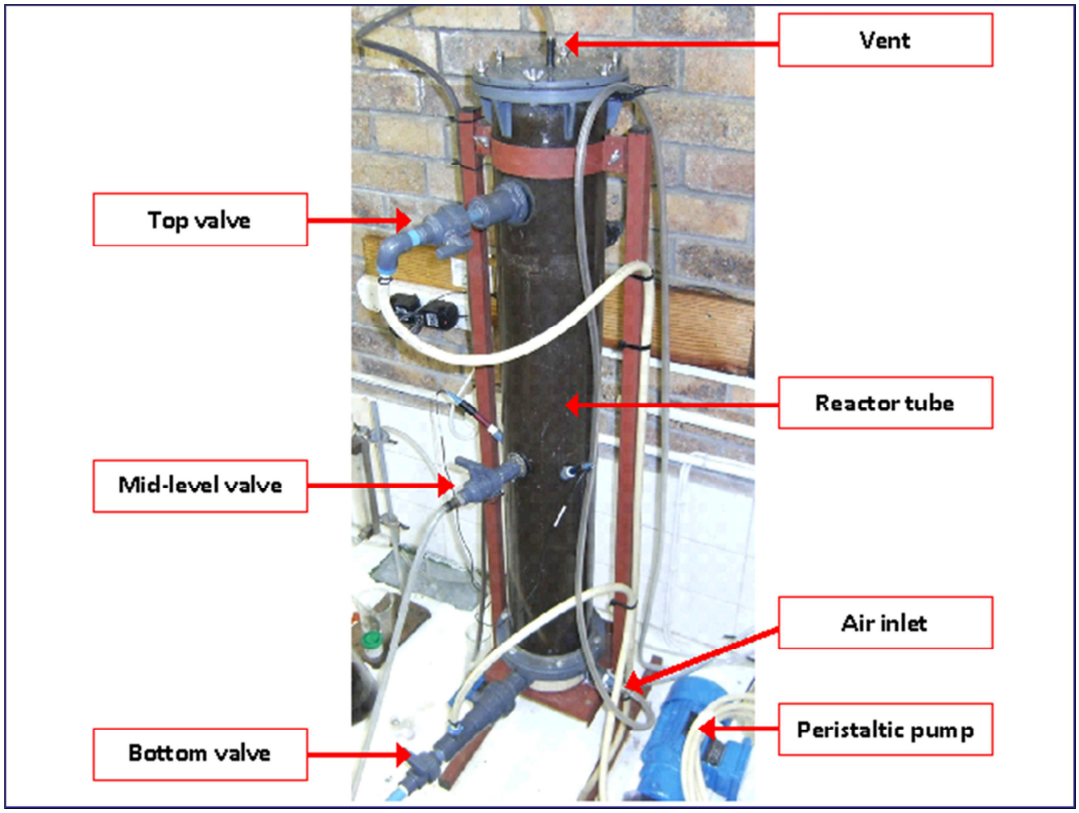


Figure 3.1: Experimental sequencing batch reactor.

3.1.1.2 Circulation

The top and bottom valves of the reactor were connected to a circulation line that consisted of 8mm tubing rigged through a 0.75 kW peristaltic pump. In addition the pump was fitted with a variable speed drive that enabled different pump rates as well as changeable pump direction.

3.1.1.3 Aeration

A nozzle was fixed into the base of the reactor. On the interior end of the nozzle a fine bubble aerator was attached and the exterior end of the nozzle was connected to an airline. The airline was fitted with a humidifier to reduce excessive evaporation from the reactor. Compressed air was supplied by an onsite compressor and maintained at a pressure of 100 kPa.

3.1.1.4 Process Monitoring

The sequencing batch reactor setup and instrumentation configuration are diagrammatically illustrated in Figure 3.2. The conditions inside the reactor were monitored by means of pH and reduction-oxidation-potential (ROP) probes. The probes were linked to an online data logger of which the logging interval could be set as required. Temperatures were measured manually with a mercury thermometer.

The initial data storage mechanism for the logger later failed during the experiment and readings had to be taken manually from the display unit until the probes and logger could be replaced. The new data logger unit monitored

- pH
- Oxidation-reduction potential (ORP)
- Temperature (T)
- Specific conductance (SC)
- Dissolved Oxygen (DO)

The oxygen utilisation rate (OUR) was measured concurrently to the above monitored parameters by a separate device. This device consisted of a control/logging processor which was linked to a separate DO probe in the reactor and a solenoid valve that was inserted in the airline. The processor maintained the DO between a set low and high concentration points. This

was facilitated by the solenoid valve which was controlled by the processor. The processor was programmed to shut the solenoid valve when the DO concentration in the system reaches the high set point. The DO concentration would decline after the valve shut. When the DO concentration of the system reached the low set point the solenoid valve would be opened. The OUR was calculated by the device based on the time between shutting and opening the valve and the set point interval.

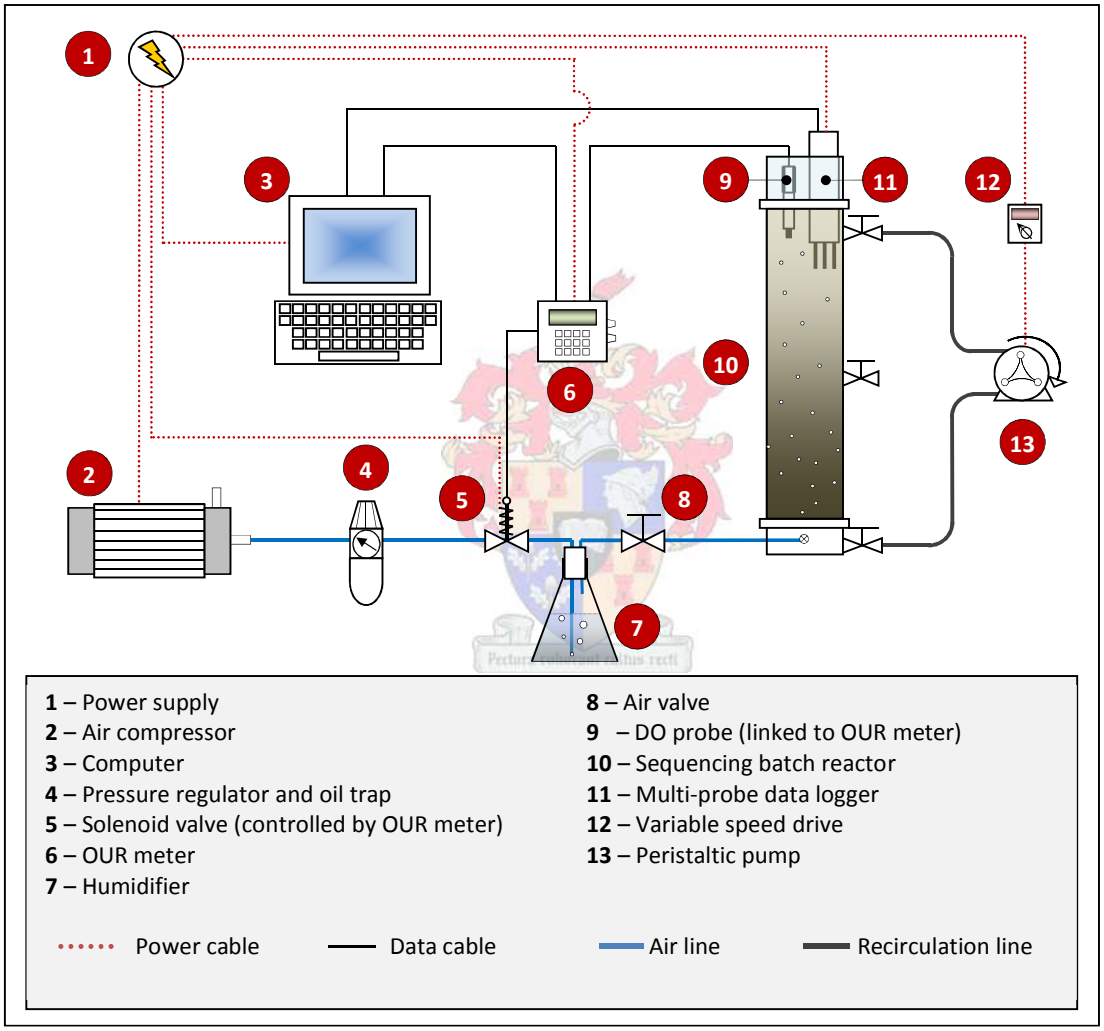


Figure 3.2: Diagrammatic layout of the sequencing batch reactor and instrumentation.

3.1.2 Operation and Control

Reactor Operation

The volume exchanges were carried out by manually withdrawing effluent from the mid-level valve and adding new feed into the top of the reactor. The volumes of effluent and feed were measured in volumetric flasks so as to determine and replace the evaporative volume losses from the reactor.

The duration of cycle phases were maintained by manually closing and opening the air valve. The air supply during aerobic phases was automated by means of a solenoid valve controlled by the OUR meter. The control of cycles and phases is illustrated in Figure 3.2.

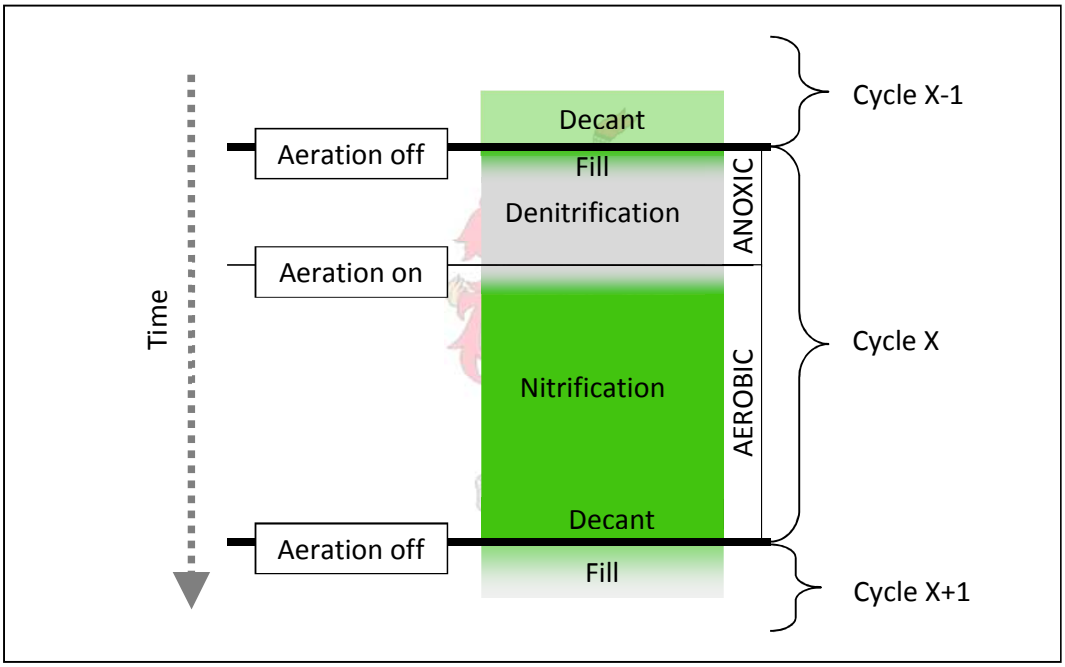


Figure 3.3: Operation of the experimental system

Process Control

The pH in the system was controlled by the inflow of urine duration of anoxic and aerobic cycles. No additional alkalinity was added other than the alkalinity in the batch feeds of urine. The temperature was not controlled initially but a heating element was later added to the system to prevent the temperature from dropping below 20°C.

3.2 BATCH EXPERIMENTS

A series of batch experiments were also carried out in a batch reactor (BR) using sludge from the sequencing batch reactor (SBR). The purpose of the experiments was to determine the effects that the high salinity and ammonia concentration had on the nitrifying organisms in the system. The BR setup and instrumentation configuration are diagrammatically illustrated in Figure 3.4.

Every batch experiment was conducted in a 3.5 l BR with compressed air supply and paddle mixer. Three litres of effluent from the SBR was centrifuged to separate the sludge. This sludge was added to the BR which was then filled to the 3.0 l mark with synthetic solution to simulate different living conditions for the sludge organisms. The synthetic solution was made up of distilled water and dissolved ammonia/salt combinations to meet the requirements as determined for each batch experiment. The saline conditions were simulated by slowly dissolving sodium chloride (NaCl) into the distilled water while measuring the specific conductivity with a conductivity meter. The sodium chloride was added to the solutions until the specific conductivity meter measured the same specific conductivity present in the sequencing batch reactor. The ammonia was supplied in the form of ammonium bicarbonate (NH_4HCO_3) which was also served as a good alkalinity supplement to assist in pH control. The ammonia and salinity of the individual batch experiments are given in Table 3.1.

Table 3.1: Salinity and ammonia-N concentrations for batch experiments.

Batch Experiment	NH_3-N	Salinity
no.	mg/l	mS/cm
1	2400	5
2	800	5
3	2400	25
4	800	25

The temperature was maintained at 20°C (± 0.2) and the pH at 7.7 (±0.1). Batch experiments were conducted for 12 hours under aerobic conditions during which OUR was measured. Samples were taken every hour and tested for FSA, NO_3^--N and NO_2^--N after which the results of the various batch experiments were compared.

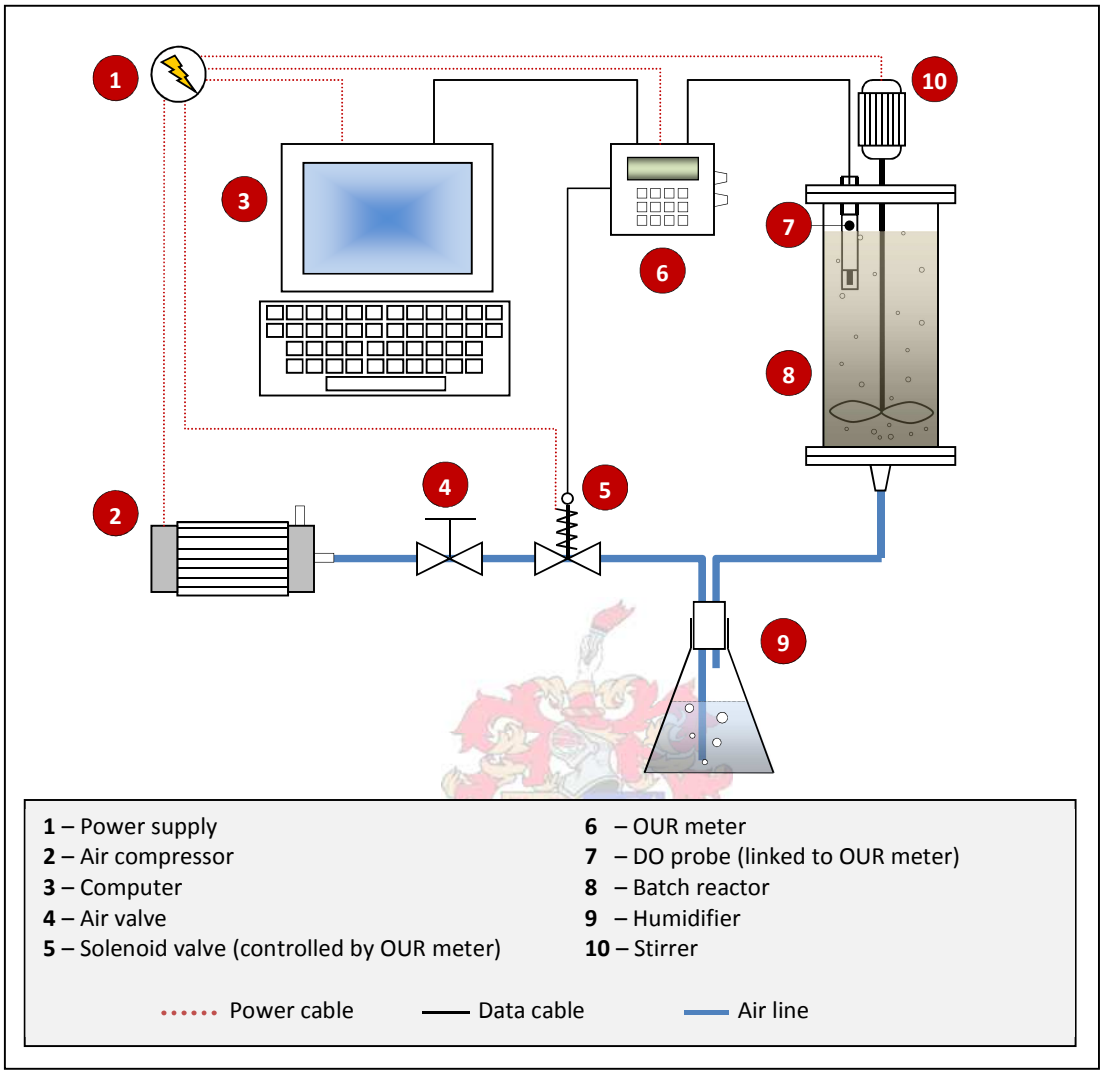


Figure 3.4: Diagrammatic layout of the batch reactor and instrumentation.

3.3 Analytical Methods

The samples collected from the sequencing batch reactor (SBR) and the batch reactor (BR) were prepared and chemically analysed to determine the concentrations of various constituents. Samples were analysed in filtered and unfiltered forms to determine the composition of both the dissolved and particulate fractions. The chemical constituents tested included TKN, FSA, Nitrite, Nitrate, COD, ortho-phosphates and alkalinity. Effluent from the SBR was analysed physically as well to determine the properties of the sludge. These physical properties included

sludge settleability, sludge volume, sludge mass, sludge volume index (SVI), total solids, volatile solids and inert solids.

3.3.1 Sampling and Sample Preparation

Sampling

Sampling was conducted whilst the system was in a fully mixed state to ensure that the samples were representative of the whole system at the particular time it was extracted. This was especially important for accurate analyses of unfiltered samples as particulates can contribute significantly to the chemical composition of the sample.

Samples were taken from the midlevel port of the reactor. Before a sample was extracted, the valve would be opened and left running for a few seconds to wash out the port and sampling pipe with effluent. Only then a sample would be taken after which the wash out effluent was returned to the reactor.

Samples that were to be analysed chemically were taken in volumes of ± 50 ml. Samples that were to be analysed chemically and unfiltered were taken in ± 150 ml volumes whereas samples to be used for physical analyses were taken in volumes of 1 000 ml. All containers used were clean and airtight. The samples were placed in a light-restricted cold-room immediately after sampling and stored at <5˚C until analyses could be performed.

Filtration

The samples that were to be analysed for dissolved constituents, were filtered using a 1.2 µm glass fibre filter first, followed by a 0.45 µm membrane filter using a suction flask and a compressor. The samples were filtered immediately after it was taken.

Dilutions

The various chemical analysis methods used had specific concentration ranges within which the chemical constituents tested for had to be in order to obtain accurate measurements. The concentration of the constituents in the samples were all well above the range of the analysis methods. Thus the samples were diluted to the range within which the method could be

applied and the result multiplied by the dilution factor. Dilutions were made stepwise using volumetric flasks and 5 ml to 10 ml pipettes to ensure accuracy of the large dilutions required for some of the methods.

Table 3.2: Dilutions of samples.

Constituent	Volume of Sample Used	Dilution Factor	Dilution Steps
TKN	5 ml	100	x10x10
FSA	5 ml	100	x10x10
Nitrite/Nitrate	10 ml	5000	x10x10x10x5
COD	10 ml	20	x10x2
Ortho-P	5 ml	50 / 100	x10x5/x10x10
Alkalinity	5 -10 ml	50 / 100	x10x5/x10x10

3.3.2 Chemical Analyses

The choice of methods selected for chemical analysis during the study was mainly determined by the availability of equipment and facility. The methods used for the analyses are based on procedures stipulated in the Standard Methods for the Examination of Water and Wastewater (SMWW, American Public Health Association, 2005) and can be consulted accordingly for detailed explanations. The chemical constituents tested for and methods applied are named and briefly discussed below.

Free and Saline Ammonia (FSA) – SMWW Method 4500-NH_3 C

FSA concentrations were determined using a titrimetric method. The method involves converting all saline ammonia (NH_4^+) in a sample to free ammonia (NH_3) then steam distilling it into a indicating boric acid (H_3BO_3) solution which turns from purple to green as the ammonia is absorbed. The boric acid solution is then titrated with a sulphuric acid solution. The boric acid solution turns back to purple and the endpoint of the titration is reached when the purple solution stops gaining intensity in colour. The concentration of ammonia-N in the solution can then be calculated from the volume of sulphuric acid titrated (Appendix A). The difficulty in this method is determining the end point of the titration as it is not always easy to determine when the colour intensity stops changing.

Total Kjeldahl Nitrogen (TKN) – SMWW Method 4500-Norg B

The TKN was determined using a macro-Kjeldahl method. TKN measures the amount of organic nitrogen as well as inorganic ammonia-N present in a sample. The procedure of this method is identical to the FSA method described above with the exception of a preceding step in which a sample is digested before steam distilled. During digestion all the organic nitrogen in the sample is converted to inorganic nitrogen which is then measured as ammonia. The amount of organic nitrogen in a sample is determined by conducting a FSA test and a TKN test on the sample and calculating difference in measured values.

Nitrite and Nitrate – SMWW Method 4500-NO3 H

Nitrite and Nitrate concentrations were determined by means of an automated colorimetric method facilitated by an auto analyser. A sample is inserted into the instrument wherein all nitrate-Nis reduced to nitrite-N by hydrazine. The nitrite then reacts with an added colouring reagent to form a coloured solution. The colour intensity of the solution is determined by the concentration of nitrite present. The solution is passed through a spectrophotometer which measures the intensity of the coloured solution. The result is compared to pre-established nitrite-N standards from which the concentration of nitrite-N in the sample is determined. The auto analyser also conducts a parallel operation on the same sample during which the reduction step is omitted. This only measures the original amount of nitrite-N present in the sample and no nitrate-N reduced to nitrite-N. The concentration of nitrate-N in the sample can be determined by calculating the difference in obtained nitrite-N values.

Chemical Oxygen Demand (COD) – SMWW Method 5220 C

The COD concentrations were determined using a closed reflux, titrimetric method. The method involves the digestion of a sample after adding $K_2Cr_2O_7$ and H_2SO_4 and then titrating with $Fe(SO_4)_2(NH_4)$. The endpoint of the titration is reached when the solution changes colour from bright yellow to dark brown. The endpoint is sudden and clear which gives a close to exact result. Errors in the result may be contributed to the step in which H_2SO_4 is added to a sample as a rapid reaction can lead to the sudden formation of vapours which may escape from the flask. Precaution is taken by adding the acid slowly so as to ensure minimum vapour losses.

Ortho-Phosphate (Ortho-P) – SMWW Method 4500-P C

Ortho-P concentrations were determined by means of a colometric method. A colouring reagent is added to the sample which reacts with ortho-P to develop a coloured solution. The intensity of the colour is determined by the ortho-P concentration in the sample. The sample is inserted in to a spectrophotometer which determines the absorbance of the coloured solution. The absorbance value of the sample is compared to pre-established standards from which the concentration ortho-P in the sample is be calculated

Alkalinity

The alkalinity was determined with a 5 point titration method (Moosbrugger et al, 1992). The sample is titrated with acid to several end points. The volume titrated at each end point is used to calculated the true alkalinity of a sample. This method differs from a standard titration in that it has various endpoints with which the alkalinity is calculated.

3.3.3 Physical Analyses

Suspended Solids

Mixed liquor effluent samples were analysed to determine the concentration of the following suspended solids components:

- Total suspended solids (TSS)
- Volatile suspended solids (VSS)
- Inorganic suspended solids (ISS)

The TSS and ISS/VSS were determined according to methods 2540 D and 2540 E (SMWW) respectively. The only deviations from these methods occurred in the separation of the solids. The original method stipulates the use of glass-fibre filter disks for separating the suspended solids from the liquid. During this study however the suspended solids were separated by means of centrifuge at greater than 3000rpm for 20 minutes.

Settleable Solids (SS)

The sludge settlability was determined according to method 2540 F (SMWW) using both the volumetric and gravimetric method. A one litre Imhoff cone was used for the volumetric technique whereas a 1 litre measuring cylinder was utilized for the gravimetric technique. Measurements were taken at settling times of 30 minutes and 60 minutes.

Sludge Volume Index (SVI)

The sludge volume index was determined according to 2710 D (SMWW). The settleable solids and total suspended solids is a prerequisite for determining SVI, hence SVI tests was conducted in conjunction TSS and SS tests.

3.3.4 Verification and Precision

Every sample was analysed twice for a given constituent (except for nitrite and nitrate) after which the average measured value was calculated for the end result. If one of the two measurements appeared to be aberrant the test would be repeated a third time to confirm or discard the result. If the average measured value appeared to be aberrant altogether, the sample would be retested completely.

Chapter 4

Development of the Experimental System

At the time that this study commenced there was no prior experimental knowledge on the biological nitrification and denitrification of pure undiluted urine. Existing theory and models on wastewater treatment and treatment systems combined with information obtained in previous studies involving urine or similar forms of high nitrogen wastewater were used as guidance on how best to approach the experimental system. Initial theories and predetermined ideas had to be adapted based on the behaviour and progress of the experimental system during the study.

The early stages of the study mainly involved attaining a stable biological system with ammonia tolerable biomass. The nitrifying organisms were of greater concern than the denitrifying organisms as they proved to be much more vulnerable to inhibition effects than initially expected. The following stage in the study entailed verifying the maximum daily feed volume, required sludge age and the optimal duration of anoxic/aerobic phases. After initial complications and setbacks the system eventually reached steady state and was operated at a sludge age of 20 days and a hydraulic retention time of the same duration. The maximum duration of the anoxic phase was established at 4 hours within a 24 hour cycle in order to compromise for the longer aerobic phase required by nitrifying organisms.

The following section discusses the initiation of the biological reactor, progress of the process and the complications involved with attaining a stable system.

4.1 Initial Perceptions on the Experimental System

4.1.1 Biological Behaviour

Biological nitrogen removal is a two phased process dependent on two different groups of bacteria. Nitrification takes place under aerobic conditions, whereas denitrification can only occur when very little or no oxygen is present. Therefore, in a a sequencing batch reactor, controlled exposure to oxygen is a vital component in the process of biological nitrogen removal to ensure that nitrification is not inhibited by a lack of oxygen and that denitrification is not inhibited by the presence of oxygen.

Oxygen utilising nitrifying bacteria are autotrophic organisms with a relatively slow growth rate. These organisms are also more sensitive to inhibition effects and are slow in recovering from unfavourable conditions. Denitrifying bacteria, on the other hand, are heterotrophic organisms with a faster rate of growth than nitrifying organisms. The duration of the nitrification phases will therefore have to be longer than the denitrification phases to balance process rates with stoichiometric requirements.

The exact duration of the anoxic and aerobic phases is something that will have to be determined while the system is in operation. It was speculated that nitrification will be the critical phase in the process of biological treatment of urine due to the slow growth rate and sensitivity of the organisms involved. Thus the duration of the anoxic phase is to be compromised based on the time required for nitrification.

The pH within a biological system dictates the efficiency of nitrification and denitrification. The optimal pH range for nitrification and denitrification is between 7.5 and 8.5. However given the chemical composition of the environment and the interaction of pH and various weak acid-base systems some inhibiting substance will form with changes in pH. Hence pH levels outside this range will hinder the efficiency of the organisms. During nitrification the pH will lower due to alkalinity reduction that occurs during the process. The process can cease completely if pH falls below the minimum working range (< pH 6) of the organisms. Some alkalinity could be regained during denitrification which would assist in extending the pH buffer of the system.

4.1.2 Urine Characteristics and Potential Effects on Biological Processes

Urine has some characteristics that will strongly influence biological nitrification. The first factor is the exceptionally high ammonia concentration of urine, which may lead to the inhibition of the nitrifying bacteria. Therefore organisms have to be slowly acclimatised to the high ammonia concentrations by introducing the urine in small quantities initially, followed gradually increase it based on the adaptability rate of the bacteria.

The pH and alkalinity of urine are further factors that are important to consider in the treatment process of urine. Fresh urine has a pH of approximately 6 which increases to 9.0 – 9.2 during urea hydrolysis in a non-sterile environment such as storage. This increase in pH can have negative implications for the treatment of urine as pH levels above 9 leads to the equilibrium shift from ammonium to ammonia, a substance which is toxic for micro-organisms. Also pH exceeding 9 falls outside the optimal working range of micro-organisms and can hamper biological processes, especially nitrification which is already a slow process. These effects have to be managed by controlling the amount of urine that enters the nitrification-denitrification system to minimize the negative impacts of strong pH changes.

Alkalinity of urine is high compared to domestic and some other wastewater. However in comparison to the amount of ammonia-N in urine that has to be oxidised, it can be expected that the process will deplete the available alkalinity before all the ammonia is oxidised. Therefore alkalinity could be a major limiting factor in the nitrification of urine. Thus the possibility of adding external alkalinity is an option that needs to be considered or might even be compulsory.

The denitrification of urine should be a relatively straight forward process due to the fast growing nature of the organisms involved. The only factor which might limit the process is the amount of organic carbon in urine. Organic carbon serves as the energy source as well as cell building for denitrifying organisms. Compared to the amount of nitrite-N/nitrate-N available, the organic carbon content is relatively low. This might lead to incomplete denitrification or only partial denitrification and even result in the formation of intermediate nitrogen oxides

which could inhibit of the process. Therefore it will be necessary for the denitrifying phase to take place before the nitrifying phase, immediately after urine enters the system. This will make all organic carbon in the urine available for nitrite/nitrate reduction.

4.2 Initiation of the Experimental System

4.2.1 Inoculation

The experimental system was inoculated with sludge from a lab scale MBR reactor at the University of Cape Town wastewater laboratory. The domestic wastewater treated in this MBR has very different characteristics to undiluted urine. It was thus foreseen that organisms in the sludge produced in this system would require time to adapt to urine feed.

4.2.2 Urine Feed

The urine used during the study was collected from urinals in an office block. The urine derived from males only and was undiluted. This collecting system produced 3.0 l to 5.0 l of urine a day during normal working days (Monday to Friday). Urine was collected in 25.0 l containers and stored at the same temperature as the main experimental system while being used as feed stock. A container of urine would normally be used for no longer than two weeks upon which it was replaced with a container of freshly collected urine.

During the time that urine was collected and stored a white precipitate (believed to be struvite) would form and accumulate at the bottom of the container. The urine in the container was not agitated during usage so as to prevent the precipitate from becoming suspended in the batch feed.

4.2.3 Reactor Start-up

The first day of reactor operation was on 25 May 2009 which initiated the start-up period that was aimed at acclimatising and establishing biomass. Only pH and ORP were monitored at this stage of the study. During the start-up stage of the reactor, the volumes of urine added, resulted in an initial process failure as organisms more likely wasn't able to cope with the high ammonia concentration that were introduced.

Upon inoculation on 25/5/2009, 2.0 l of urine was added to the experimental system. One day later, on 26/05/2009, an additional 2.0 l of urine was added. However, not enough time was allowed for the first batch of ammonia to be oxidised. This caused a sudden high ammonia concentration which inhibited the bacteria and forced pH to above 9.0. The reactor was operated in this state with no further urine added in the expectation that the biomass would adjust. However this was to no avail. After three weeks there were still no notable changes in pH or ROP, which indicated that nitrification was not occurring and that the organisms had failed to adjust (Figure 4.1). The inverted peak in ORP was due to an aeration failure.

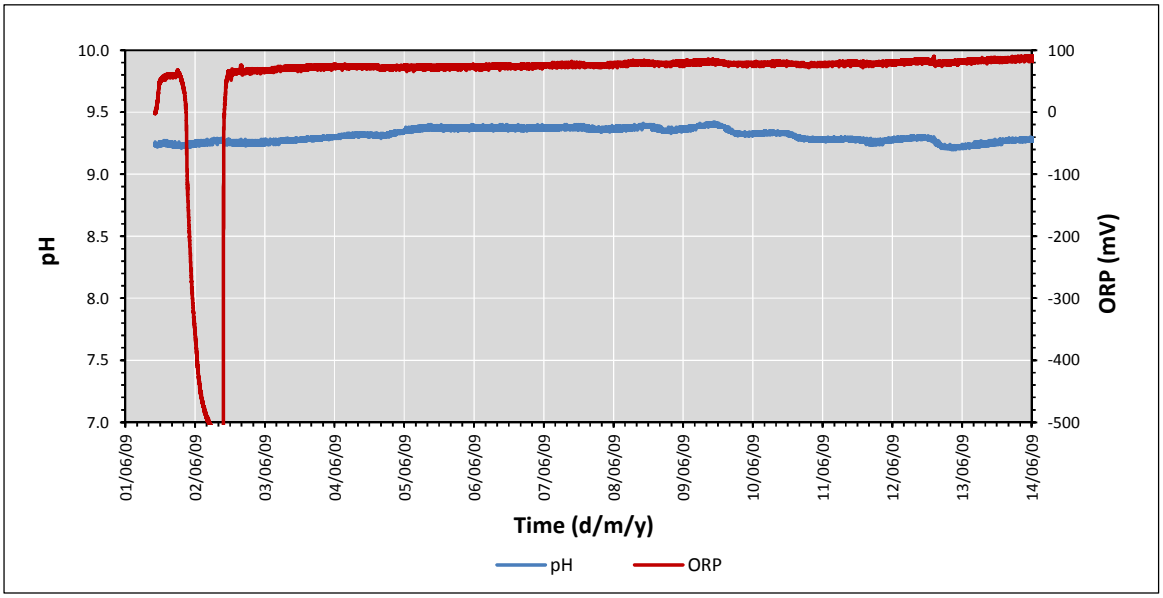


Figure 4.1: pH and ORP profiles of the system during a 2 week period (01/06/2009 to 14/06/2009).

The problem was addressed by decanting 10.0 l of effluent and replacing the discharged volume with fresh sludge form the UCT MBR (15/06/2009). From this point onwards only small volumes of urine (0.5 l) were added to the reactor per cycle (period between volume exchanges). Based on pH and ROP responses it was evident that the system had recovered (Figure 4.2). The pH decline during cycles indicated nitrification with concomitant consumption of alkalinity. The ROP increase during cycles was indicative of nitrite and/or nitrate formation and the decrease in ammonia.

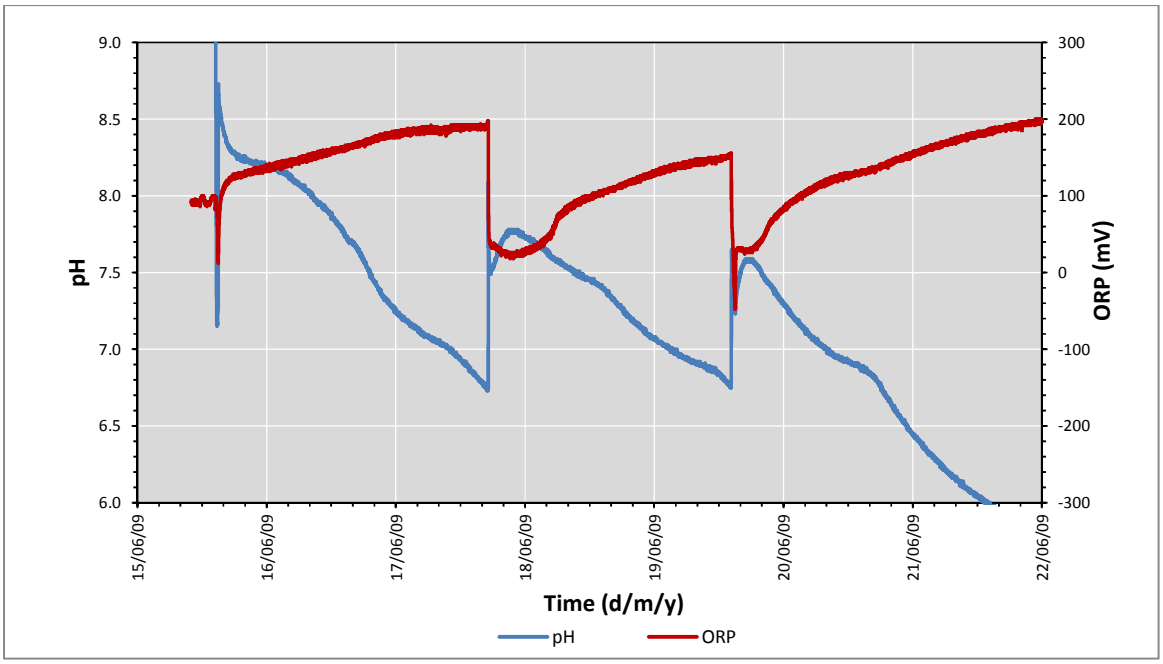


Figure 4.2: pH and ORP responses after re-inoculation of the reactor (15/06/2009) with fresh activated sludge.

New cycles were only initiated when the pH dropped to approximately 7.0. Cycles lasted for longer than 24 hours in the period following re-inoculation as the system was still accumulating nitrifying biomass capable of processing the urine feed. As biomass adapted to system conditions, nitrification rate improved and cycle times became shorter.

At 02/07/2009 (week 6), the system was operating at two cycles a day with 0.5 l urine feed per cycle (Figure 4.3). At 12/07/2009 (week 7) cycles were changed back to 1 cycle a day and the exchange volume was increased to 1.0 l of urine per cycle. The system responded well as nitrification was achieved within 24 hours. The temperatures varied between 10°C and 18.8°C from week 4 to week 7. Effects of the temperature variation during week 4 and 5 can not accurately be linked to effects on the pH and ORP as the system was still in a early stage after re-inoculation; new biomass was still acclimatising to system conditions. During the first three days of week 6 (30/06/2009 – 02/07/2009) the temperature varied between 12°C and 14°C and the nitrifying capacity of the system was at 0.5 l urine per day. On 02/07/2009 the temperature increased to 18.5°C which coincided with the ability of the system to process two 0.5 l bathes of urine in one day. This could be linked to the temperature dependency of the biological process as a higher temperature is expected to increase the reaction rate.

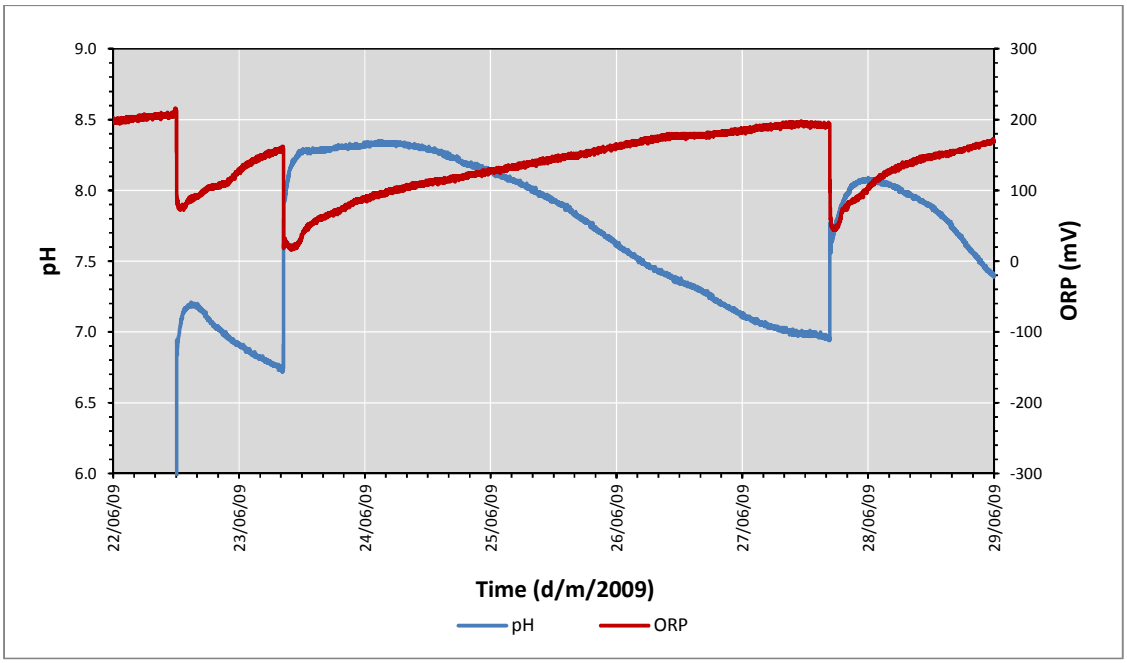


Figure 4.3: 0.5 l per cycle at two cycles per day

Sludge was not wasted from the system initially to accumulate a sufficient mass of autotrophic biomass. However, as the system progressed, sludge was wasted in order to establish a constant sludge age and prevent accumulation of endogenous biomass and inert residue. Sludge was wasted with effluent. Therefore sludge age was equal to the hydraulic retention time of the system. This was motivated by the intention of developing a practical system which can be implemented and operated with minimal complexity.

51 days (15/07/2009) after initiation of the experimental system the first anoxic phase was introduced into the cycles so that denitrifcation could establish. After the addition of new urine the aeration would be turned off for 1 hour permitting anoxic conditions. On 21/07/2009 (51 days after initiation) the anoxic phase was increased to 1.5 hours and by 22/07/2009 it was noticed that a 15 mm thick floating sludge blanket had formed at the top of the reactor during the anoxic phase. This floating sludge was as a result of the formation of nitrogen gas which were entrapped in flocks of sludge, floating them to the surface. This was seen as an indication of denitrification.

65 days after initiation (29/07/2009) the exchange volume was stepped up to 1.25 l. The system appeared to be capable of nitrifying this amount urine still in one day and was maintained at that exchange volume for the time being (Figure 4.4).

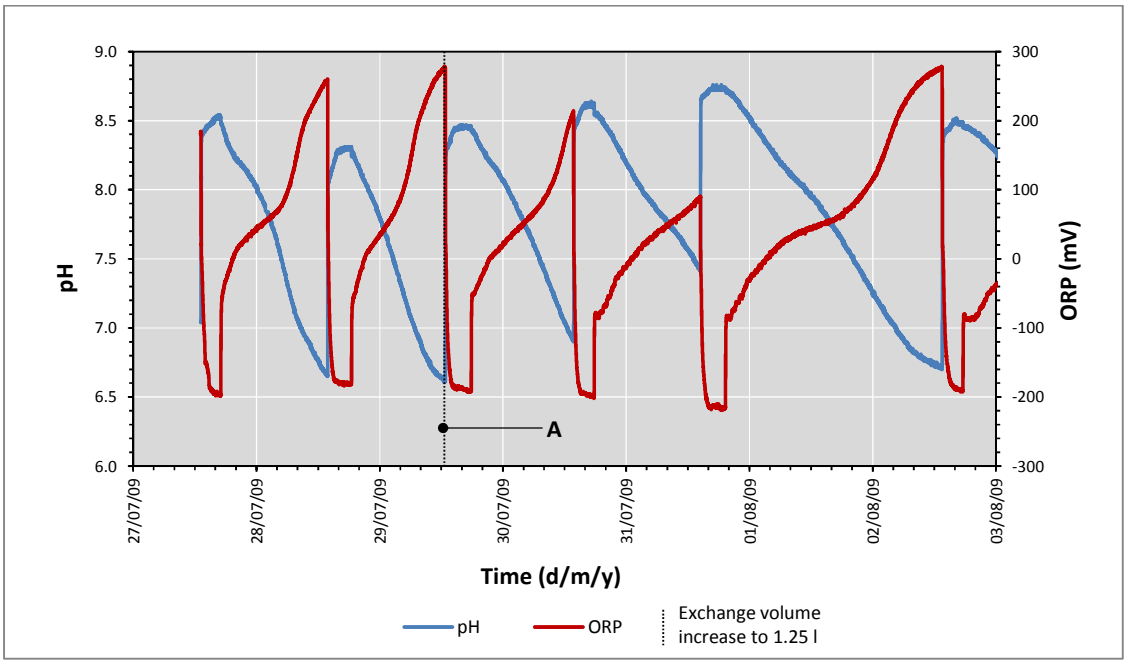


Figure 4.4: Nitrification of 1.25 l urine a day

During week 12 (August 2009) the online data logger failed. The pH and ROP information was limited to manual daily readings. In the weeks that followed it was attempted to build up the nitrifying capacity of the system by gradually increasing the exchange volumes. 111 days after initiation (13/09/2009), the exchange volume was again increased from 1.25 l to 1.5 l. The system was capable of nitrifying the first two batches at 1.5 l per day, however 114 days after initiation (16/09/2009) the system slowed down and the batches required 2 days to be nitrified. It was speculated that the system needed time to re-adjust and therefore the reactor was maintained at 1.5 l batches every two days. 123 days after initiation (25/09/2009) the system regained its capacity to nitrify batches in one day. Temperature during this time (13/09/2009 to 25/09/2009) varied between 13˚C and 19˚C.

The system was maintained at a daily exchange volume of 1.5 l from 25/09/2009 to 17/10/2009. At 18/10/2009 the exchange volume was again increased to 1.75 as it was assumed that the organisms were well adapted to the conditions in the system. The system responded well and on day 147 (19/10/2009), the batch size was increased to 2.0 l. The system

was able to nitrify the batch within 24 hours again. 150 days after initiation (22/10/2009) the batch size was increased to 3.0 l. The system was capable of operating at this batch volume until 06/11/2009 when there was sudden "breakdown" in the process as the system required 2-3 days to nitrify batches. 182 days after initiation (23/11/2009) the batch size was reduced to 2.0 l in an attempt to restore the process. However the system still required 2 days to nitrify. 187 days after initiation (28/11/2009) the batch size was reduced back to 1.0 l and has been operating at this exchange volume since. The temperature during this period (22/10/2009 – 28/11/2009) varied between 19˚C and 25˚C.

4.2.4 System stability

pH Control

The ability to sustain a stable batch system relied on maintaining the pH within a workable range for nitrification. The pH at the start of cycles consistently had to be low enough to ensure buffer capacity for the increase in pH associated with the addition of urine feed and subsequent denitrification. If the pH at the start of the aerobic phase was too high above the minimum level, the associated slower rate of nitrification would ensue for a large part of the aerobic phase. This created the dilemma in which the overall rate of nitrification was insufficient to ensure that the pH was reduced to an adequately low level for the initiation of the new cycle.

The initiation of a new cycle, by the addition of urine followed by denitrification, would result in a higher pH at the start of the aerobic phase than in the previous cycle. With every following cycle the pH would creep further beyond the optimal range until the pH in the system was completely beyond the range in which nitrification could occur. This would lead to a breakdown in the aerobic process and the accumulation of ammonia. The pH would have to be adjusted after a number of cycles in order for the process to recover and the batch operation to continue. It was this approach which led to the system failure during the initiation stage of the system.

The aerobic phase could be prolonged until the pH lowered to an acceptable level for the initiation of a new cycle. This method was adopted in the early stages of the reactor operation

before the daily load of urine became known. As the SRT was dependant on HRT ad hoc changes in cycle time could result in uncontrolled sludge age and inevitably an unstable system. The aerobic phase could be extended by omitting the anoxic phase. pH increase, resulting from denitrification, would be prevented and the cycle duration would not be altered making it possible to maintain the sludge age. This would however require higher COD concentrations at the start of the aerobic phase. The nitrifying organisms would possibly also have to compete with COD utilising heterotrophic organisms for oxygen during the aerobic phase. This was however the method reverted to when the system indicated signs of instability as it was vital for the sludge age to be maintained. Omitting the anoxic phase was also not conducted for more than two consecutive cycles in order to prevent excessive build-up of nitrite/nitrate. The system was also not sampled during these situations until stability was achieved again.

Sub-optimal pH levels (<pH 7.0) at the end of cycles proved to be less problematic in the operation of the system than pH levels above optimal range at the start of cycles. The pH regularly dropped below 7.0 during the aerobic phase during times when system conditions were more favourable. The decrease in process rate at the end of a cycle did not have the same knock-on effect as a slower rate at the start of a cycle. The system would correct itself within the next cycle when urine addition and denitrification elevated the pH to the upper levels of the optimal range. It was therefore preferred that aerobic phases started at pH 8.0 levels and ended at below pH 7.0 levels rather than starting at above pH 8.0 levels and ending with above pH 7.0 levels.

Temperature

Initially the reactor temperature of the experimental system was dependent on the climate of the building. The laboratory was without climate control or insulation and consequently the system was vulnerable to fluctuating temperatures. The temperatures recorded in the system during the study ranged from a minimum of 10°C and to a maximum of 35°C. The temperature in the experimental system is illustrated in Figure 4.5.

The temperature varied with time of day as well as with weather and seasonal changes. This meant that temperature variations occurred during phases of a cycle as well as from one cycle to the next.

The variation of temperature clearly affected the process rate. The process was established during a period of warmer temperatures and performed adequately. However the onset of a colder period lead to prolonged system temperatures of below 20°C. This resulted in a process rate decrease which led to poor system performance that verged on process failure. The process temperature was eventually controlled above 20°C by introducing a thermostat-controlled heating element. Figure 4.5 indicates variation (decrease) in the process temperature and the more stable operation between 20°C and25°C (eventually) after the introduction of the temperature control mechanism.

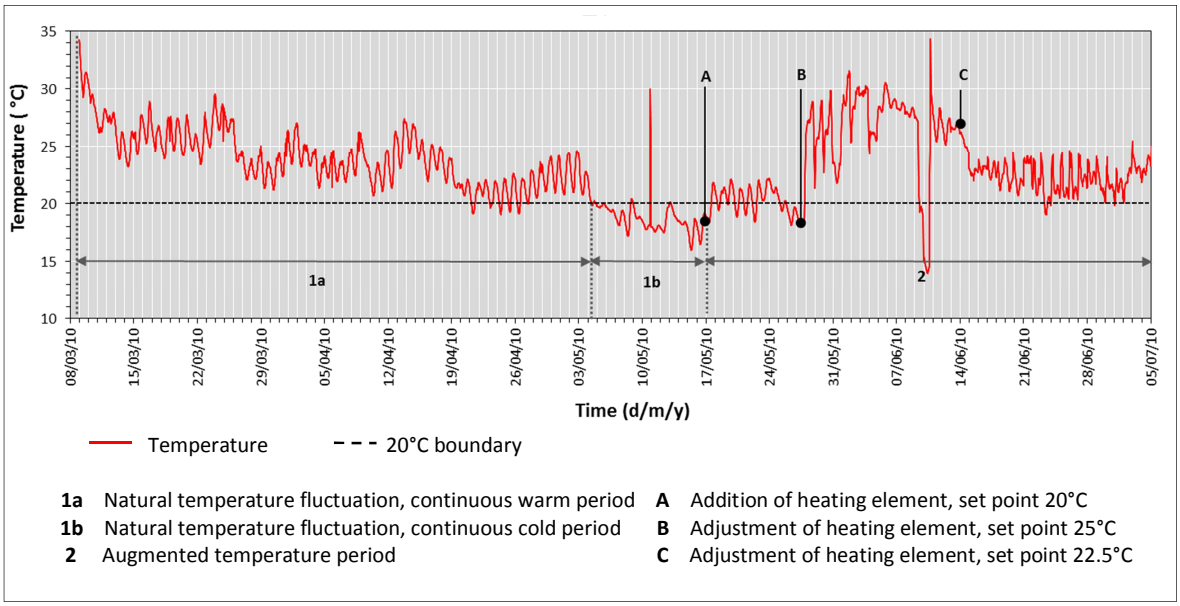


Figure 4.5: Temperature profile of the experimental system.

Chapter 5

Analysis of the Continuous Online Measurements

The experimental SBR was operated continuously for a period of 669 days. During the study a series of online measured data was collected from the experimental system, which constituted an essential part of the study. The non-quantified information deriving from observations made during the operation of the experimental system also proved valuable. Combined, these results and observations provided much insight into the nitrification and denitrification of undiluted urine. This section describes and explains the results obtained during this study.

5.1 pH DATA

The online measurements are represented on graphs in which the measured parameter is on the vertical axis (y- axis) plotted against time on the horizontal axis (x-axis). The data is plotted in two categories based on time scale. The first type displays unit of time in hours for illustration of measured data over the duration of individual cycles. The second type displays unit of time in days to represent the data over of consecutive cycles.

5.1.1 Rationale

pH is a measure of the hydrogen ion activity in an aquatic solution and can be defined mathematically as follows:

$$pH = -\log(H^+) = -\log \gamma \bullet [H^+]$$

where: (H^+) = *hydrogen ion activity*

$[H^+]$ = *hydrogen ion concentration (mol/l)*

γ = *activity coefficient*

The hydrogen ion activity is directly proportional to the concentration of free hydrogen ions by a factor equal to the activity coefficient. The value of pH is therefore related to the concentration of free hydrogen ions and changes in hydrogen ion concentration are reflected by pH change. The concentration of hydrogen ions is a function of the acid-base equilibriums present in the system.

The hydrogen ion concentration in a system is affected by alkalinity. Alkalinity absorbs hydrogen ions and therefore serves as a buffer against changes in pH resulting from increases in hydrogen ion concentration. The extent to which hydrogen ions can be absorbed depends on the amount of alkalinity in the system at a given time. Once alkalinity becomes depleted the hydrogen ions will accumulate and pH will decrease. The addition of alkalinity can increase pH of a system by absorbing hydrogen ions until equilibrium is reached. Adding more alkalinity to a system does not necessarily result in further pH increase but extends the buffer capacity of the system.

The pH changes during biological nitrification and denitrification are indicative of the presence of these biological processes as well as the rate at which the processes occur. The pH is therefore one of the main indicators through which biological progress in the experimental system was monitored.

5.1.2 Experimental System pH Profile

The pH profile of the experimental system is characterised by cyclical repetitions of rapid peaking increases in pH followed by much slower decreases which resides for greater part of the cycle. The increases in pH correspond to anoxic phases whereas decreases in pH are associated with aerobic phases.

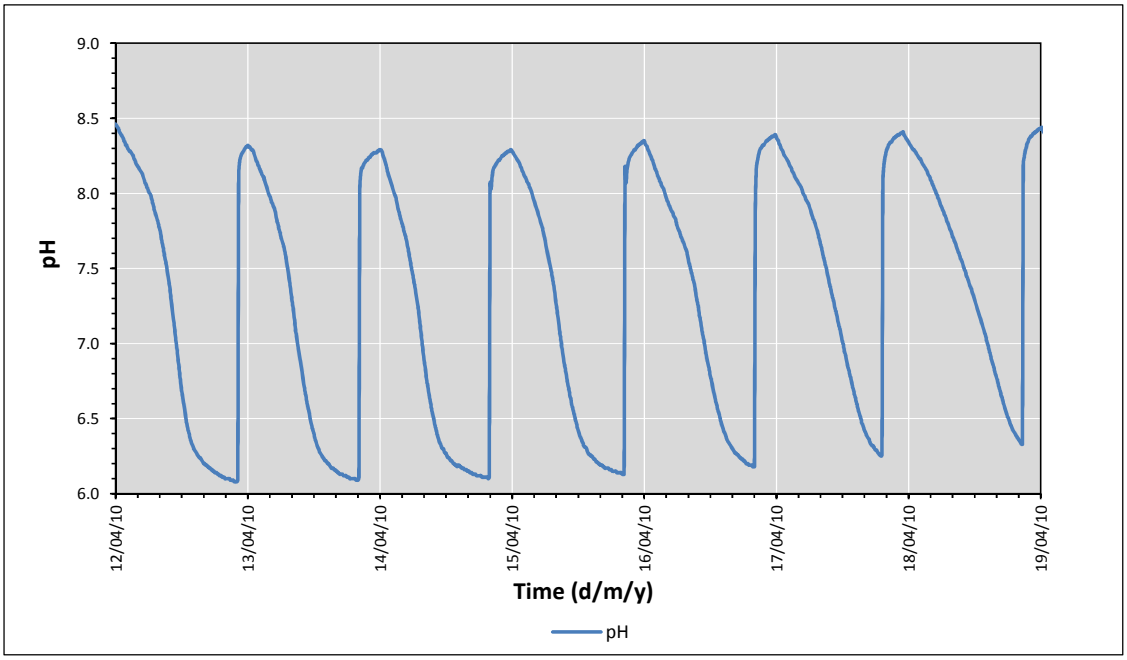


Figure 5.1: pH profile of the stable system over a period of 7 days.

A typical cycle pH profile is illustrated in Figure 5.1 and although variations occur in the cycle profiles, as observed during the study, the given profile represents the base form.

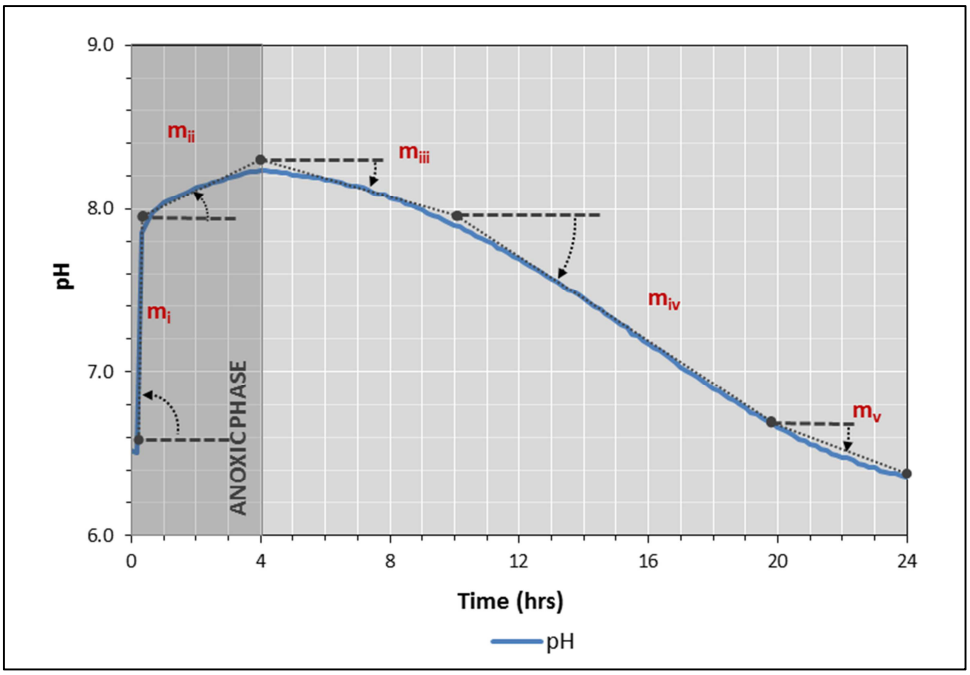
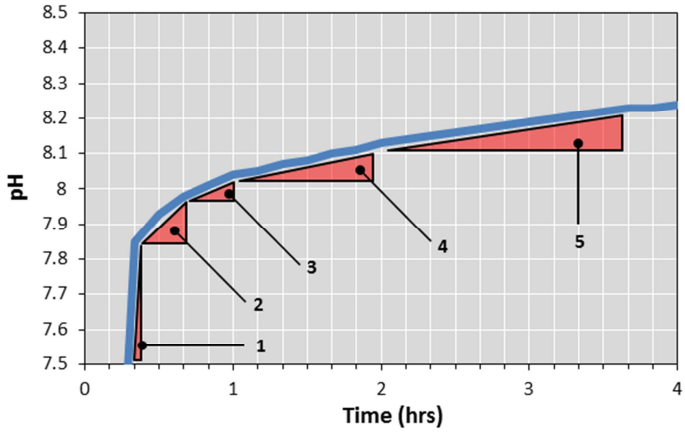


Figure 5.2: Typical pH profile during a 24 hour cycle, 1.0l urine feed, 4.0hr anoxic, 20.0hr aerobic (28/04/2010).

Upon the initiation of a new cycle, by the addition of urine, pH rises sharply and rapidly (m_i, Figure 5.2). This sharp rise in pH ensues for approximately 10 minutes (0.7 % of cycle time) after the batch feed as the urine is circulated and mixed completely into the system.

After the initial pH increase, associated with the feed procedure, there is a further increase in pH during the remainder of the anoxic phase (m_{ii}, Figure 5.2). The rate of this secondary pH increase is significantly slower than the rate of the initial increase and declines as pH rises further.

At a closer glance of the anoxic phase (Figure 5.3), the pH rate of change and variation thereof, over the extent of the phase, is evident. The intial rapid pH increase (section 1, Figure 5.3) associated with the feed procedure causes the pH to increase by more than one pH point, from 6.3 to 7.85, at a rate of 8 pH/hr due to rapid mixing. Thereafter the rate declines to 0.39 pH/hr (section 2, Figure 5.3) during which the pH increases to 8.0. At pH above 8.0 the rate of change readily declines fom 0.18 to 0.06 pH/hr (section 3,4,5, Figure 5.3) bringing the pH to 8.24 by the end of the anoxic phase.

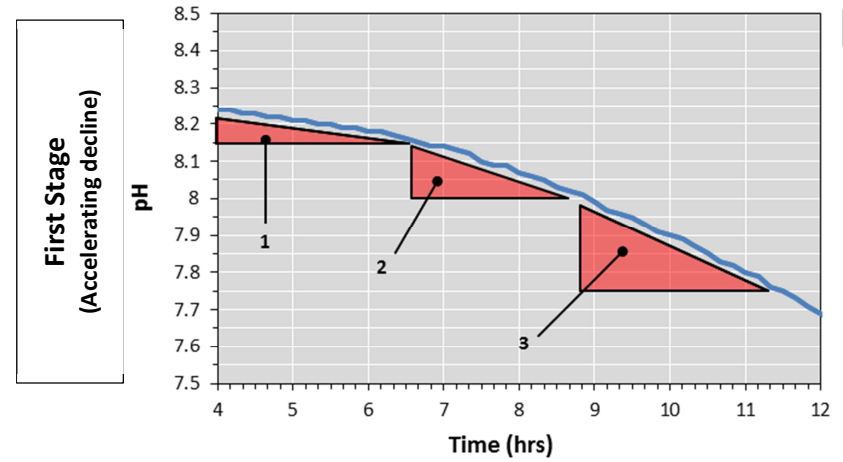


Section	Gradient
1	8.04
2	0.39
3	0.18
4	0.09
5	0.06

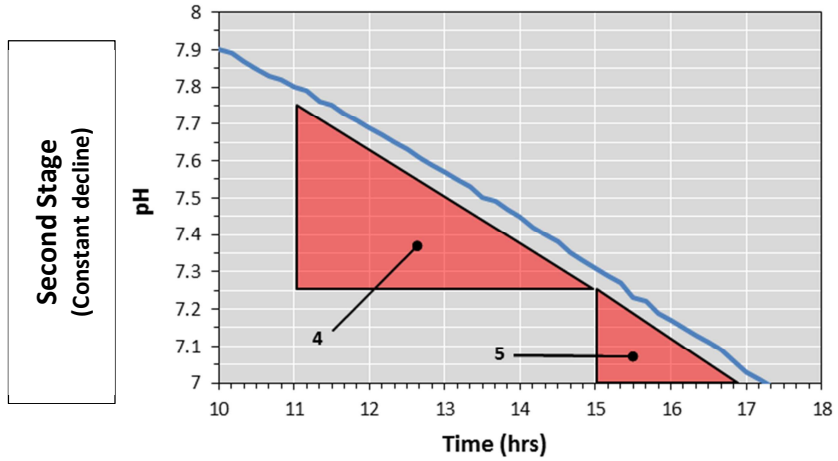
Figure 5.3: Anoxic phase pH profile (enlarged from figure 5.2)

The aerobic phase is characterised by an overall decrease in pH, which can be divided into three stages based on the rate of pH change. Referring to Figure 5.2 the rate of pH declines at the beginning of the aerobic phase, constituting the first stage, is normally slower (m_{iii}) compared to the general cycle rate. This slow rate of pH change gradually progresses to a faster rate as pH decreases. The second stage of the aerobic phase is marked by a maximum decline (m_{iv}). The pH declines at a faster rate towards the lower boundary of the operating pH range, upon which the aerobic cycle enters the third stage. The third stage is represented by a decrease in the rate of pH change (m_v). The pH decreases at a constantly declining rate for the remainder of the aerobic cycle. The pH profile levels out until reaching 6.2 (±0.1) from which there is no further significant change.

The detailed gradient of the pH change, during the three stages of the aerobic phase, is depicted in Figure 5.4. As the aerobic phase commences, the gradient is -0.036 pH/hr (section 1, Figure 5.4) which then doubles to -0.070 pH/hr (section 2, Figure 5.4). The gradient further inclines by three times the initial gradient to -0.097 (section 3, Figure 5.4), during the transition from the first to the second stage which transpires to a maximum of 0.13 pH/hr. This rate ensues nearly unchanged for the whole second stage. This rate of change slows down again and the gradient levels when the pH decreases below 7.0. This is the third stage of the aerobic phase and is virtually an inverse first stage.



Section	Gradient
1	-0.036
2	-0.07
3	-0.10
4	-0.13
5	-0.13
6	-0.13
7	-0.10
8	-0.06



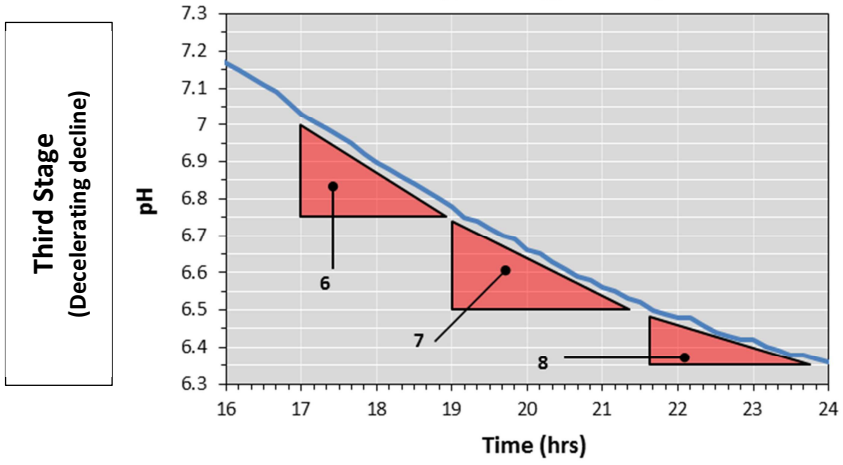


Figure 5.4: Aerobic phase pH profile (enlarged from Figure 5.2)

5.1.3 System pH Behaviour

In view of the observed pH fluctuations that the system was subjected to, it becomes clear that alterations occurred in the levels of alkalinity. These alterations were brought about by chemical changes which can be attributed to the volume exchanges and biological activity in the system as will be discussed in section 5.1.3.1 to 5.1.3.2.

5.1.3.1 pH Increase

The initial increase in pH is owed to the manner of feed procedure and the characteristics of the hydrolysed urine used as feed. The urine contains alkalinity but also has an elevated pH of 9.1 (±0.1) which derives from its high ammonia concentration. The addition of urine replenishes the alkalinity of the system that was consumed in the previous cycle and increases the ammonia concentration. This leads to a reduction in the concentration of hydrogen ions and subsequently the pH increases. The steep gradient of the pH increase can be explained by the way in which volume exchanges were conducted. After decantation of the effluent the feed was added to the system all at once thus creating a sudden influx of urine. The recycle pump operated at a maximum rate of 3.5 L/minute which means that it circulated the reactor volume almost twice in 10 minutes. Therefore mixing in the reactor was rapid relative to the duration of the anoxic phase and pH increased accordingly.

The slower secondary increase in pH, which continues for the greater part of the anoxic phase, is indicative of the presence of biological denitrification in the system. This is because the process of denitrification involves the consumption of hydrogen ions in the chemical reaction where nitrite or nitrate is reduced to nitrogen gas and as a result the pH increases further.

Denitrification most likely follows soon after new feed is added to the system proviso that residual oxygen from the aerobic phase is sufficiently depleted (i.e. < 0.5 mg/L). If this is the case then the primary increase in pH and the transition between the primary and secondary pH increase is the combined effect of new feed and denitrification.

In order to clarify the primary and secondary pH increases, the pH profile illustrated in Figure 5.5 is considered. This was observed during a stage of the study when normal operation

procedure was deviated from by omitting the anoxic phase in the selected cycle (to compensate for the higher pH at the end of the previous cycle). The new cycle was initiated by conducting a volume exchange but aerobic conditions were maintained throughout for the duration of the cycle. This fully aerobic cycle (indicated on Figure 5.5) displayed a similar pH gradient after the urine batch feed as the pH gradients of adjacent anoxic aerobic cycles. The effect of omitting the anoxic phase (between 02/07 and 03/07) was that the maximum pH of this cycle was noticeably lower than the average maximum pH of the prior and subsequent cycles which did have anoxic phases. The urine used as feed derived from the same unchanged storage container and therefore the feed had the same characteristics for all the cycles displayed in Figure 5.5. The feed was thus not responsible for the difference in the pH profile. Over the duration of the study a number of cycles were operated in the same manner and resulted in similar outcomes as described above.

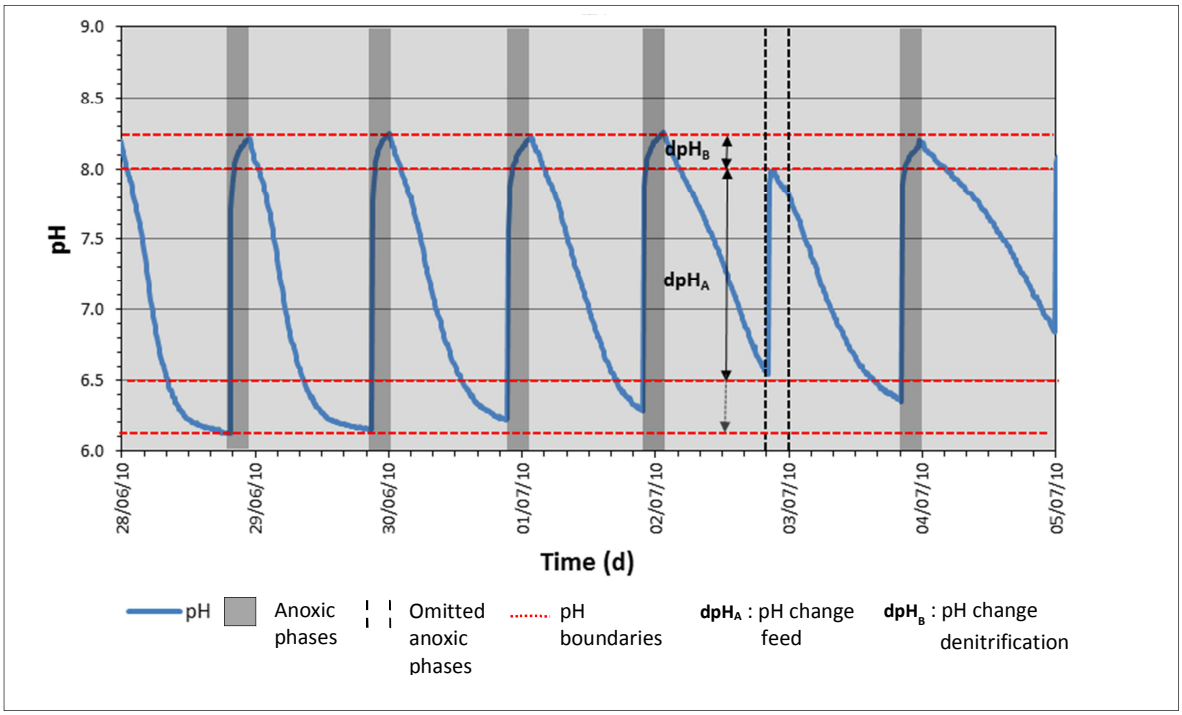


Figure 5.5: The effect denitrification on the pH profile.

Based on the above it can be assumed that denitrification is present in the system as the secondary increase in pH does not occur in the absence of an anoxic phase but recurs when an anoxic phase is introduced in the following cycle (this can be a useful test in a system where pH is the only data measurement to work from). The absence of oxygen, which is one of the

prerequisites for denitrification, is required for the secondary pH increase. Secondly it can be established that the primary increase in pH is mainly attributed to feed and that denitrification has a insignificant contribution to the initial increase.

During the unaerated (anoxic) period, hydrogen ions are consumed in the process during which nitrite/nitrate is converted to nitrogen gas. The hydrogen ion concentration is therefore reduced further which leads to a further decrease in pH. The rate of the secondary increase in pH is significantly slower than the initial rate as it is dependent on the progress of the biological processes to facilitate chemical changes and not sudden influx of chemical altering substances as in the case of urine batch feeds. The decrease in rate of the secondary pH incline, with a rise in pH, could indicate:

- The inhibition of organisms by increased pH levels (i.e. the pH increasing outside of optimal pH range);
- The formation or increase of inhibiting substances with an increase in pH
- The formation or increase of inhibiting substances with the progress of denitrification
- Depletion/decline in available nitrate/nitrite concentration to the extent that the organisms become inhibited
- Depletion/decline of the available carbon (COD) to the extent that the organisms become inhibited

5.1.3.2 pH Decline

The pH decrease during aerobic phases occurs when the available amount of alkalinity is incapable of neutralising the amount of hydrogen ions produced during the oxidation of ammonia. The amount hydrogen ions produced is proportional to the amount of ammonia oxidised hence the rate of nitrification can be determined by the rate of pH change if nitrification is the dominant pH altering process (similarly denitrification rate can be determined during anoxic phases). The optimal pH range for nitrification in the system was observed to be between 7.0 and 8.0 based on the rate of pH change and the premise that only nitrification was accountable for the pH decrease in the aerobic phase. This pH range concurs with optimal nitrification pH ranges recorded in literature.

5.1.3 pH and the Effect of Temperature

Temperature proved to be one of the key limiting factors of nitrification performance and overall system performance ability. Warmer periods, as indicated by A in Figure 5.6, lead to an increase in the rate of nitrification and would result in lower end-of-cycle pH. The inverse effect (B - Figure 5.6) would occur when colder conditions occurred and prompted slower nitrification rates. The varying temperature thus made it difficult to maintain the system pH within optimal range.

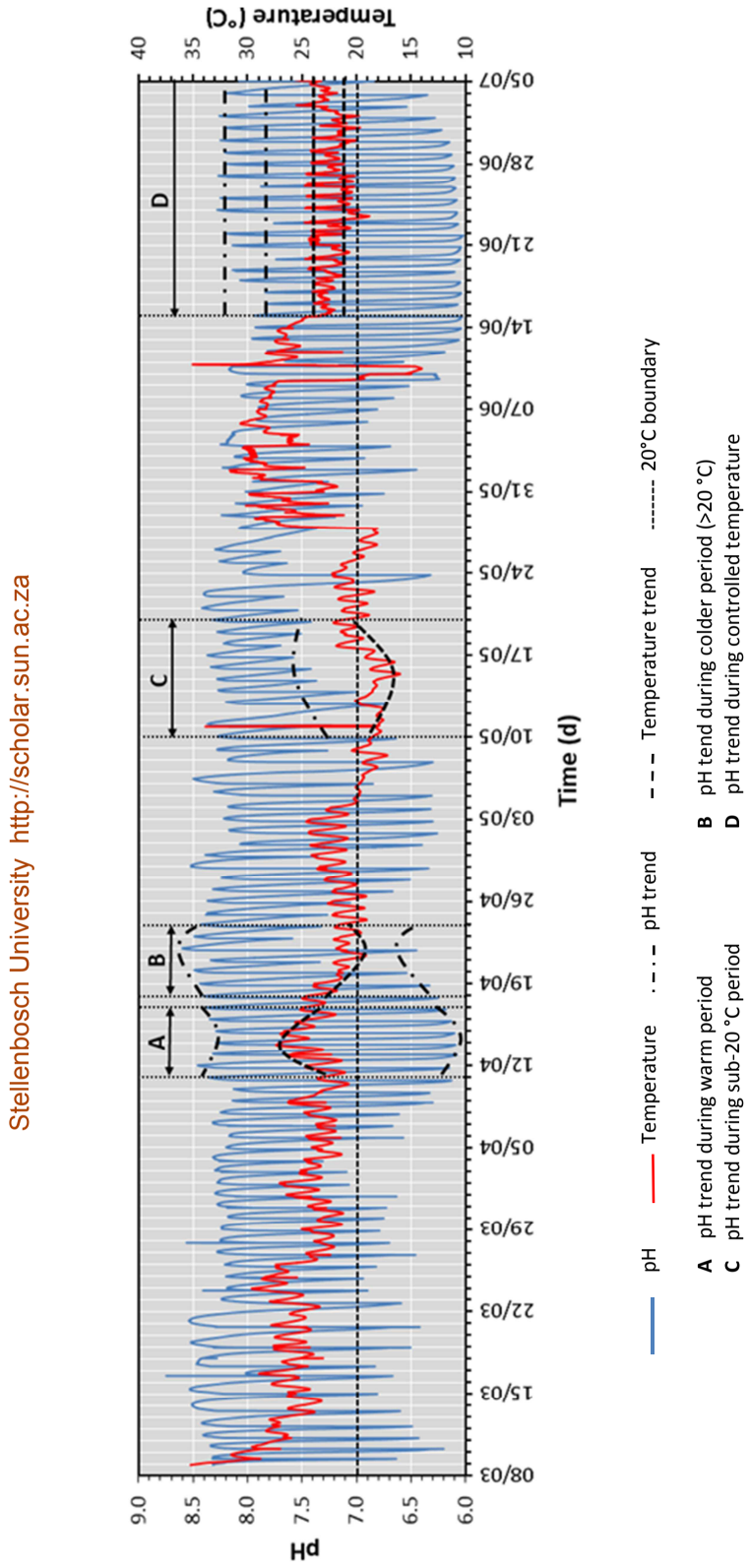


Figure 5.6: Long term pH profile and temperature variation.

A slower nitrification rate due to low temperatures would result in higher end-of-cycle pH and cause an elevated starting pH in the following aerobic phase. In turn this would lead to pH conditions further beyond optimal nitrification range. The overall nitrification rate would then be reduced leading to yet a higher end-of-cycle pH than before. Figure 5.7 illustrates the effect of sustained drop in temperatures (A_i) and the resulting "pH creep" in the reactor. The upper boundary of the pH increases towards pH 8.5 (B_{ia}, Figure 5.7) whereas the lower boundary (B_{ib}, Figure 5.7) moves further away from pH 6.0 which constitutes pH creep.

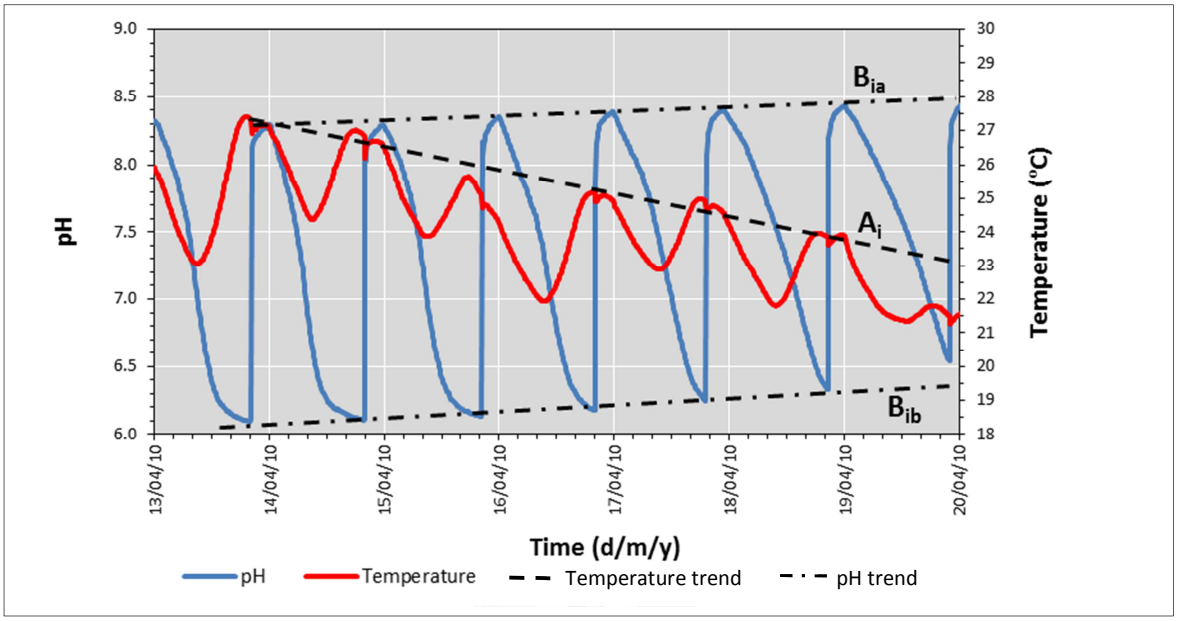


Figure 5.7: pH profile during sustained cold period showing decrease in process rates and "pH creep".

The cyclical nature of the system temperature allowed for the system to recover when warmer periods followed as illustrated in Figure 5.8. The gradual increase in temperature (Aii, Figure 5.8) results in a faster nitrification rates. This in turn causes a lower pH at the end of cycles leading to a gradually reducing lower pH boundary (B_{iib} , Figure 5.8). In turn there is a greater buffer against pH increases at the start of cycles which results in the downward trend of the upper pH boundary (B_{iia} , Figure 5.8).

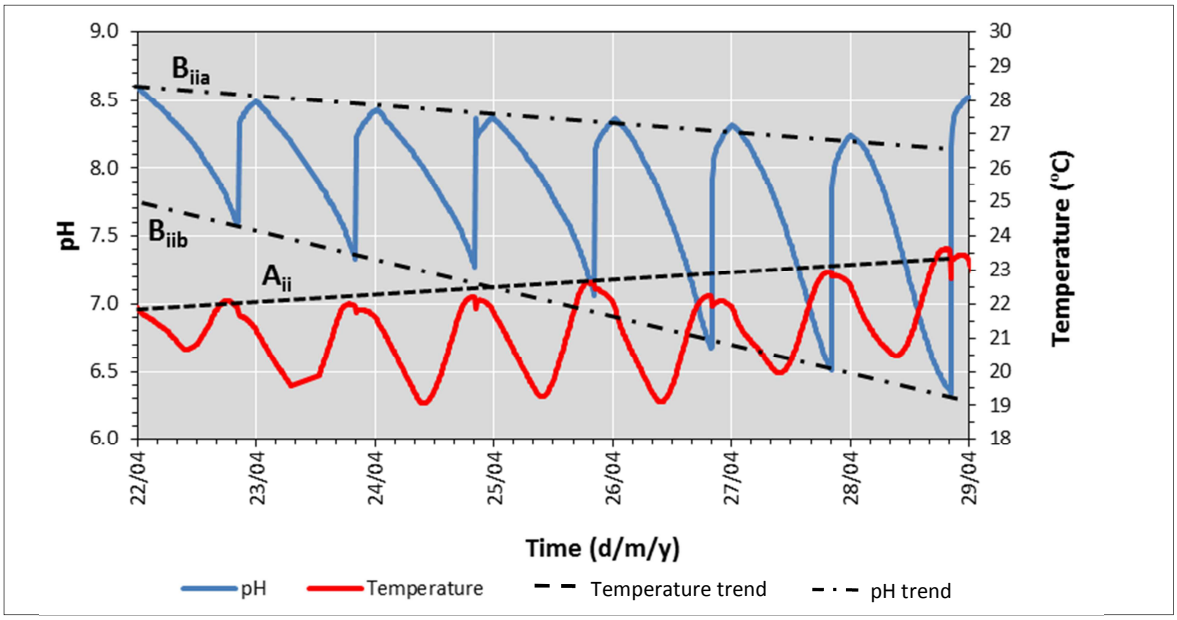


Figure 5.8: pH profile during continues warm period showing a recovery of the system.

When temperatures were augmented, after a prolonged cold period, the system recovered rapidly as shown in Figure 5.9 from point B onward. The overall gradient in the pH profile increase significantly after the temperature augmentation (mii, Figure 5.9) compared to the pH profile before point B. This illustrates how sensitive the system can be to the effects of temperature.

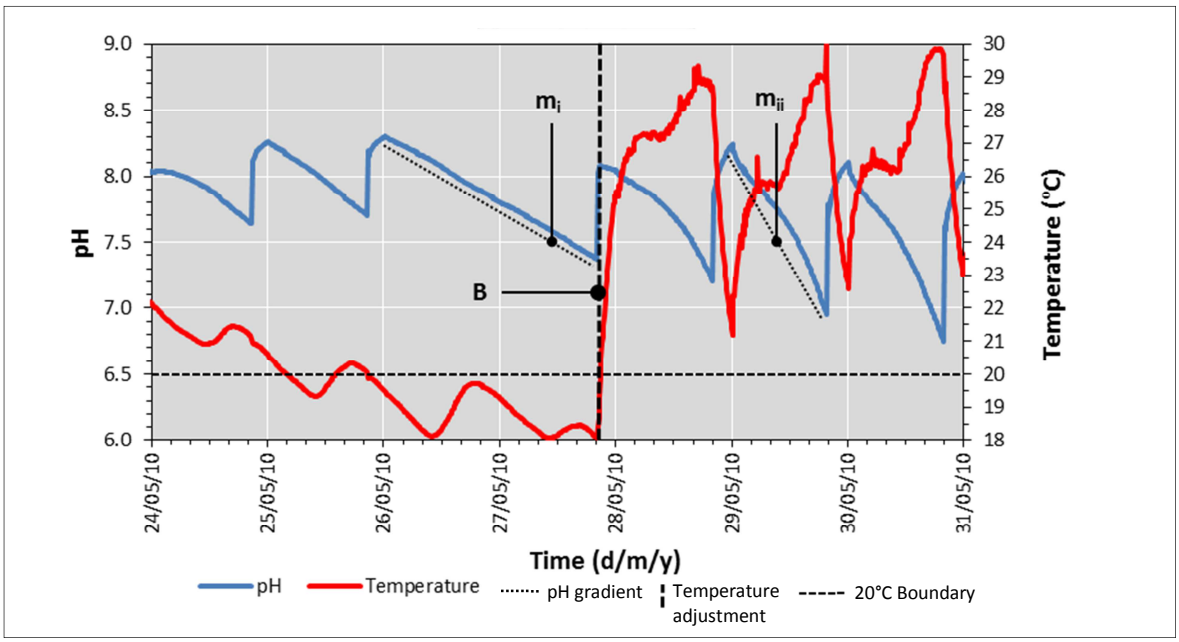


Figure 5.9: The recovery of the system by the augmentation of temperature by means of a heating element.

5.2 OXIDATION-REDUCTION POTENTIAL (ORP)

5.2.1Rationale

The oxidation-reduction potential is a measure of the tendency of a chemical solution to donate electrons (oxidation potential) or gain electrons (reduction potential). ORP measurements does not give an exact account of concentration in oxidation or reduction agents but rather the intensity in ability ("potential") of electron transfer that can occur between chemical species in an aquatic system. ORP measurements are in units of mV (millivolt) and in systems where the amount of electrons that can be donated is equal to the amount of electrons that can be accepted the ORP will be measured as 0.0 mV (i.e. oxidising agents and reducing agents are balanced).

Positive ORP readings signify that the system has a tendency to gain/receive/accept electrons and therefore has an oxidation potential. The oxidation agents in the system are capable of absorbing more electrons than reducing agents can produce. The system is therefore capable of attracting electrons which induce a positive electrical flow and subsequent voltage reading. Rise in ORP indicate chemical change in the system that increases its capability of attracting electrons. This translates into an increase in oxidation agents and/or a decrease in reducing agents. Decreases in oxidising agents and/or increases in reducing agents will accordingly decrease ORP.

Negative values in ORP indicate a tendency in the system to donate/yield/supply electrons and thus a system that has a reduction potential (negative oxidation potential). The reducing agents in the system are capable of donating more electrons than the oxidising substances can accept and electron transfer capability of the system trends toward donating electrons. When chemical changes occur in the system that decreases reducing agents and/or increases oxidation agents then ORP will increase (become less negative).

In a system where bio-chemical processes such as nitrification and denitrification are prevalent, there are a range of chemical species involved which influence the ORP. Nitrification and

denitrification are essentially a sequence of redox reactions during which electrons are exchanged to ultimately alter the oxidation state of nitrogen.

Aerobic processes such as nitrification are usually coupled with a system in a state of reduction potential (increasing or positive ORP). Oxygen serves as the oxidising agent which absorbs electrons and, in the case of nitrification, ammonia serves as the reducing agent which donates electrons. The resulting compounds are nitrate and nitrite which are oxidation agents that serve as the primary electron acceptor during anoxic conditions. Denitrifying anoxic conditions are coupled with oxidation potential in the system. Organic carbon (COD) serves as reduction agent during both anoxic and aerobic conditions which are oxidised in processes facilitated by heterotrophic organism activity.

5.2.2 ORP Profile

The ORP profile that corresponds inversely to the pH profile is used to illustrate and explain the ORP tendency as observed during the study. The ORP profile of the experimental system contains features which are reflective of the phases in which the system is operated.

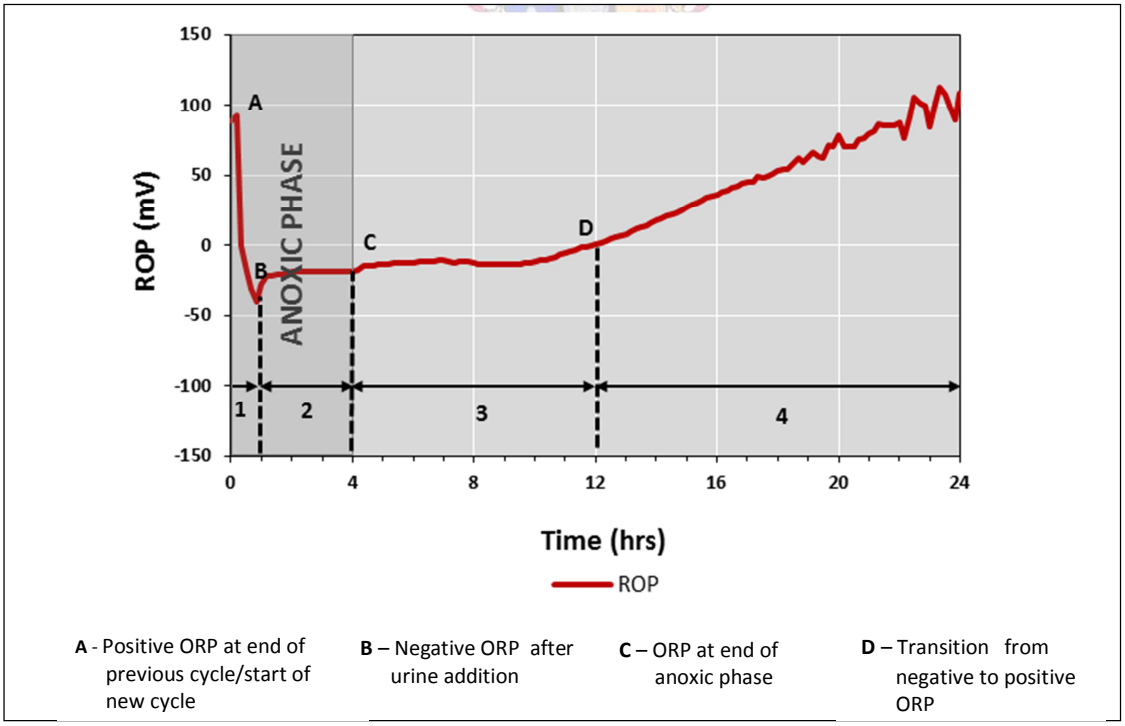


Figure 5.10: Typical ORP profile during a 24 hour cycle, 1.0l urine feed, 4.0hr anoxic, 20.0hr aerobic (28/04/2010).

The system ORP is positive (A, Figure 5.10) at the end of a cycle prior to the start of the new cycle. The addition of a batch of urine results in a steep decline (Section 1, Figure 5.10) in the ORP, leading to a negative ORP (B, Figure 5.10) after feed. The inverted peak at B, which divides section 1 and 2, is a common appearance in ORP profiles as observed during the study. In some cases the peak extends for a longer duration during which the ORP remains unchanged or decreases with a very slight gradient to form a horizontal base in the profile. The ORP increases after the peak phenomenon but remains negative for the duration of the anoxic phase (Section 2, Figure 5.10). Following the anoxic phase the ORP remains negative during initial stage of aerobic phase (Section 3, Figure 5.10) however it gradually increases until making the transition from negative to positive (D, Figure 5.10). From this point onward (Section 4, Figure 5.10) the ORP ascends at a markedly higher rate than previous until the end of the cycle.

5.3 Oxygen Utilisation Rate (OUR)

The oxygen utilisation rate measures the amount of oxygen used by aerobic organisms during a time interval. The units of OUR are expressed as $mgO_2/L/hr$. OUR is directly related to the respiration rate of organisms and thus an indicator of their level of activity. During the study the OUR was measured on a regular basis for the duration of individual aerobic phases.

5.4 Specific Conductance

The system was subjected to levels of salinity that were higher than in average domestic wastewater. High inorganic salt concentrations are inhibitory to nitrifying organisms according to literature and the effect thereof on this system was evident. One of the problems encountered in the operation of the system was the increase of salinity resulting from evaporative water loss. The water balance of the system had to be maintained by monitoring the volume and adding water to make up for evaporative losses. Even with a humidifier the volumes lost was notable during warm periods.

Chapter 6

Analytical Results

Urine feed, effluent and samples from the reactor were analysed throughout the course of the experiment. The aim of the chemical analyses was to determine the efficiency of nitrogen conversions and removal as well as to establish the rate and stoichiometry of the biochemical processes.

Influent urine and effluent samples were periodically analysed to evaluate the difference in concentrations of the various constituents and so evaluate the long term progress of the experimental system.

Routine 24-hour tests, during which multiple samples were taken at intervals during anoxic and aerobic phases of a cycle and analysed, were also conducted. These tests were conducted to establish the chemical changes that occurred over the duration of individual cycles and determine the rate and efficiency during phases.

6.1 INTRODUCTION

6.1.1 Objectives of Analytical Procedures

The aim of chemical analyses was to establish chemical changes in the system over the long term and the short term. The long term changes refer to the quality and consistency of the effluent which reflect the capacity and stability of the system. The short term changes describe individual cycles which indicate the rate of chemical conversion associated with biological processes.

6.1.2 Sampling Process

The experimental system was sampled on a periodical basis during the course of the study. The periodic sampling sessions involved the collection of a urine feed sample and a consecutive set of samples at intervals over the duration of a cycle. The first and last sample of the set consisted of effluent from the preceding cycle and effluent from the end of the particular cycle. These effluent samples were chemically analysed in filtered and unfiltered form and also analysed for suspended solids. The remainder of samples were chemically analysed in the unfiltered form only.

6.1.3 Chemical Analyses

The choice of chemical analyses was based on the major chemical constituents involved in the bio-chemical processes of nitrification and denitrification. The focus was on organic carbon- and nitrogen compounds. Ortho-phosphates were also tested for as it was a prerequisite for determining alkalinity.

The COD was used as the main indicator of organic carbon levels. Although the COD test measures all substances oxidised by dichromate, the majority thereof is organic matter. Nitrogen was tested for as TKN and FSA-N as well as Nitrite-N and Nitrate-N. The organic nitrogen could be calculated as the difference between TKN and FSA-N.

Filtered samples only contain chemical constituents in the dissolved form whereas unfiltered samples consist of both soluble and particulate chemical constituents. The COD content of

particulate matter was determined as the difference in COD between filtered and unfiltered samples:

$$COD_{particulate} = COD_{unfiltered} - COD_{filtered} \quad (6.1)$$

Likewise the nitrogen content of the particulate matter was determined as the difference in TKN between filtered and unfiltered samples:

$$N_{particulate} = TKN_{unfiltered} - TKN_{filtered} \quad (6.2)$$

6.1.4 Physical Analyses

The suspended solids (SS) tests served as a basis for determining the physical differences in particulate matter of which sludge comprises. It is assumed that all particulate matter in the system derives from biological growth as urine feed contained only dissolved matter. Precipitate that accumulated at the bottom of urine feed storage tanks was discarded and precipitate that formed inside the system is presumed negligible. Therefore volatile suspended solids (VSS) component of the particulates is considered to be biomass only whereas inorganic suspended solids (ISS) are inert residue from organism decay. The biomass contributes approximately 15 % of their VSS mass to the ISS mass when conducting the total suspended solids (TSS) test (Ekama and Wentzel, 2004). This phenomenon is compensated for by adjusting the VSS and ISS results accordingly:

$$VSS^* = VSS/(1-0.15) \quad (6.3)$$

and

$$ISS^* = TSS - VSS^* \quad (6.4)$$

with

VSS^* = Measured VSS adjusted

ISS^* = Measured ISS adjusted

The average ratio of COD and N to suspended solids is determined from the chemical analyses of particulates and the concentration of solids.

$$TKN/TSS = TKN_{particulate}/TSS \quad (6.5)$$

6.2 Chemical Analyses of Urine Feed

The results of chemical analyses performed on urine samples are illustrated in Figure 6.1. Nitrogen was present as FSA-N and organic nitrogen. FSA-N ranged from 4 382-6 188 mgN/l whereas organic nitrogen ranged from 140-1 288 mgN/l. The majority of organic nitrogen in fresh urine derives from urea which is transformed to ammonia when hydrolysis occurs. Therefore the low organic nitrogen levels in relation to FSA-N indicate a high degree of urine hydrolysis. Nitrite-N and nitrate-N were not detected in any urine samples. COD in urine exhibited large variations as levels ranged between 3 926 mgO/l and 11 000 mgO/l.

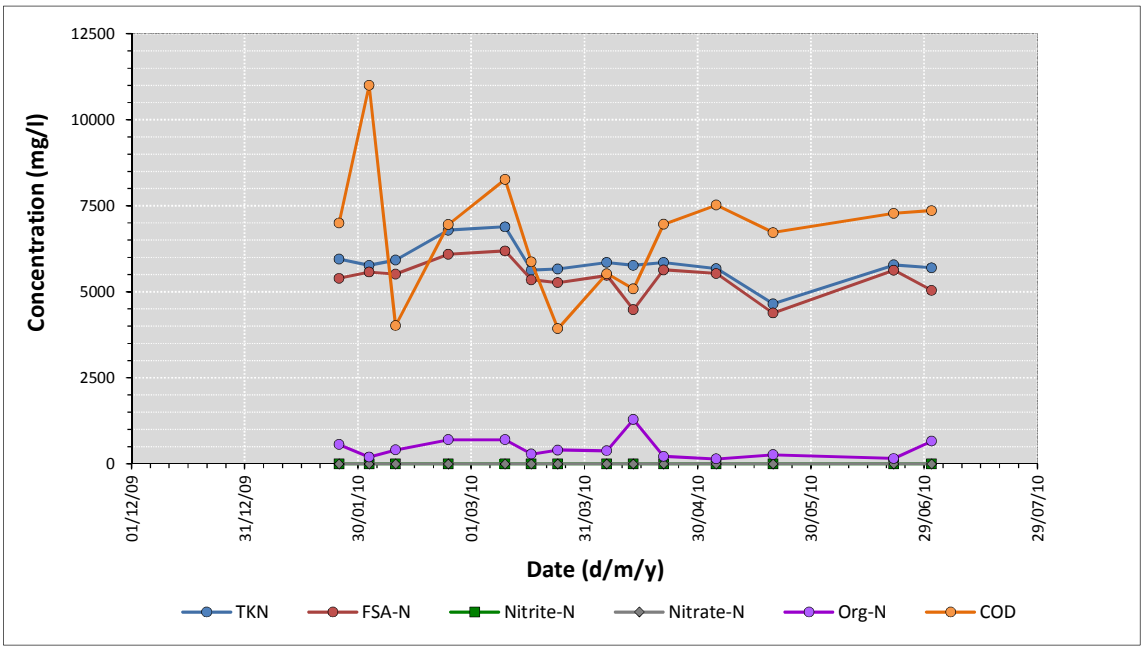


Figure 6.1: Concentration of nitrogen compounds and COD in urine samples

The observed alkalinity of urine is illustrated in Figure 6.2 in relation to TKN and organic nitrogen. The alkalinity ranged between 8 850 mg/l and 14 296 mg/l whereas pH was in the 8.9 to 9.1 range. The hydrolysis of urea is a major source of alkalinity in urine. Therefore the level of alkalinity in urine is proportional to the amount of urea and the degree of hydrolysis. Point A in Figure 6.2 illustrates a scenario where the observed alkalinity is notably lower than average. This can be related to the comparatively high amount of urea present (indicated by organic nitrogen) that has not been hydrolysed to produce bicarbonate.

Incomplete hydrolysis however does not impede on full alkalinity potential of urine as residual urea hydrolyses in the system thereby releasing the remainder of alkalinity. This finding, although not the focus of the study, indicates that the analytical methods, e.g. five point titration, for determining alkalinity is not accurate where urea has not been hydrolysed.

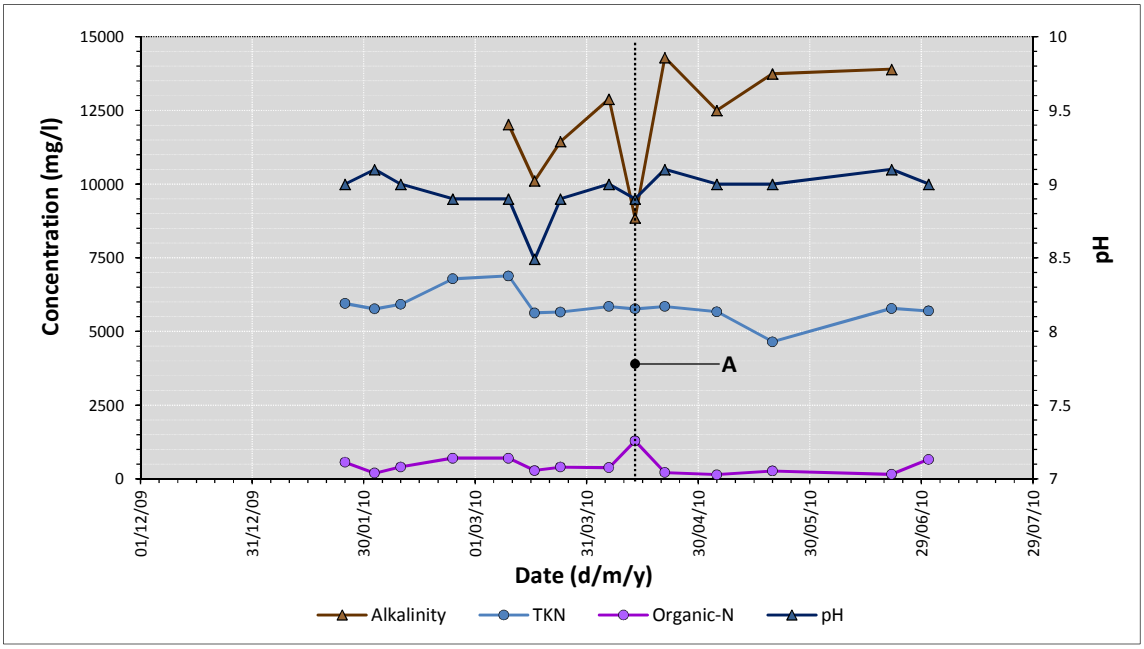


Figure 6.2: Alkalinity of urine in relation to TKN and organic nitrogen.

6.3 CHEMICAL ANALYSES OF EFFLUENT

Effluent samples were analysed for the same constituents as urine and the results are illustrated in Figure 6.3 (i.e. the last sample of a sample set collected over the duration of a cycle and not the first sample which is effluent from the preceding cycle).

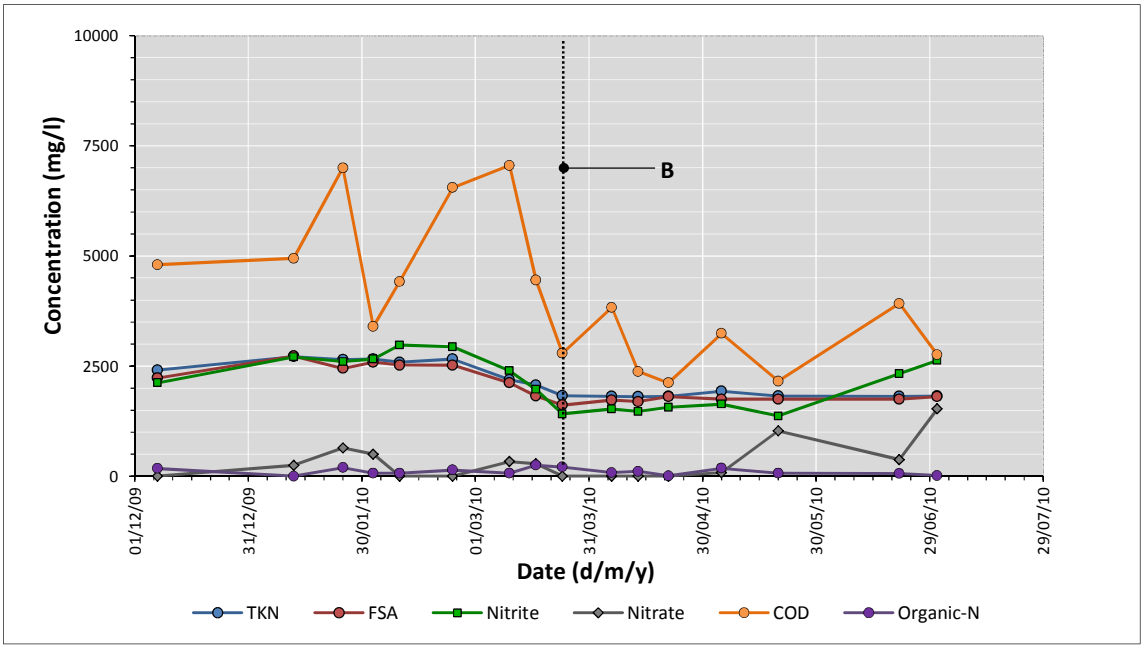


Figure 6.3: Effluent nitrogen and COD concentrations.

The initial effluent results varied but eventually reached stability as indicated by point B. This point of stability is recognised as the stage at which the system reached steady state. The difference in effluent characteristics is evident upon comparing the levels and variation of constituents prior to and after steady state.

6.3.1 Effluent COD

The effluent COD levels prior to steady state averaged at approximately 6000 mg/l and exhibited a degree of variation similar to influent urine COD levels. Under steady state conditions the average COD concentration reduced to approximately 3000 mg/l with less prominent variation.

6.3.2 Effluent nitrogen compounds

FSA-N and nitrite-N levels initially exceeded 2 500 mgN/l but reduced to concentrations of less than 2 000mgN/l after reaching steady state. These two compounds were present at

similar concentrations thus resulting in an average FSA-N to nitrite-N ratio of approximately 1:1. Nitrate-N levels were very low in comparison to nitrite-N and at times not present. The nitrite-N and nitrate-N levels did however increase notably as seen in last three points of the sequence.

The relatively high levels of FSA-N and nitrite-N in the effluent are as a result of incomplete/partial nitrification. This indicates inhibition of both autotrophic ammonia oxidisers (AAOs) and autotrophic nitrite oxidisers (ANOs) which limited the efficiency of ammonia and nitrite conversion. ANOs typically have a greater growth rate than AAOs which means that they can convert nitrite to nitrate faster than AAOs can convert ammonia to nitrite. Therefore nitrification in an ideal activated sludge system is ultimately dependent on the work rate of AAOs rather than that of ANOs. This was not the case in this experimental system as the relatively high nitrite levels in the effluent shows that ANOs were incapable of oxidising the substance at the rate that it was produced thus leading to an accumulation of nitrite. Therefore it is apparent that, although AAOs and ANOs were both inhibited, the inhibition of ANOs was greater.

Inhibition can most likely be attributed to numerous substances which in combination with physical conditions (temperature, pH etc.) created a stringent environment for the organisms. One of the major causes of inhibition can presumably be related to organism substrate and products. Ammonia and nitrous acid (product of ammonia oxidation) serve as substrate for AAOs and ANOs respectively but also inhibits the organisms especially when present in high concentrations. Additionally ANOs are also susceptible to inhibition by hydroxylamine (intermediate of ammonia oxidation) and nitrate. Given the high levels of the various nitrogen compounds which make up the substrates and products of the organisms, it is very probable that inhibition by these substances were the dominant limitation in organism growth and ultimately the ability to fully convert nitrite to nitrate.

6.3.3 Effluent alkalinity

The effluent alkalinity is illustrated in Figure 6.4 with COD, TKN and organic-N. Steady state is indicated by point C. The decrease in TKN effluent levels suggests a higher degree of ammonia oxidation during steady state which means that more alkalinity was utilised.

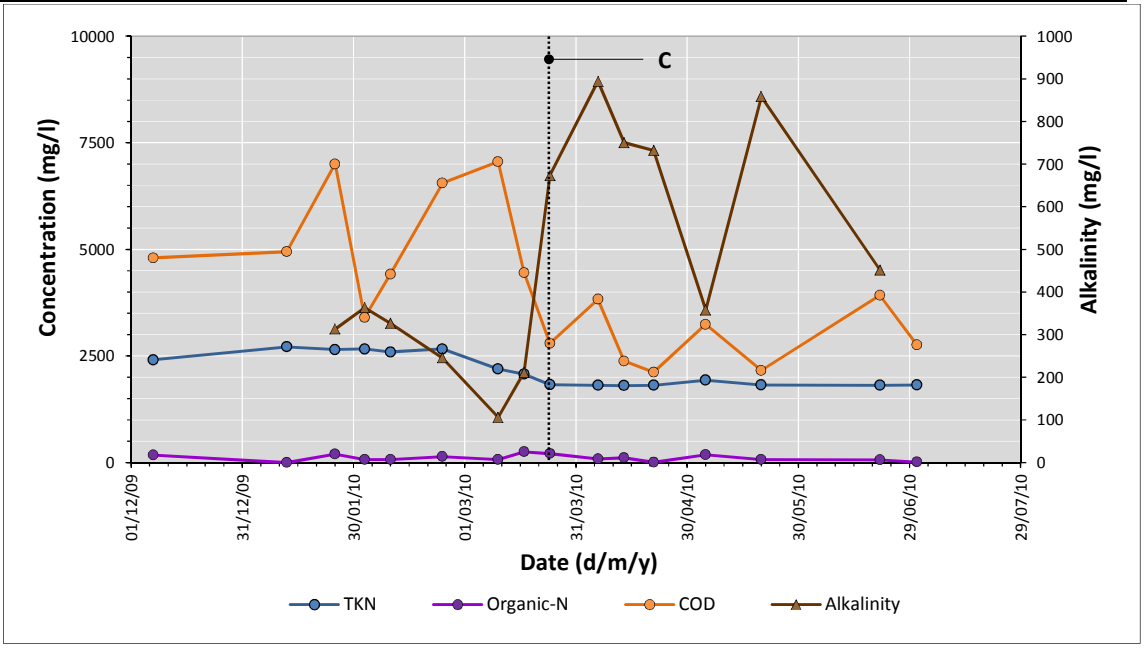


Figure 6.4: Effluent alkalinity in relation to COD, TKN and Org-N.

Figure 6.4 however, shows that effluent alkalinity levels were higher during steady state which indicates that more alkalinity was available during this period. This poses the question of where the additional alkalinity was derived from. Table 6.1 shows the alkalinity levels of urine, samples taken at the end of anoxic phases and samples taken at the end of aerobic phases (effluent).

Table 6.1: Alkalinity levels after anoxic and aerobic phases

Sample		Alkalinity (as mg $CaCO_3$/l)			
No	Date	Urine	EndAnoxic	End Aerobic	dAlk
1	01-12-2010	#	1129	#	#
2	25-1-2010	#	1512	313	1199
3	02-02-2011	#	1455	363	1092
4	09-02-2010	#	1467	327	1140
5	23-02-2010	#	1392	246	1146
6	10-03-2010	12025	1368	106	1262
7	17-03-2010	10108	1349	211	1138
8	24-03-2010	11450	1245	673	572
9	06-04-2010	12888	1154	894	260
10	13-04-2010	8851	1343	750	593
11	21-04-2010	17297	1882	732	1150
12	05-05-2010	12501	961	358	603
13	20-05-2012	13747	1339	859	480
14	21-06-2010	13897	1034	452	582
15	01-07-2010	#	#	#	#
All	Average	12529	1331	483	863
1 to 7	Average	11067	1382	261	1163
8 to 15	Average	12947	1280	674	606
Samples 1 to 7 before steady state. Samples 1 to 8 during steady state					

The alkalinity of urine feed during steady state was somewhat higher, but the alkalinity after the anoxic phase during the same period was not. Therefore, during the steady state period, urine alkalinity and alkalinity gained through denitrification did not result in higher alkalinity levels at the start of the aerobic phases. The higher effluent alkalinity may possibly be as a result of a higher degree of COD oxidation. It appears that higher effluent alkalinity levels correspond to lower effluent COD levels and vice versa. The oxidation of organics produces bicarbonate (HCO_3^-) which contributes to the total alkalinity through the carbonate system. Therefore more alkalinity is produced with an increase in the amount of organics oxidised.

6.4 Chemical Analyses of 24-Hour Sample Sets

The chemical analysis of sample sets taken at intervals over the duration of individual cycles was aimed at establishing the chemical changes that occurred in the system during anoxic and aerobic phases. One of the main challenges of these results was the level of accuracy that was obtainable. The changes in constituent concentrations over a cycle were small relative to the base level of the constituents. The high chemical concentrations in samples called for large dilutions in order to get within the concentration range of test methods. This meant that a certain degree of error was inevitable. The error may be small in comparison to the base level concentrations but significant compared to change in concentration over a cycle. This is explained by the following scenario:

Assume that the TKN concentration at the end of a cycle is 2 000 mgN/l. This constitutes the base level TKN concentration in the system and effluent. During the volume exchange, 1.0 l of effluent is withdrawn from the 20.0 l system and 1.0 l of urine is added again with a TKN concentration of 6 000 mgN/l. Therefore the TKN in the system at the start of the cycle is:

= (19.0 l x 2 000 mgN/l + 1.0 l x 6 000 mgN/l)/20.0 l

= 2 200 mg

During the cycle the TKN concentration is reduced to 2 000 mgN/l again through nitrification. Therefore the change in the TKN concentration during the cycle is 200 mgN/l. If the TKN chemical analyses of samples are 95% accurate then an error of 5% is made. 5% of 2000 mgN/l amounts to 100mgN/l but 100 mgN/l is 50% of the change in TKN concentration over a cycle. This means that error in measurements makes it difficult to determine accurately the chemical concentration changes in samples taken over the extent of a cycle as a small error

in measurement can overshadow the change from one sample to the next. This also makes it nearly impossible to calculate a mass balance. This has to be taken in consideration when evaluating the results.

6.4.1 Typical cycle profile

The change in chemical concentration for various constituents is illustrated in figure 6.5. This was the first set of samples taken within the steady state period (24/03/2010). The measured pH during the cycle is also displayed as indication of the system progress. The measured alkalinity at the start of the aerobic phase was 1 245 mgCaCO3/l and 673 mg$CaCO_3$/l at the end. The average temperature during the cycle was 27.2 °C.

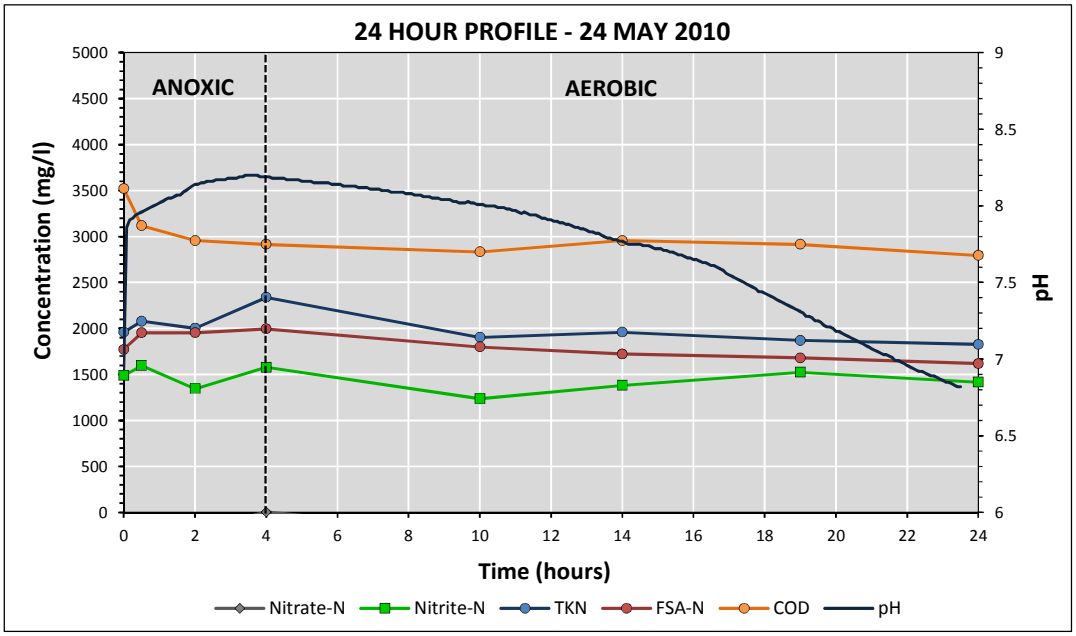


Figure 6.5: Change in chemical concentrations during cycle (24/03/2010)

The first point in the profile sequence shows the state of the system just prior to the addition of urine. The addition of urine results in a pH increase along with increases in TKN and FSA-N concentration. No nitrate-N was detected in samples which mean that nitrite-N was the primary electron acceptor during the anoxic phase. Therefore denitrification ensued through the reduction of nitrite. The change in nitrite-N concentration during the anoxic phase does not clearly show the progress of denitrification through a decrease in nitrite-N. A decrease in COD (associated with the utilisation of organics as carbon source) is evident however. The secondary increase in pH during the anoxic phase is also a strong indicator of

denitrification. During the aerobic phase there is a gradual decrease in TKN and FSA-N which results from nitrification. An increase in nitrite-N is visible in the profile from hour 10 onwards. The increase in nitrite should theoretically be proportional to the decrease in FSA-N but establishing this from observed results is difficult due to the analytical errors.

Figure 6.6 shows a set of results obtained from a cycle 12 days after the previous results. The temperature during this cycle was ranged between 21.8°C and 24.5°C. The alkalinity at the start of the aerobic phase was 1154 mg$CaCO_3$ and 894 mg$CaCO_3$ at the end.

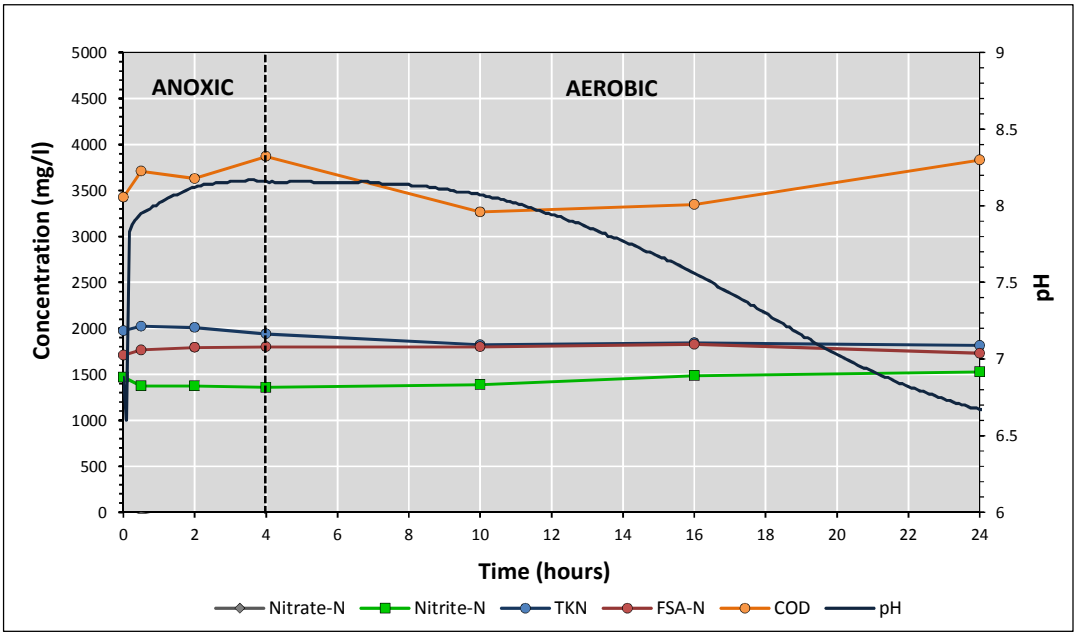


Figure 6.6: Change in chemical concentrations during cycle (06/04/2010)

As with the previous set of results nitrate-N was not present. The decrease in nitrite-N during the anoxic phase is however more noticeable along with the characteristic secondary pH increase. The aerobic nitrification phase brings about a decrease in TKN and an increase in nitrite-N. A feature that stands out in this cycle is the marginal increase in pH that occurs during the first 2 hours of the aerobic phase. This is presumably as a result of increase in alkalinity which possibly derives from residual urea hydrolysis or organics oxidation. Both of these notions are likely if the analytical results are accurate. TKN levels are marginally higher than FSA-N at the start of the aerobic phase (which indicates that some nitrogen is still in the form of organic urea) but is hydrolysed during the initial period of the aerobic phase. This results in TKN levels reducing to the same concentration as FSA-N 10 hours into the cycle

(approximately the same time that the pH starts falling). Similarly the COD concentration decrease during the same period which reflects the oxidation of organics and the production of bicarbonate. The inconsistency in COD measurements does however foil confirmation of the latter notion.

6.4.2 Relationship between pH and ammonia oxidation during cycles

The change in pH and the rate at which change occurs dictates nitrification and results in a varying rate of ammonia oxidation. This is illustrated in Figure 6.7 which shows the results obtained during a cycle marked by a relatively rapid decrease in pH brought about by a period of warmer system temperatures. The decrease in FSA-N and increase in nitrite-N occurs most rapidly during the initial period of the aerobic cycle when the pH is still above 7.0. Once the pH drops below 7.0 there the changes in FSA-N and nitrite-N is significantly less.

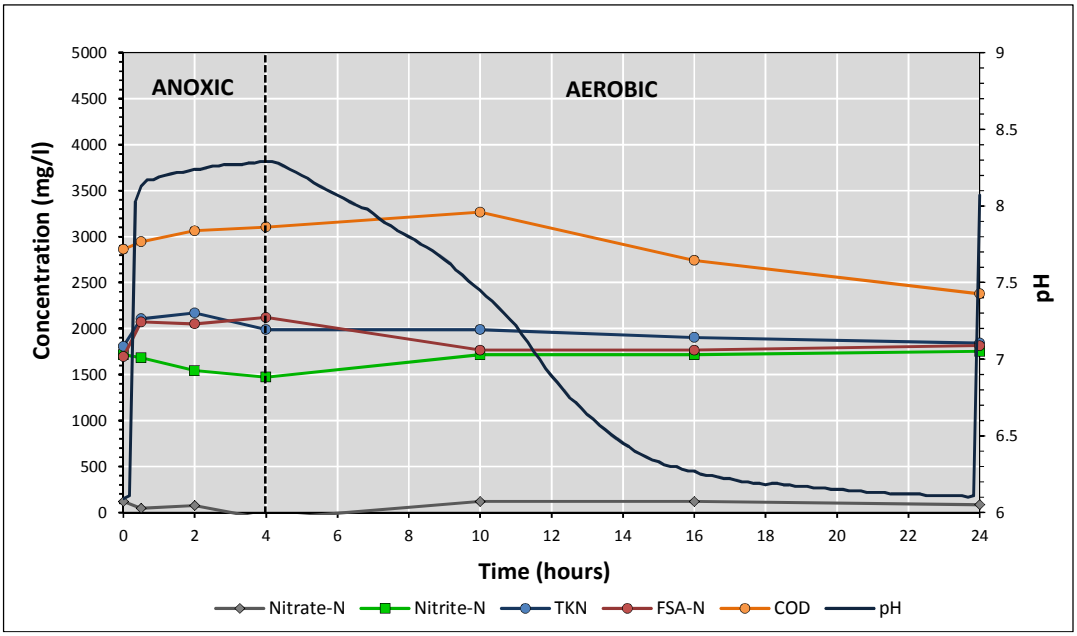


Figure 6.7: Change in chemical concentration during cycle 13/04/2010.

This confirms that the optimal pH for nitrification in this system is between 7 and 8. The change in pH is a direct result of ammonia oxidation of which the rate is closely related to pH decline rate. The marginal decrease in FSA-N at a pH of below 6.5 indicates the proximate end of nitrification and consequently the slowing in pH decline. From previous observations it was determined that pH change comes to a standstill when the pH reaches approximate

6.2 to 6.1. Therefore based on pH and FSA-N decline trend observed in Figure 6.7, it is reasonable to assume that no ammonia oxidation occurs once pH decline ceases.

6.4.3 Nitrite-N and Nitrate-N levels

The inconsistency in the levels of nitrate-N from cycle to cycle reflected the inhibition of nitrite oxidisers. No nitrate-N was observed during certain times which were possibly due to the absence of nitrite oxidisers brought about by extended periods of inhibition and the consequent wash out of the organisms. When nitrate-N was detected in the system the level thereof was significantly lower relative to nitrite-N as illustrated in Figure 6.8.

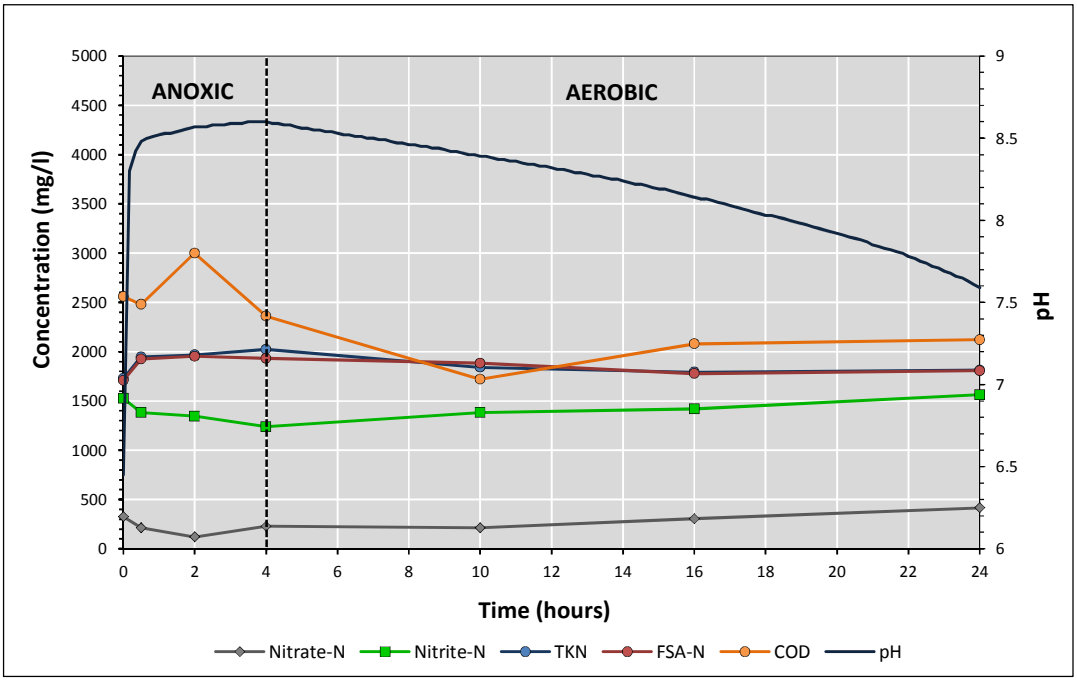


Figure 6.8: Change in chemical concentration during cycle 21/04/2010.

Nitrate is the preferred electron acceptor under anoxic conditions which would suggest that nitrite would only be utilised once nitrate becomes depleted. This does not appear to be the case as seen in Figure 6.8 as a decrease in nitrite-N occurs while nitrate-N is present suggesting that nitrite and nitrate was utilised simultaneously. This may be due the fact that nitrite is more readily available in the system than nitrate. Alternatively this anomaly may be as a result of analytical error.

The results of the aerobic phase of the cycle show an increase in both nitrite-N and nitrate-N. These increases appear to occur proportionally which means that ammonia- and nitrite

oxidation transpires at approximately equivalent rates. It results in the net difference between the two constituents remaining similar. This incidence is evident in every cycle profile where nitrate is observed.

6.4.4 The effect of extended anoxic phases

The duration of anoxic phases was limited to 4 hours as result of the aerobic phase time required to consistently reduce pH to a sufficiently low level so as to buffer the pH increase associated with urine addition. The denitrification capacity of the system was therefore limited. The duration of the anoxic phase was extended by 4 hours during a sampled cycle in order to explore the effect of extended denitrification. The results are illustrated in Figure 6.9.

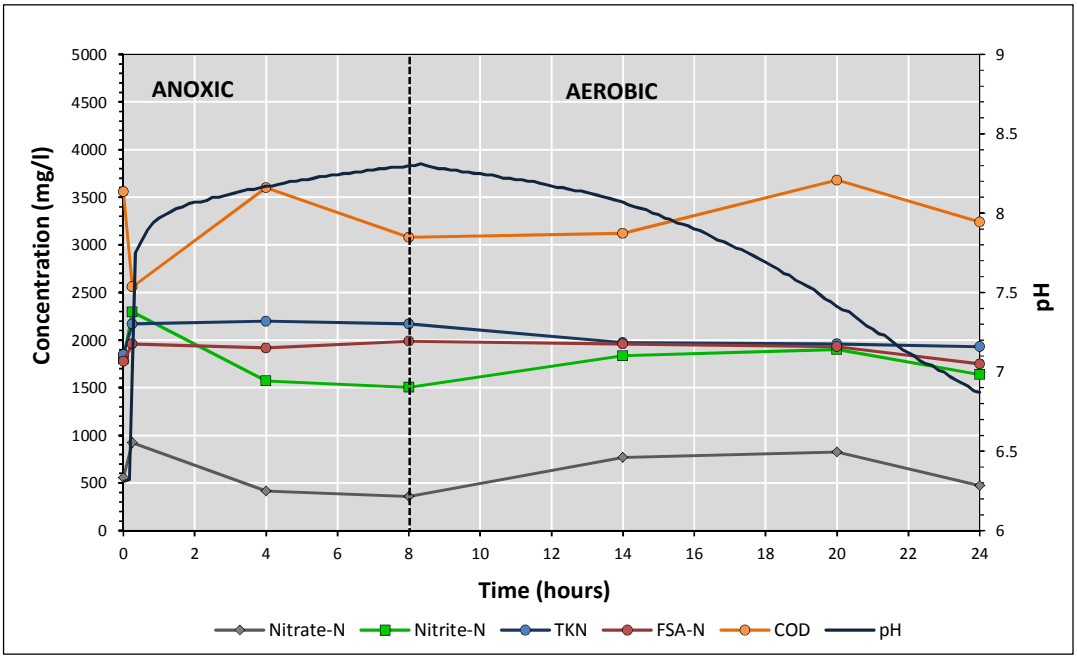


Figure 6.9: Extended anoxic phase during cycle 05/05/2010.

The change in nitrite-N and nitrate-N during the anoxic phase is somewhat distorted by the second point in the series as it should theoretically be lower than the first point. None the less it appears that denitrification does continue throughout the extended period as the nitrate-N and nitrite-N concentrations decrease from hour 4 to hour 8. The pH also continues to increase during this period. The TKN and FSA-N levels during the anoxic phase remained relatively constant but net difference in concentration indicates the presence of some organic nitrogen which can be interpreted as unhydrolysed urea. This difference between the two constituents diminishes once the aerobic phase commences. The same

observation can be made from Figure 6.6. This could indicate that the hydrolysis of residual urea, during the anoxic phase, is marginal.

6.5 Chemical and Physical Analyses of Sludge Solids

Unfiltered samples were analysed for inert suspended solids (ISS), volatile suspended solids (VSS) and total suspended solids (TSS). TSS is essentially the sum of ISS and VSS and therefore dependant on the levels thereof. The ISS and VSS are of principal interest for establishing the characteristics of the sludge.

The ISS content of wastewater sludge typically consists of inert particulate substances which enter the system as part of the influent wastewater (external sources) or forms inside the system through biological and chemical processes (internal sources).

Undiluted urine as the influent wastewater to the experimental system did not contain significant amounts particulate matter which could contribute to the ISS content of the sludge. Therefore the sludge ISS had to derive from within the system mainly as endogenous residue from biomass decay (endogenous respiration). It is possible that struvite also contributed to the ISS of the sludge but this would have been negligible as struvite precipitation occurred in the urine storage tanks before entering the system thus limiting the precipitation potential in the system. The struvite precipitation potential would also have been further limited by the lower pH (relative to pH of urine in storage tanks) at which the system was operated.

The VSS content of sludge comprises organic solids from influent wastewater or is internally generated in the form of biomass. The VSS in sludge from the experimental system is assumed to be only internally generated particulate organic matter as the influent urine did not contain any observable organic solids. Therefore it is assumed that internally generated particulate organic matter in the system is mainly biomass. The biomass would consist of both active (live) and inactive (dead) bacteria. Inactive biomass becomes hydrolysed into substrate for active biomass. The VSS test does however not distinguish between active and inactive biomass.

Figure 6.10A shows the VSS, ISS and TSS measurements which are plotted against sampling time. The same results were plotted on a numeric scale based on the order of sampling to delineate sample points better as shown in Figure 6.10B. Before steady state the solids concentration varies between 1 700mg/l and 3 300 mg/l with an initial high inert solids contribution. This indicates that a high degree of endogenous respiration which produces endogenous residue manifests as ISS. This is possibly due to the adjustment of the organisms to system conditions during which organism decay is high relative to organism growth. During steady state the total solids concentration ranged between 1100 mg/l and 2000 mg/l. The VSS fraction averaged at more than 80% of the TSS which indicates that majority of sludge consisted of biomass.

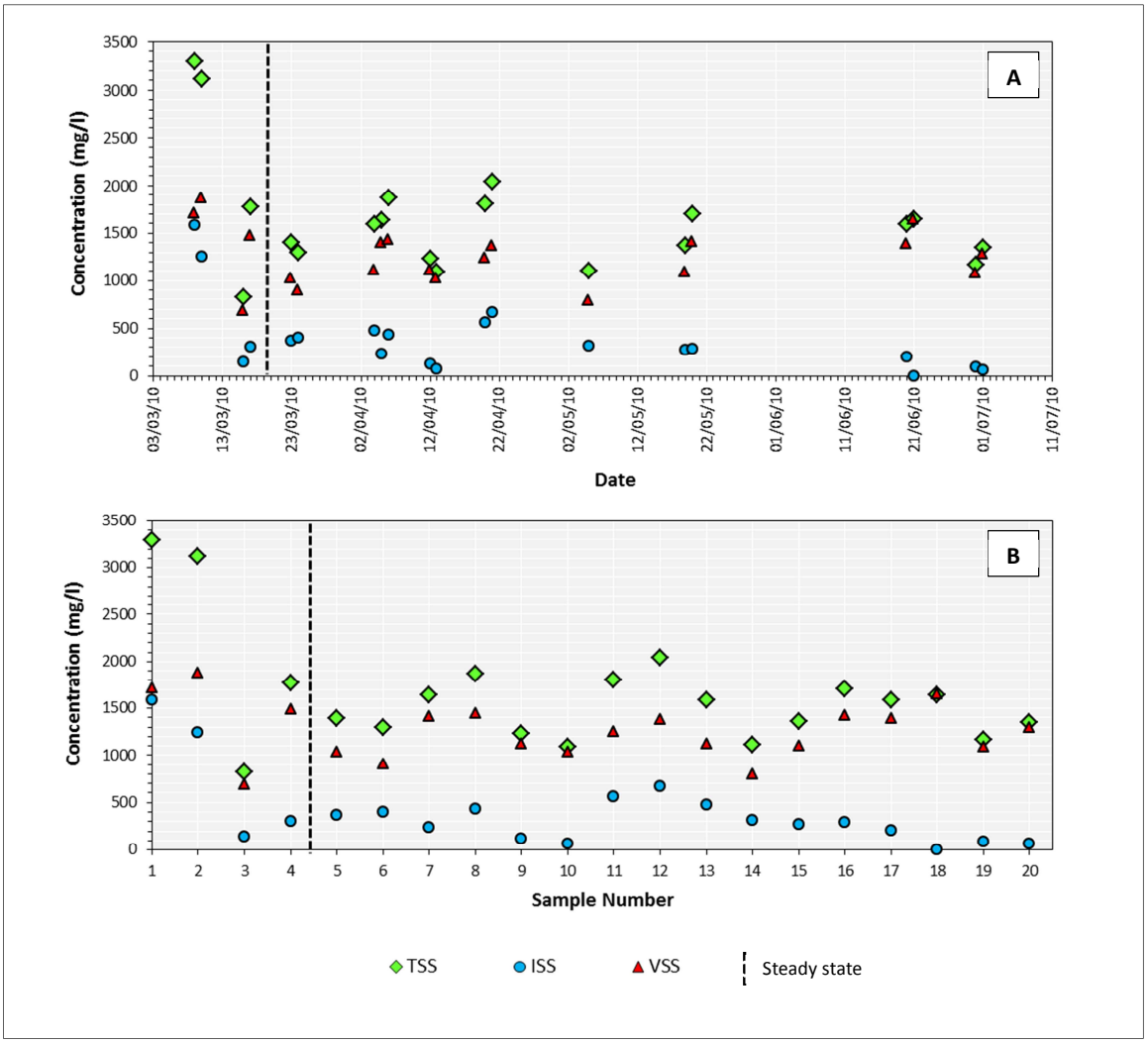


Figure 6.10: Measured TSS, ISS and VSS in experimental system.

The COD and TKN content of the sludge was determined by comparing filtered and unfiltered samples. The difference in COD and TKN measurements between filtered and unfiltered samples was attributed to sludge and related to the measured sludge solids as summarised in Table 6.2. The COD and TKN ratios were only calculated in relation to the TSS as it cannot be established what the individual contributions of VSS and ISS are to COD and TKN. The first 4 results in the table was obtained before steady state which is why different sets of statistical parameters were calculated as shown at the bottom of the table.

Interpretation of the sludge COD and TKN content poses a challenge as the data shows a high degree of variation. The observed values do however give an indication of the probable ranges of the COD and TKN.

Table 6.2: Measured solids, COD and TKN of sludge.

Sample No	Date	TSS	ISS	VSS	ISS*	VSS*	COD	TKN	VSS/TSS	ISS/TSS	ISS/VSS	COD/TSS	TKN/TSS	TKN/COD
		mgTSS/l	mgISS/l	mgVSS/l	mgISS/l	mgVSS/l	mgCOD/l	mgN/l	mgVSS/mgTSS	mgISS/mgTSS	mgISS/mgVSS	mgCOD/mgTSS	mgN/mgTSS	mgN/mgCOD
1	2010/03/09	3294	1842	1452	1586	1708	#	308	0.519	0.481	0.928	#	0.094	#
2	2010/03/10	3118	1528	1590	1247	1871	#	224	0.600	0.400	0.667	#	0.072	#
3	2010/03/16	826	244	582	141	685	607	336	0.829	0.171	0.206	0.735	0.407	0.6
4	2010/03/17	1776	522	1254	301	1475	3036	98	0.831	0.169	0.204	1.709	0.055	0.0
5	2010/03/23	1398	523	875	369	1029	243	252	0.736	0.264	0.358	0.174	0.180	1.0
6	2010/03/24	1298	532	766	397	901	1133	420	0.694	0.306	0.440	0.873	0.324	0.4
7	2010/04/05	1639	446	1193	235	1404	766	49	0.856	0.144	0.168	0.467	0.030	0.06
8	2010/04/06	1866	645	1221	430	1436	766	84	0.770	0.230	0.299	0.411	0.045	0.11
9	2010/04/12	1230	286	944	119	1111	1492	273	0.903	0.097	0.108	1.213	0.222	0.18
10	2010/04/13	1096	223	873	69	1027	1935	217	0.937	0.063	0.067	1.766	0.198	0.11
11	2010/04/20	1807	747	1060	560	1247	1080	252	0.690	0.310	0.449	0.598	0.139	0.233
12	2010/04/21	2036	873	1163	668	1368	800	147	0.672	0.328	0.488	0.393	0.072	0.184
13	2010/04/04	1588	643	945	476	1112	320	252	0.700	0.300	0.428	0.202	0.159	0.787
14	2010/05/05	1108	434	674	315	793	1360	168	0.716	0.284	0.397	1.227	0.152	0.124
15	2010/05/19	1365	434	931	270	1095	720	140	0.802	0.198	0.246	0.527	0.103	0.194
16	2010/05/20	1701	500	1201	288	1413	1320	126	0.831	0.169	0.204	0.776	0.074	0.095
17	2010/06/20	1589	410	1179	202	1387	1880	119	0.873	0.127	0.146	1.183	0.075	0.063
18	2010/06/21	1642	201	1441	0	1642	960	21	1.000	0.000	0.000	0.585	0.013	0.022
19	2010/06/30	1166	249	917	87	1079	1240	182	0.925	0.075	0.081	1.063	0.156	0.147
20	2010/07/01	1347	257	1090	65	1282	2760	357	0.952	0.048	0.050	2.049	0.265	0.129
1 to 4	Average	2253	1034	1220	819	1435	1822	242	0.695	0.305	0.501	1.222	0.157	0.293
1 to 4	Min	826	244	582	141	685	607	98	0.519	0.169	0.204	0.735	0.055	0.032
1 to 4	Max	3294	1842	1590	1586	1871	3036	336	0.831	0.481	0.928	1.709	0.407	0.553
1 to 4	Standard Dev	1168	771	447	707	526	1717	107	0.160	0.160	0.358	0.689	0.167	0.368
1 to 4	Coeff. of Var.	0.52	0.75	0.37	0.86	0.37	0.94	0.44	0.23	0.52	0.71	0.56	1.07	1.26
5 to 20	Average	1492	463	1030	284	1208	1173	191	0.816	0.184	0.246	0.844	0.138	0.241
5 to 20	Min	1096	201	674	0	793	243	21	0.672	0.000	0.000	0.174	0.013	0.022
5 to 20	Max	2036	873	1441	668	1642	2760	420	1.000	0.328	0.488	2.049	0.324	1.038
5 to 20	Standard Dev	283	196	198	192	226	637	108	0.108	0.108	0.164	0.540	0.087	0.278
5 to 20	Coeff. of Var.	0.19	0.42	0.19	0.68	0.19	0.54	0.56	0.13	0.59	0.67	0.64	0.63	1.15

6.6 BATCH EXPERIMENTS

A series of batch experiments were conducted in separate reactors with artificial substrate solutions and sludge from the main system. The batch systems were operated for 12 hours each during which samples were collected hourly and tested for FSA-N, nitrite-N and Nitrate-N. The aim of the batch experiments was to determine how different levels of FSA and salinity affect the performance of ammonia- and nitrite oxidising organisms. The FSA concentrations and salinity of the batch experiments are summarised in Table 6.2. The nitrite-N and nitrate-N levels were used as main indicators.

Table 6.3: FSA concentrations and salinity of batch experiments.

Batch Experiment	NH_3-N	Salinity	Condition
no.	mg/l	mS/cm	-
1	2400	5	High ammonia, low salinity
2	800	5	Low ammonia, low salinity
3	2400	25	High ammonia, high salinity
4	800	25	Low ammonia, high salinity

The first batch experiment was conducted under low saline (i.e. no added salinity) conditions and an initial FSA-N concentration of 2 400 mgN/l. The second batch experiment was also conducted under low saline conditions but the initial FSA-N concentration was lowered to 800 mgN/l.

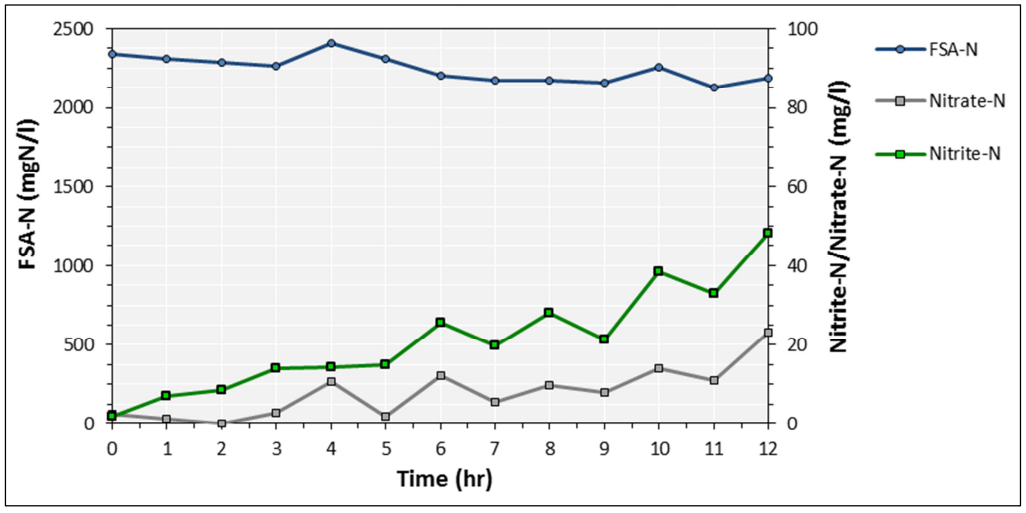


Figure 6.11: Chemical analyses of batch experiment 1.

Results from the first batch experiment are shown in Figure 6.10. The FSA-N declines steadily as nitrite-N and nitrate-N increases. The formation of nitrate-N however lags behind nitrite-N which indicates that nitrite production is faster than the conversion thereof to nitrate. Consequently there is an accumulation of nitrite. The final nitrite-N and nitrate-N concentrations are 48 mgN/L and 23 mgN/L respectively.

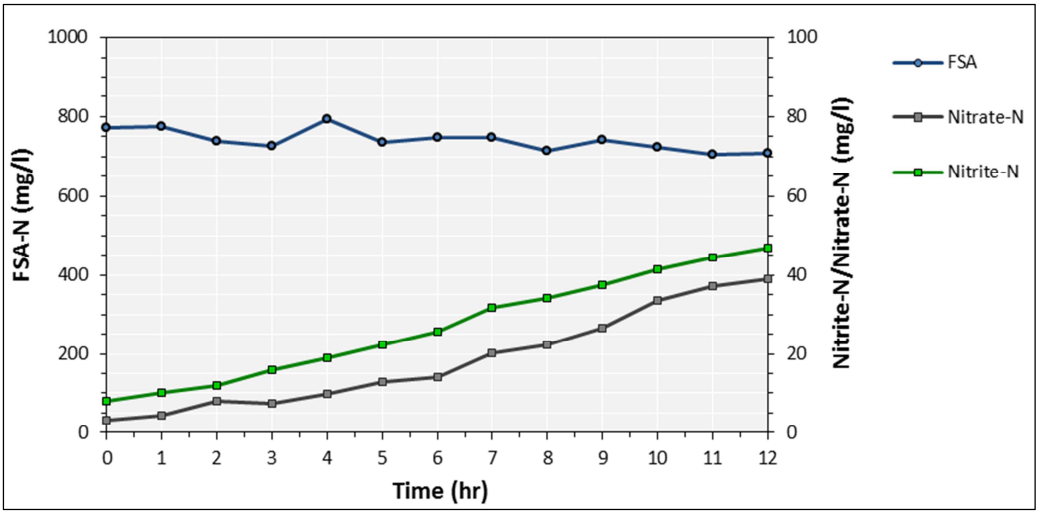


Figure 6.12: Chemical analysis of batch experiment 2.

The results from the second batch experiment are illustrated in Figure 6.11. The results are similar to the first test showing accumulation of nitrite-N and a lag in the production of nitrate-N. The main dissimilarity however is the notably smaller lag between nitrite-N and nitrate-N levels. It appears that the conversion of nitrite to nitrate occurred at a faster rate thus resulting in the production of more nitrate than the first batch experiment. The final nitrite-N concentration was 47 mgN/l and the final nitrate-N was 39 mgN/l.

The third and fourth batch experiments were conducted under saline conditions and aimed at simulating the same level of salinity as in the main system. The FSA-N concentration of batch experiment 3 was adjusted to 2400 mgN/l (same as batch experiment 1) and 800 mgN/L for batch experiment 4 (same as batch experiment 2). Batch experiment 3 is comparable to the main experimental system based on the similar salinity level and FSA concentration.

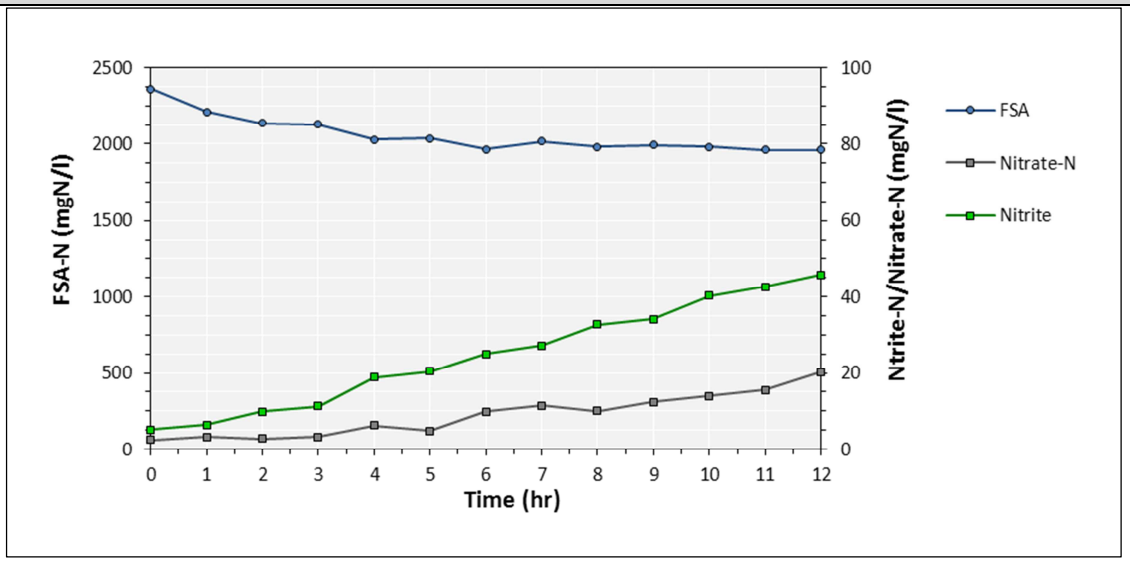


Figure 6.13: Chemical analyses of batch experiment 3.

Figure 6.12 displays the results of batch experiment 3 which shows a lag in nitrate production and nitrite accumulation similar to batch experiment 1. The overall rate of nitrite- and nitrate production is somewhat lower leading to a lower final nitrite-N and nitrate-N concentrations to that of batch experiment 1.

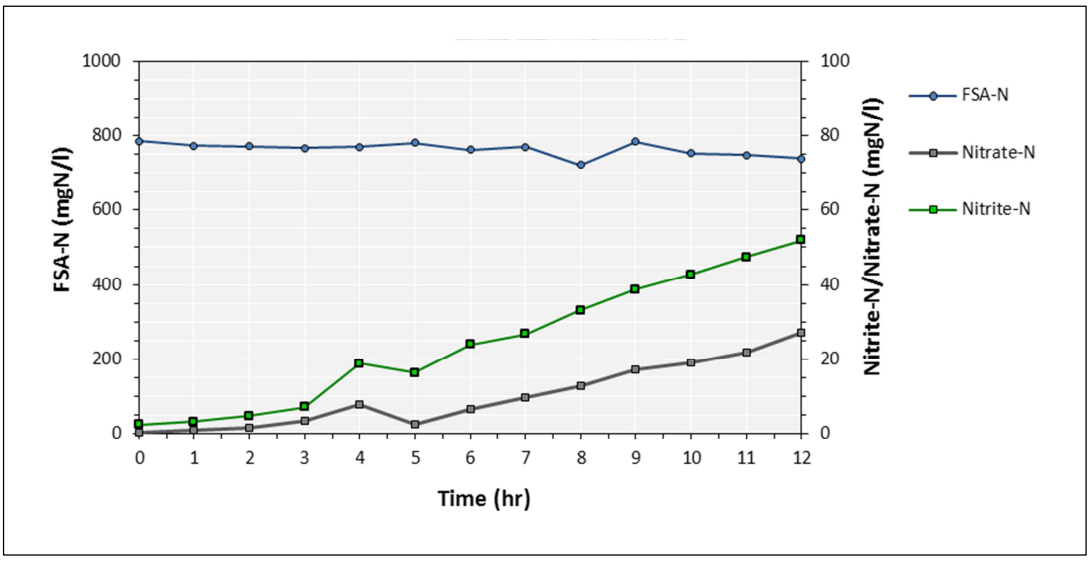


Figure 6.14: Chemical analyses of batch experiment 4.

The fourth batch experiment produced higher final nitrite-N and nitrate-N concentrations than batch experiment 3 but lower than that of batch experiment 2. This indicates that nitrite and nitrate production rates are marginally greater under reduced FSA levels but hampered by higher levels of salinity.

Table 6.4: Batch experiment final Nitrite-N and Nitrate-N concentrations.

Batch Experiment	Final Nitrite-N	Final Nitrate-N	Nitrite-N + Nitrate-N
No	mgN/L	mgN/L	mgN/L
1	48.3	23.1	71.4
2	46.8	39.1	85.9
3	45.8	20.3	66.1
4	51.9	27.2	79.1

The final nitrite-N and nitrate-N concentrations of the batch experiments are compared in Table 6.1. The combined nitrite-N and nitrate-N values are also given in this table which reveals that nitrogen oxidation progressed best in batch experiments 2 and 4. This could probably be attributed to the significantly lower FSA levels under which these experiments were conducted. The major dissimilarity between 2 and 4 is the difference in final nitrite-N concentration. The saline experiment produced 30% less nitrate than the low-saline experiment.

The batch experiments confirm that nitrifying organisms are affected adversely by both high FSA and salinity levels. However it does appear as if ANOs are affected more severely especially by high salinity levels.

Chapter 7

Conceptual Model

This section sets out to explain the model for biological nitrification and denitrification of urine in a SBR system. A model was developed in a spreadsheet by means of a time step integration method. The model is aimed at simulating reactor processes over a 24 hour cycle in incremental time steps of 10 minutes. The techniques and assumption used to develop the model are explained.

7.1 INTRODUCTION

The bacteria facilitated biochemical processes which define an activated sludge system are dependent on various factors that can be categorised by the groups of organisms involved. These factors are related to the biological behaviour and requirements of the organisms. Every group of organisms have different requirements with respect to substrate and environment. This essentially defines the functional roles of organism groups. The development of a model is centred around the mathematical description of the biological behaviour of functional organisms and the quantification of influential factors. Organisms may perform differently from one system to the next, but the biological fundamentals of activated sludge processes remain valid and can be used as the platform for developing a model of an unfamiliar system. Data from experimental work serves in verification of parameters and estimation of unknowns which assists in refining and calibrating a model specific to the system.

7.2 MODEL DEVELOPMENT

Activated sludge systems are in reality very intricate and it is not always possible to determine all variables or represent every biological mechanism in detail. Therefore various simplifications have to be made in developing a model. The simplifications are based on reasonable assumptions and principles that make it possible to bridge complexities and create a model that is theoretically plausible and practically representative of the real system.

The development of this model is based on the fundamentals of activated sludge systems. It involves the biological activity of organisms, chemical changes and conversions, and the interactions that occur within the system environment. In order to explain the approach used to develop the model, the system is broken down into its various components which it consists of, as explained in the following sections.

7.3 ORGANISMS AND SLUDGE COMPOSITION

7.3.1 Organism Classification in the Model

Many different species of bacteria make up the microbial population of an activated sludge process. The characteristics of the organisms, with respect to biological behaviour,

requirements and functional roles, differ from one species of bacteria to the next and therefore have to be deliberated in order to develop a plausible model. The identification of every individual species of bacteria is impractical (virtually impossible) but grouping organisms by type and similarity, provides an adequate approach to recognising the significance of the diversity in bacterial population composition. Bacteria are grouped and every group is identified as a separate entity with a specific functional role and set of attributes (concentration, growth, decay…) which collectively describe multiple types of similar organisms as one. Similarities in organisms can be found in their metabolic processes and requirements which in effect determine their role in an activated sludge system. Metabolism therefore serves as a good basis for classifying organisms. For the purpose of modelling, organisms were divided into the following groups based on their metabolism defining their functional roles:

Heterotrophs

This group of organisms are primarily responsible for the removal of organic carbon (measured as COD) from wastewater. The same group of organisms also facilitate the conversion of nitrate/nitrite to nitrogen gas. Under aerobic conditions the organisms use oxygen as terminal electron acceptor. This is illustrated in Figure 7.1.

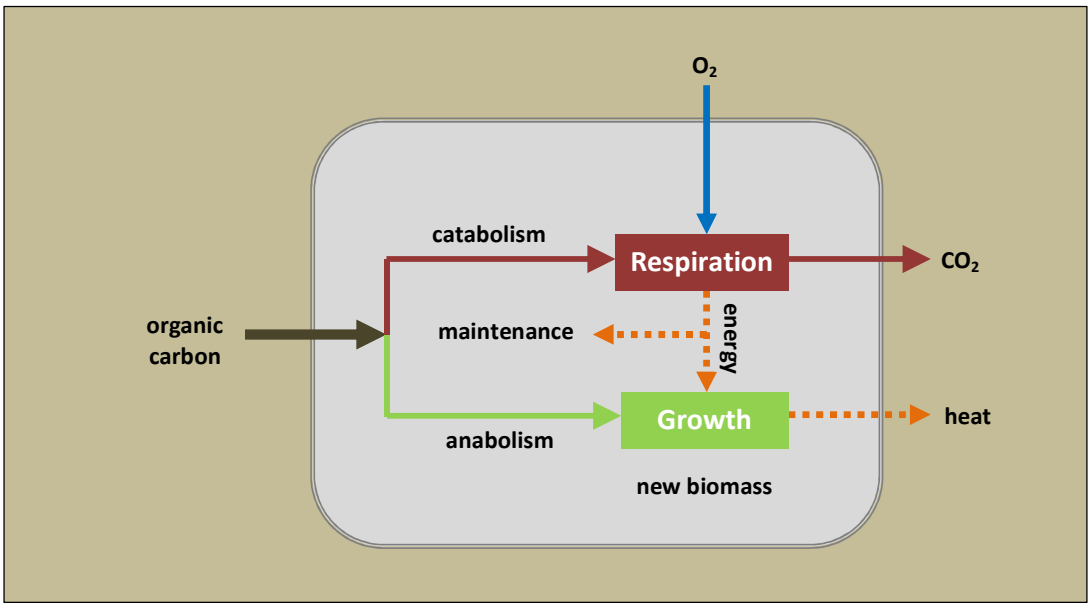


Figure 7.1: Metabolism of heterotrophic organism under aerobic conditions.

However when oxygen is not available the organisms can revert to available nitrite or nitrate as electron acceptor. This is illustrated in Figure 7.2.

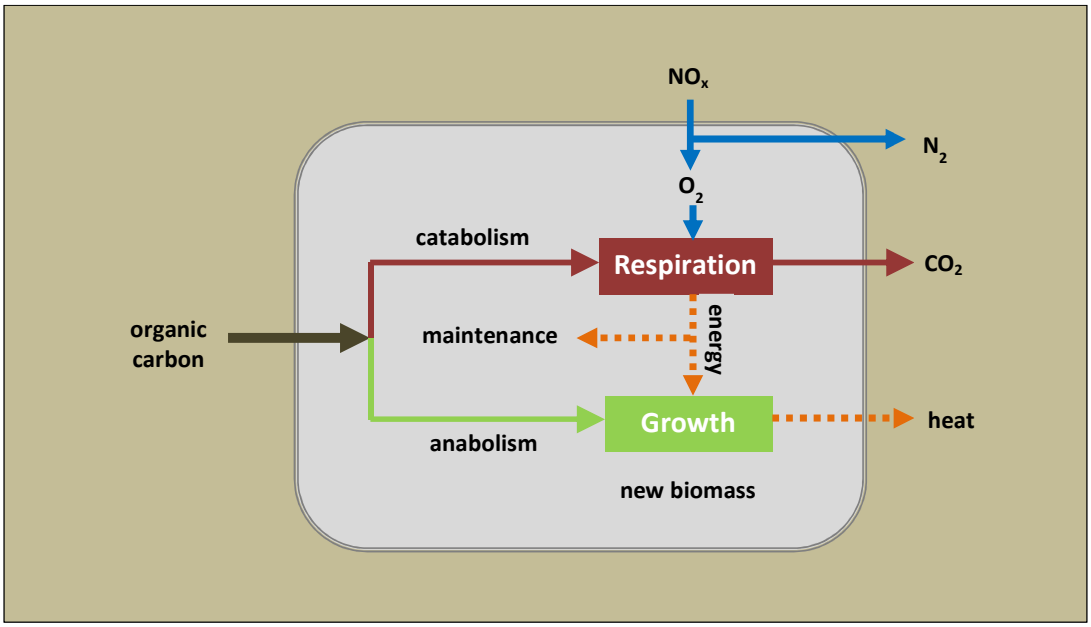


Figure 7.2: Metabolism of heterotrophic organism under anoxic conditions.

These organisms are therefore modelled as one entity with different sets of attributes for aerobic and anoxic conditions.

Autotrophs

Organisms of this group are responsible for nitrification under aerobic conditions. Autotrophic nitrifiers are subdivided into two types. The first type is the ammonia oxidisers which convert ammonia to nitrite. This is illustrated in Figure 7.3.

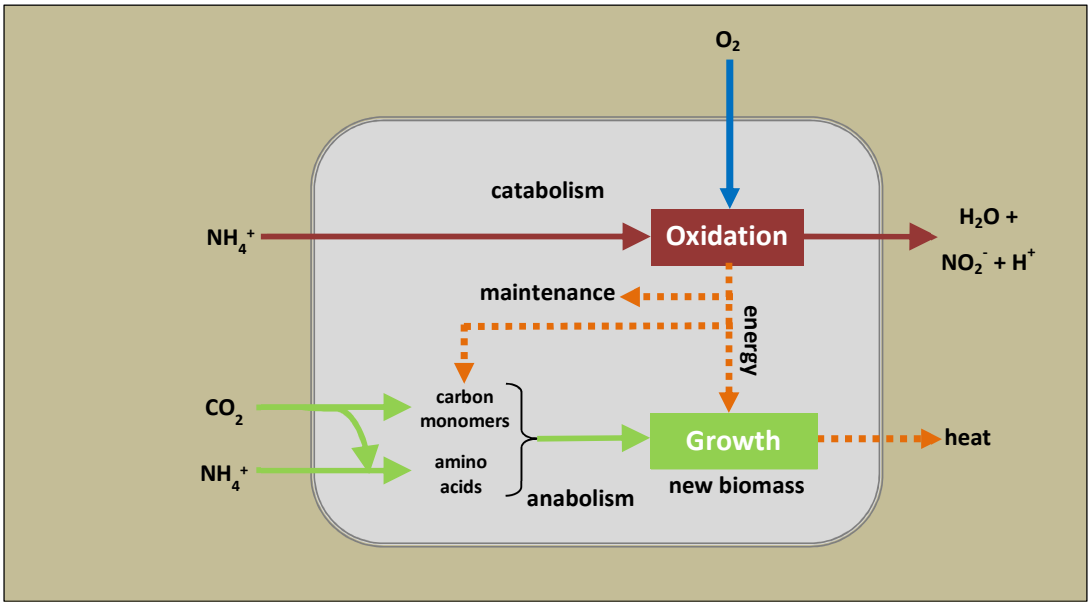


Figure 7.3: Metabolism of autotrophic ammonia oxidisers.

The second type of autotrophic nitrifiers is nitrite oxidisers which convert nitrite to nitrate. These organisms are therefore inherently dependant on ammonia oxidisers if there is no other source of nitrite in the system. The metabolism of nitrite oxidisers is illustrated in Figure 7.4.

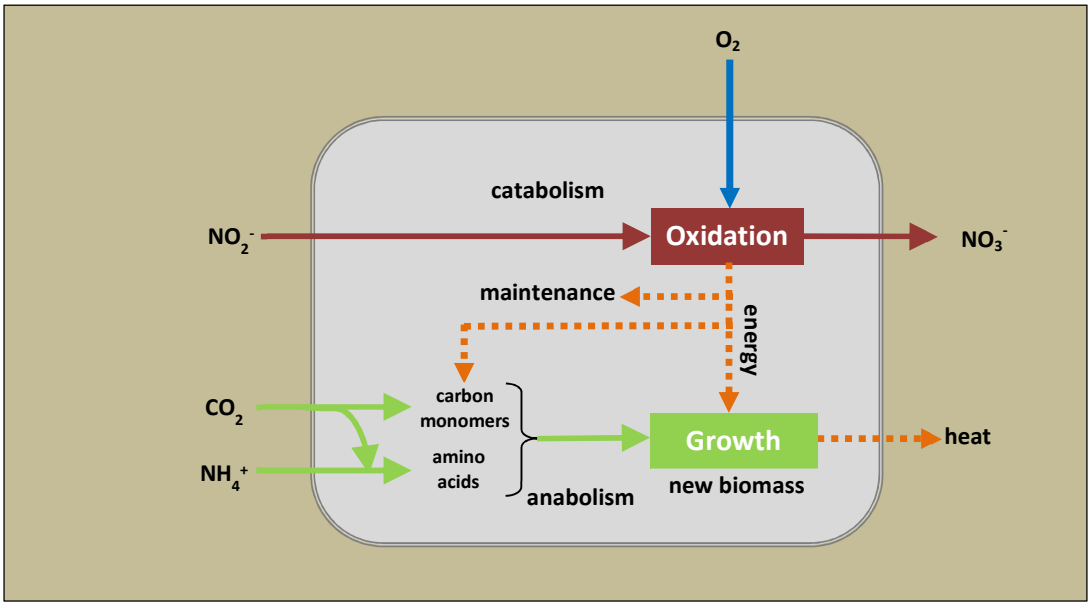


Figure 7.4: Metabolism of autotrophic nitrite oxidisers.

Nitrification is normally modelled as one step in which the amount of ammonia oxidised is considered proportional to the amount of nitrate formed without any residual intermediate nitrite. However, in the urine treatment reactor it was evident that nitrification is not

complete. Therefore, the reactions of ammonia oxidisers and nitrite oxidisers had to be considered as two separate processes in the model.

7.3.2 Sludge Composition

The sludge solids in the system consists of volatile suspended solids (VSS) and inert suspended solids (ISS). For modelling purposes it is assumed that all sludge in the system derives from biological growth (VSS) and decay as influent urine contains no particulate matter that could contribute to the sludge solids. The VSS is therefore considered to consist of heterotrophic organisms and autotrophic organisms (ammonia oxidisers and nitrite oxidisers) only. Any other biomass was assumed negligible.

For modelling purposes (and due to lack of any other information) the VSS fractionation into the three groups of organisms was determined through trial and error. It was found that the best results are obtained with 40 % off VSS allocated to heterotrophic organisms, 30 % to ammonia oxidisers and 30 % to nitrite oxidisers. In activated sludge systems generally the contribution of autotrophic nitrifying organisms to the sludge mass is considered negligible. However given the nature of the wastewater used for the study, with its high ammonia content, it can be expected that the AAO and ANO make up a significantly larger fraction of the sludge.

Biological decay results in inactive biomass which hydrolyses to become new substrate for active organisms. The fraction of the inactive biomass which is not biodegradable becomes endogenous residue which contributes to the ISS content of the sludge. The reason for incorporating an inactive fraction of biomass is to facilitate the hydrolysis in the model. It was envisaged that when organisms die off, it first has to be broken down (hydrolysed) before producing substrate or endogenous residue. Hydrolysis takes place at a certain rate which may be slower than the rate at which organisms dies off and therefore resulting in a fraction of the VSS that consists of inactive organisms.

7.4 KINETICS

7.4.1 Growth and Substrate Conversion

Growth of the various groups of organisms in the system was modelled using Equation 7.1:

$$\frac{dX}{dt} = \mu \times X \qquad (7.1)$$

Where:

$\frac{dX}{dt}$	rate of change in biomass concentration over (M/V/T)
μ	specific growth rate (1/T)
X	initial concentration of biomass (M/V)

The specific growth rate is derived from the maximum growth rate by incorporating a kinetic function which describe the effect of rate limiting environmental factors on the growth rate of the organisms. The kinetic functions can be of various forms depending on the environmental factors but Monod kinetics (Monod, 1949) are typically used as shown in the case of substrate as environmental factor:

$$\mu = \mu_{max} \times f(S) = \mu_{max} \times \frac{S_s}{S_s + k_S^H} \qquad (7.2)$$

Where:

μ	specific growth rate (1/T)
μ_{max}	maximum growth rate (1/T)
f(S)	substrate kinetic function
S_s	substrate concentration (M/V)
k_S^H	substrate saturation constant (M/M)

Substrate utilisation is modelled by using the growth equation in combination with a yield constant as shown in Equation 7.3:

$$\frac{dS}{dt} = \frac{dX}{dt} \times Y = \mu \times X \times Y \quad (7.3)$$

Where:

$\frac{dS}{dt}$	rate of change in substrate concentration over incremental period of time (M/V/T)
Y	yield coefficient (MX/MS)
X	initial concentration of biomass (M/V)

7.4.2 Decay

Decay of organisms in the system is modelled by using a simple first order kinetic function as shown in Equation 7.4 (Henze et al, :

$$\frac{dX}{dt} = -b \times X \quad (7.4)$$

Where:

$\frac{dX}{dt}$	rate of change in biomass concentration over incremental period of time (M/V)
b	decay constant (1/T)
X	initial concentration of biomass (M/V)

7.4.3 Hydrolysis

The hydrolysis of particulate matter (hydrolysable organic solids) into substrate is modelled using a similar function as for growth. This function is given in Equation 7.5:

$$\frac{dS}{dt} = k_{hX} \times \frac{\frac{X_S}{X_B}}{K_X + \frac{X_S}{X_B}} \times X_B \quad (7.5)$$

Where:

$\frac{dS}{dt}$	rate of change in substrate concentration over incremental period of time (M/V/T)
k_{hX}	maximum specific hydrolysis rate (M/M/T)
K_X	hydrolysis half saturation constant (M/M)
K_S	concentration of hydrolysable solids (M/V)
K_B	concentration of biomass (M/V)

In the model inactive biomass was considered to be hydrolysable solids (X_S) and X_B comprised only of active heterotrophic biomass.

7.5 Environmental Influences and Inhibitions

7.5.1 Heterotrophs

Anoxic and Aerobic Environments

The heterotrophic organism utilises organic carbon as substrate (electron donor). However the organisms utilise different terminal electron acceptors under aerobic and anoxic conditions namely oxygen and nitrate/nitrite respectively. The availability of these substances impact on the growth rate of the organisms and have to be incorporated into the model. The effect of oxygen concentrations under aerobic conditions was described by a kinetic term which was introduced to the growth equation:

$$f(S^H_{O_2}) = \frac{S_{O_2}}{S_{O_2} + k^H_{O_2}} \tag{7.6}$$

Where:

$f(S^H_{O_2})$ oxygen function describing the effect of oxygen concentration on growth of the heterotrophic organisms

S_{O_2} concentration of oxygen (M/V)

$k^H_{O_2}$ oxygen half saturation constant (M/V)

Under anoxic conditions the concentration of nitrite/nitrate may affect the growth of the organisms and this was incorporated into the model using a function of the same form (Monod) as for oxygen:

$$f(S^H_{NO_X}) = \frac{S_{NO_X}}{S_{NO_X} + k^H_{NO_X}} \tag{7.7}$$

Where:

$f(S^H_{NO_X})$ nitrite/nitrate function describing the effect of nitrite/nitrate concentration on growth of the heterotrophic organisms

S_{NO_X} concentration of nitrate/nitrite (M/V)

$k^H_{NO_X}$ nitrite/nitrate half saturation constant (M/V)

Temperature

Temperature can have an impact on the growth and decay rates of heterotrophic organisms. Since the experimental system underwent quite significant fluctuations in temperature it was necessary to incorporate temperature effects into the model. The effect of temperature on growth rate was incorporated by means of the following function:

$$f(T) = e^{K_H(T-20)} \quad (7.8)$$

Where:

f(T)	temperature function
K_H	temperature constant (1/T)
T	temperature

The function for the effect of temperature on decay is identical to that of growth. However, different temperature constants apply used under aerobic and anoxic conditions.

pH

Organisms have an optimal pH range for growth beyond which there is a decline in growth rate. Modelling the effect of varying pH on the growth rate of the heterotrophic organisms was done by means of the following pH function:

$$f(pH) = \frac{K_{pH}}{(K_{pH} + I)} \quad (7.10)$$

and

$$I = I^{|opt.pH-pH|}-1 \quad (7.11)$$

Where:

K_{pH}	temperature constant (1/T)

Inhibition

Certain substances in the system may be toxic to the heterotrophic organisms and therefore inhibit growth. High salinity of the system was identified as a possible inhibiting factor. The extent of inhibition in the experimental system could however not be determined or quantified.

It was clear that salinity did not fluctuate significantly in the experimental system and therefore it was speculated that if inhibition from high salinity did occur, it would be at a constant rate. Therefore an inhibition function, f(I), was incorporated into the model. This function merely consisted of a constant factor which could be changed as required to best suit the model. If no inhibition by salinity occurred this, factor could be set to 1.

7.5.2 Autotrophs

The effect of substrate-, ammonia/nitrite-, oxygen, temperature and variation thereof, on autotrophic organisms, were incorporated into the model by utilising the same functions as for the heterotrophic organisms. The constants in these functions were substituted with constants specific to ammonia- and nitrite oxidisers.

pH and inhibition

One of the major differences between the heterotrophic organisms and autotrophic organisms is the inhibition of the autotrophic organisms by its own substrates as well as the sensitivity to pH and salinity (as determined in batch experiments). Deterministic calculation of pH, as a result of biological and chemical processes, was beyond the scope of the current study. This type of calculation would not be best approached in a spreadsheet, but rather through a programming platform capable of solving multiple simultaneous equations.

The autotrophic organisms were responsible for nitrification and therefore also the changes in pH. As pH was continuously measured during the study there was an extensive collection of data available. Changes in pH and rates of change are related to nitrification rates and therefore the performance of nitrifying organisms (specifically ammonia oxidisers). It was decided to use the pH data and devise a function which could describe the effect of both pH and inhibitions on the organisms. From this data the rate of change in pH for different pH intervals was determined for a range of temperatures between 20°C and 30°C. The result is graphically illustrated in Figure 7.5.

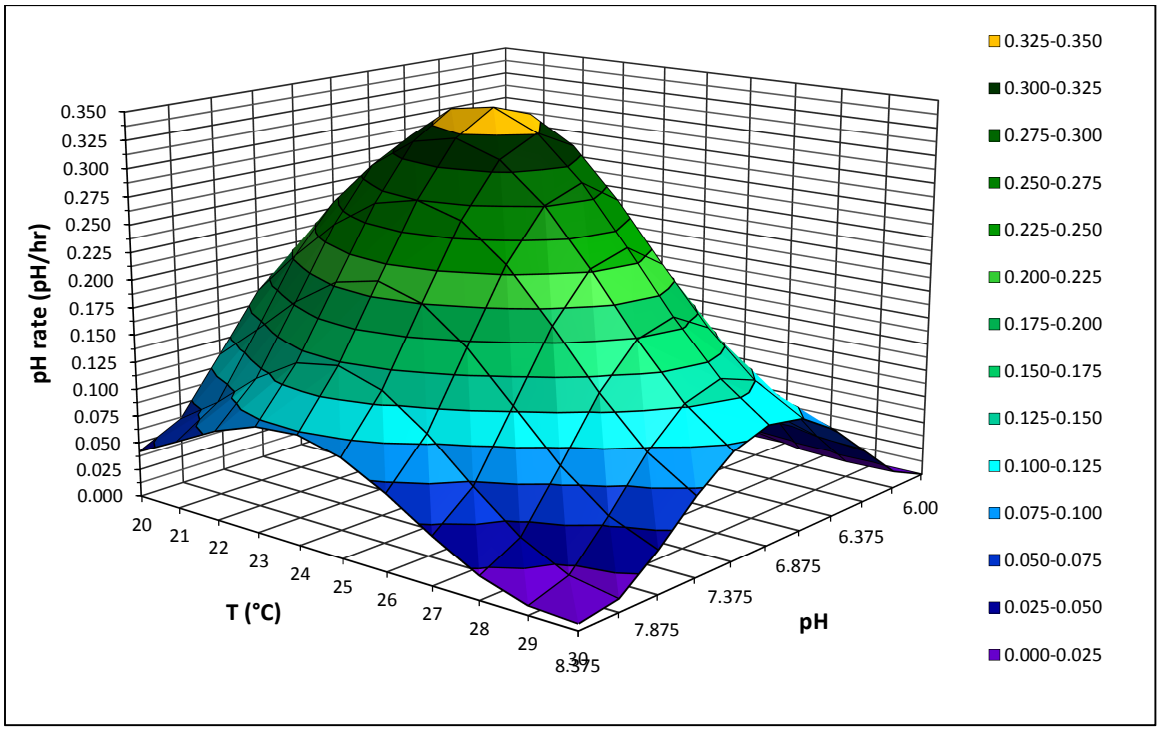


Figure 7.5: Rate of pH change relative to pH intervals and temperature

The function describing the rate of pH change for different temperatures is as follows:

$$pH_{rate} = A \times pH^4 + B \times pH^3 + C \times pH^2 + D \times pH + E \quad (7.11)$$

and

$$A = a_1 \times T^6 + a_2 \times T^5 + a_3 \times T^4 + a_4 \times T^3 + a_5 \times T^2 + a_6 \times T + a_7 \quad (7.12)$$

$$B = b_1 \times T^6 + b_2 \times T^5 + b_3 \times T^4 + b_4 \times T^3 + b_5 \times T^2 + b_6 \times T + b_7 \quad (7.13)$$

$$C = c_1 \times T^6 + c_2 \times T^5 + c_3 \times T^4 + c_4 \times T^3 + c_5 \times T^2 + c_6 \times T + c_7 \quad (7.14)$$

$$D = d_1 \times T^6 + d_2 \times T^5 + d_3 \times T^4 + d_4 \times T^3 + d_5 \times T^2 + d_6 \times T + d_7 \quad (7.15)$$

$$E = e_1 \times T^6 + e_2 \times T^5 + e_3 \times T^4 + e_4 \times T^3 + e_5 \times T^2 + e_6 \times T + e_7 \quad (7.16)$$

The constants for Equations 7.12 to 7.17 are given in Table 7.1.

Table 7.1: Constants for pH equation

a_1	-2.94E-06	b_1	8.75E-05	c_1	-9.70E-04	d_1	4.75E-03	e_1	-8.66E-03
a_2	4.91E-04	b_2	-1.46E-02	c_2	1.62E-01	d_2	-7.90E-01	e_2	1.44E+00
a_3	-3.38E-02	b_3	1.00E+00	c_3	-1.11E+01	d_3	5.42E+01	e_3	-9.86E+01
a_4	1.22E+00	b_4	-3.63E+01	c_4	4.01E+02	d_4	-1.96E+03	e_4	3.57E+03
a_5	-2.47E+01	b_5	7.31E+02	c_5	-8.08E+03	d_5	3.94E+04	e_5	-7.17E+04
a_6	2.63E+02	b_6	-7.77E+03	c_6	8.58E+04	d_6	-4.18E+05	e_6	7.61E+05
a_7	-1.15E+03	b_7	3.40E+04	c_7	-3.76E+05	d_7	1.83E+06	e_7	-3.33E+06

Once pH_{rate} is calculated it is normalised by dividing it by the maximum pH_{rate}, (0.344/hr) to give the pH factor that is finally incorporated into growth function.

7.6 Modelling Procedure

7.6.1 Method

The model was generated in a spreadsheet and implemented a time step integration method to calculate system changes for 10 minute intervals over a 24 hour period. The changes in the system over a time increment were incorporated into the system condition at the start of the interval to form the starting conditions for the following interval. This is graphically illustrated in Figure 7.6.

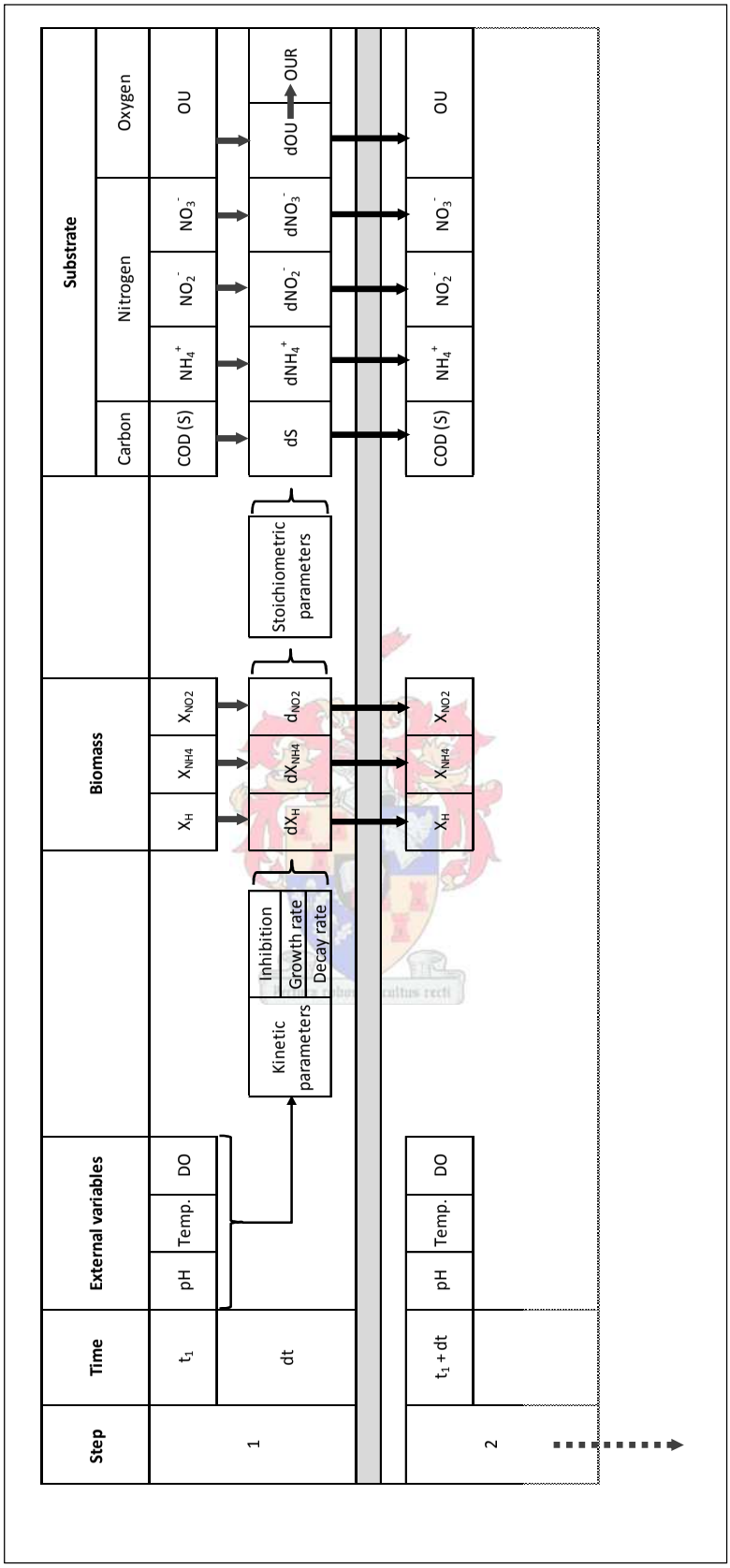


Figure 7.6: Time step integration method used in model.

The model consisted of an input section, a time step calculation section and an output section which graphically illustrated the output of the model in various plots.

7.6.2 Inputs

The system constraints have to be defined as part of the model. This includes time step intervals, cycle- and phase durations, system- and exchange volume as well as sludge retention time. The initial system conditions were required to define a starting point of the model. This was provided by defining the wastewater characteristics and sludge characteristics as part of the input. The kinetic and stoichiometric constants also formed part of the input.

7.6.3 Calibration

The model contains a significant number of input variables in terms of the kinetic and stoichiometric constants. Many of these variables were obtained from literature which typically did not give a single value but a range of values (Table 7.2). Therefore the model was calibrated by using experimental data on the system such as the measured sludge concentration and substrate concentration. The model variables were then calibrated until it best described the observed system.

The pH and oxygen levels were not modelled but the actual observed pH and oxygen levels were instead incorporated as part of the time step calculation. Therefore these time step parameters reflected the actual changes in the experimental system and served as a guide for calibration of the model.

Table 7.2: Kinetic and stoichiometric constants (at 20°C) from literature.

Parameter	Symbol	Definition	Unit	Value 1	Reference	Value 2	Reference	Value 2	Reference
Biomass	f_H	Endogenous residue fraction of heterotrophic biomass	-			0.2	[4]	0.2	[6], p. 48
	f_{IOHO}	ISS fraction of OHOs	-			0.15	[4]		
Growth	μ_H^{max}	Maximum specific growth rate of heterotrophic biomass	1/d	4.0-8.0	[1], p.75				
	$\mu_{H(NO3)}^{max}$	Maximum specific growth rate of heterotrophic biomass (anoxic)	1/d	3.0-6.0	[1], p.95	1.0 - 4.5	[5], p.114		
	μ_{NH4}^{max}	Maximum specific growth rate of ammonia oxidisers	1/d	0.6 -0.8	[1], p.85	0.33-0.65	[4]	0.76	[6], p.48
	μ_{NO2}^{max}	Maximum specific growth rate of nitrite oxidisers	1/d	0.6-1.0	[1], p.85				
	μ_A	Maximum specific growth rate for nitrification (ammoinia & nitrite oxidisers combined)	1/d	0.6-0.8	[1], p.86	varies	[5], p.90		
Decay	b_{H20}	Endogenous respiration rate of aerobic heterotrophic biomass (decay)	1/d	0.1-0.2	[1], p.75	0.24	[4]	0.2496	[6], p.48
	$b_{H(NO3)20}$	Endogenous respiration rate of anoxic heterotrophic biomass (decay)	1/d	0.05-0.1	[1], p.95	0.24	[4]	0.2496	[6], p. 122
	b_{NH4}	Endogenous respiration rate of ammonia oxidisers (decay)	1/d	0.03-0.06	[1], p.85				
	b_{NO2}	Endogenous respiration rate of nitrite oxidisers (decay)	1/d	0.03-0.06	[1], p.85				
	b_{A20}	Endogenous respiration rate of nitrifiers (ammonia and nitrite oxidisers combined)				0.04	[4]		
	η_H	Anoxic reduction factor for heterotrophic growth	-	0.8	[3]				
	η_{NH4}	Anoxic reduction factor for ammonia oxidisers decay	-	0.5	[2]				
	η_{N02}	Anoxic reduction factor for nitrite oxidisers decay	-	0.5	[2]				
Stiochiometry	f_{cvH}	COD/VSS ratio aerobic heterotrophs	mg COD/mg VSS			1.48	[4]	1.5	[6], p.48
	$f_{cvH(NO3)}$	COD/VSS ratio of anoxic heterotrophs	mg COD/mg VSS			1.48	[4]	1.5	[6], p. 122
	Y_H	Yield coefficient of aerobic heterotrophic biomass	mg COD(X)/mg COD	0.5 - 0.7	[1], p.75	0.67	[4]		
	$Y_{H(NO3)}$	Yield coefficient of anoxic heterotrophic biomass	mg COD/mg COD	0.4 - 0.6	[1], p.95	0.67	[4]		
	$Y_{H,NO3-N}$	Yield coefficient of anoxic heterotrophic biomass	mg COD/mg NO_3-N	1.6-1.8	[1], p.95				
	Y_{NH4}	Yield of ammonia oxidisers per NO2-N	mg COD/mg NO_2-N	0.24	[1], p.85				
	Y_{NO2}	Yield of nitrite oxidisers per NO3-N	mg COD/mg NO_3-N	0.24	[1], p.85				
	Y_{Hv}	Yield coefficient of aerobic heterotrophic biomass	mg VSS/mg COD			0.45	[4]	0.45	[6]
	$Y_{hv(NO3)}$	Yield coefficient of anoxic heterotrophic biomass	mg VSS/mg COD			0.45	[4]	0.45	[6]
	$Y_{NH4,V}$	Yield of ammonia oxidisers per NO3-N formed	mg VSS/mg NO_3-N	0.10-0.12	[1], p.85				
	$Y_{NO2,V}$	Yield of nitrite oxidisers per NO3-N formed	mg VSS/mg NO_3-N	0.05-0.07	[1], p.85				
	Y_A	Yield of autotrophic nitrifying organisms (ammonia and nitrite oxidisers)	mgVSS/gFSA			0.1	[5], p.90		
	$i_{N,BM}$	Nitrogen content of inert solids	mg N/mgCOD	0.086	[1], p.76				
	$i_{N,XI}$	Nitrogen content of biomass	mg N/mgCOD	0.06	[1], p.76				
Affinity constants	k^H_{O2}	Afinity constant for oxygen of heterotrophic biomass	mg O_2/L	0.5 - 1.0	[1], p.75				
	$k^H_{O2(NO3)}$	Afinity constant for oxygen inhibition of heterotrophic biomass under anoxic conditions	mg O_2/L	0.1 - 0.5	[1], p.95				
	k^{NH4}_{O2}	Affinity constant for oxygen of ammonia oxidisers	mg O_2/L	0.5-1.0	[1], p.85				
	k^{NO2}_{O2}	Affinity constant for oxygen of nitrite oxidisers	mg O_2/L	0.5-1.5	[1], p.85				
	k^A_{O2}	Affinity constant for oxygen of nitrifiers (ammoinia & nitrite oxidisers combined)	mg O_2/L	0.5-1.0	[1], p.85				
	k^H_{Ss}	Afinity constant for organic substrate of heterotrophic biomass	mg COD/L	5.0 - 30.0	[1], p.75				
	$k^{H(NO3)}_{Ss}$	Afinity constant for organic substrate of heterotrophic biomass	mg COD/L	10.0 - 20.0	[1], p.95				
	k^{NH4}_{NH4}	Affinity constant for ammonia of ammonia oxidisers	mg NH_4-N/L	0.3-0.7	[1], p.85			5.0	[2]
	k^{NO2}_{NO2}	Affinity constant for nitrite of nitrite oxidisers	mg NO_2-N/L	0.8-1.2	[1], p.85				
	k^A_{NH4}	Affinity constant for ammonia of nitrifiers (ammoinia & nitrite oxidisers combined)	mg NH_4-N/L	0.3-0.7	[1], p.85	1.0	[5], p.90	2.0	[2]
	k^H_{NO3}	Afinity constant for NO_3 of heterotrophic biomass	mg NO_3-N/L	0.2-0.5	[1], p.76				
pH	k_{pH}	pH constant for heterotrophs	-	150-250	[1], p.75				
Temperature	K_H	Temperature constant for heteterotrophs (aerobic)	1/°C	0.06-0.10	[1], p.75				
	K_{NH4}	Temperature constant for ammonia oxidisers	1/°C	0.08-0.12	[1], p.85				
	K_{NO2}	Temperature constant for nitrite oxidisers	1/°C	0.07-0.10	[1], p.86				
	K_A	Temperature constant for nitrifiers (ammoinia & nitrite oxidisers combined)	1/°C	0.07-0.11	[1], p.87				
	$K_{H(NO3)}$	Temperature constant for heteterotrophs (anoxic)	1/°C	0.06-0.12	[1], p.85				
	Θn	Temperature coeficient for growth and substrate afrinity of ANO's	-			1.123	[5], p.90	1.04	[6]
	Θb	Temperature coeficient for endogenous respiration of ANO's	-			1.029	[5], p.90	1.04	[6]

[1] Henze, M., Harremoës, P., la Cour Jansen, J., Arvin, E. (1997). Wastewater Treatment, 2nd ed., Springer-Verlag, Berlin, Germany.
[2] Moussa,M.S., Hooijmansa, C.M., Lubberdinga,H.J., Gijzena,H.J., van Loosdrecht, M.C.M. (2005). Modelling nitrification, heterotrophic growth and predation in activated sludge.
[3] Henze, M., Gujer, W., Mino, M., van Loosdrecht, M.C.M. (2000). Activated Sludge Models ASM1, ASM2, ASM2d and ASM3. IWA Publishing, London
[4] Marais, GvR., Ekama, G.A. (1976) The activated sludge process Part 1 - Steady state behaviour. *Water SA 2 (4) 163-200* .
[5] Henze, M., van Loosdrecht, M. C. M., Ekama, G. A., Brdjanovic, D. (2008). Biological Wastewater Treatment, IWA Publishing, London, UK.
[6] Van Haandel, A., Van der Lubbe, J. (2007). Handbook biological wastewater treatment: design and optimisation of activated sludge systems. Quist Publishing, Netherlands.

7.8 MODELLING RESULTS

Modelling the system proved to have various difficulties and the results have various imperfections. Some of the better results were obtained by modelling the system as observed on 21-06-2010. This instance will therefore be used to discuss the model results. The following kinetic and stoichiometric constants were used for this model run:

Table 7.3: Kinetic and stoichiometric parameters used for model run 21/06/2010

Parameter	Symbol	Unit	Value	Typical range as per literature
Sludge Fractionation				
VSS fraction as Ammonia oxidisers	$f_{X,ANH4}$	-	0.3	
VSS fraction as Nitrite oxidisers	$f_{X,ANO2}$	-	0.3	
VSS fraction as COD utilising Heterotrophs	$f_{X,HCOD}$	-	0.4	
Autotrophic ammonia oxidisers				
Max growth rate of ammonia oxidisers	μ_{NH4}^{max}	1/d	0.80	0.33 - 0.8
Decay rate of ammonia oxidisers	b_{NH4}^{max}	1/d	0.03	0.03 - 0.06
Affinity constant for ammonia of ammonia oxidisers	$k^{NH4}_{NH4,20}$	mg NH_4-N/L	0.70	0.3 - 0.7
Affinity constant for oxygen of ammonia oxidisers	k^{NH4}_{O2}	mg O/L	1.00	0.5 - 1.0
Temperature constant for ammonia oxidisers in growth (μ)	$K_{NH4,\mu}$	1/°C	0.12	0.08 - 0.12
Temperature constant for ammonia oxidisers in endogenous respiration (b)	$K_{NH4,b}$	1/°C	0.12	0.08 - 0.12
Yield of ammonia oxidisers per NO3-N formed	$Y_{NH4,V}$	mg VSS/mg FSA-N	0.12	0.10 - 0.12
Yield of ammonia oxidisers per NO2-N	Y_{NH4}	mg COD/mg FSA-N	0.24	0.24
COD/VSS Ratio	f_{CV}	mgCOD/mgVSS	2.000	
Model Inhibition/calibration factor	I		0.1	
Autotrophic nitrite oxidisers				
Max growth rate of nitrite oxidisers	μ_{NO2}^{max}	1/d	0.60	0.6 - 0.1
Decay rate of nitrite oxidisers	b_{NO2}^{max}	1/d	0.06	0.03 - 0.06
Affinity constant for nitrite of nitrite oxidisers	k^{NO2}_{NO2}	mg NO_2-N/L	1.20	0.8 - 1.2
Affinity constant for oxygen of nitrite oxidisers	k^{NO2}_{O2}	mg O/L	1.50	0.5 - 1.5
Temperature constant for nitrite oxidisers in growth (μ)	$K_{NO2,\mu}$	1/°C	0.10	0.07 - 0.10
Temperature constant for decay of nitrite oxidisers in endogenous respiration(b)	$K_{NO2,b}$	1/°C	0.10	0.07 - 0.10
Yield of nitrite oxidisers per NO3-N formed	$Y_{NO2,V}$	mg VSS/mg NO_2-N	0.07	0.05 - 0.07
Yield of nitrite oxidisers per NO3-N	Y_{NO2}	mg COD/mg NO_2-N	0.24	0.24
COD/VSS Ratio	f_{CV}	mgCOD/mgVSS	3.429	
Model Inhibition/calibration factor	I		0.1	
Heterotrophs				
Optimum pH	pH_{opt}		8.00	
pH constant	K_{pH}		200.00	150 - 250
COD/VSS ratio of biomass	f_{CV}	mgCOD/mgVSS	1.48	1.48 - 1.5
Endogenous residue fraction of biomass	f_H	-	0.2	0.2
Model Inhibition/calibration factor	I		0.075	
Aerobic				
Max growth rate	μ_H^{max}	1/d	6.00	4.0 - 8.0
Aerobic decay rate of heterotrophs	b_H^{max}	1/d	0.24	0.1 - 0.24
Affinity constant for organic substrate	$k^S_{H,20}$	mg COD/L	20.00	5.0 - 30.0
Affinity constant for oxygen	k^N_{O2}	1/°C	1.00	0.5 - 1.0
Temperature constant for growth (μ)	$K_{H,\mu}$	1/°C	0.10	0.06 - 0.10
Temperature constant for decay (b)	$K_{H,b}$	1/°C	0.10	0.06 - 0.10
Yield (VSS) of heterotrophs	$Y_{H,V}$	mg VSS/mg COD	0.45	0.45
Yield (COD) of heterotrophs	Y_H	mg COD(X)/mg COD	0.67	0.67
Anoxic				
Max growth rate	$\mu_{H(NO3)}^{max}$	1/d	0.70	0.5 - 0.7
Anoxic decay rate of heterotrophs	$b_{H(NO3)}^{max}$	1/d	0.10	0.01 - 0.2496
Affinity constant for organic substrate	$k^{H(NO3)}_{S,20}$	mg COD/L	20.00	0.05 - 0.24
Affinity constant for oxygen (oxygen as inhibitor)	$k^{H(NO3)}_{O2}$	mg O2/L	0.50	10.0 - 20.0
Affinity constant for Nitrate(/Nitrite)	$k^{H(NO3)}_{NO3}$	mg NO3-N/L	0.50	0.1 - 0.5
Temperature constant for growth (μ)	$K_{H(NO3),\mu}$	1/°C	0.12	0.2 - 0.5
Temperature constant for decay (b)	$K_{H(NO3),b}$	1/°C	0.12	0.06 - 0.12
Yield (VSS) of heterotrophs	$Y_{HV(NO3)}$	mg VSS/mg COD(S)	0.45	0.45
Yield (COD) of heterotrophs	$Y_{H(NO3)}$	mg COD(XB)/mg COD(S)	0.67	0.4 - 0.7
Yield (COD) of heterotrophs	$Y_{H(NO3),NO3}$	mg COD(XB)/mg NO_3-N	1.80	1.6 - 1.8
Hydrolysis - Aerobic				
Hydrolysis constant , dissolved solids	k_h	1/d	12.00	3 - 20
Hydrolysis constant , suspended solids	k_h	1/d	1.00	0.6 - 1.4
Hydrolysis constant	k_{hX}	mgCOD(X)/(mgCOD(XB)•d)	1.00	0.6 - 1.4
Hydrolysis saturation constant	K_X	mgCOD(X)/(mgCOD(XB)	0.035	0.02 - 0.05
Hydrolysis - Anoxic				
Hydrolysis constant , dissolved solids	k_h	1/d	7.50	1 - 15
Hydrolysis constant , suspended solids	k_h	1/d	0.28	0.15 - 0.4
Hydrolysis constant	k_{hX}	mgCOD(X)/(mgCOD(XB)•d)	0.28	0.15 - 0.5
Hydrolysis saturation constant	K_X	mgCOD(X)/(mgCOD(XB)	0.035	0.02 - 0.05

7.8.1 Substrate

One of the main modelling difficulties was to match the modelled changes in substrates (COD, FSA-N, Nitrite-N, Nitrate-N) to measured values. Figure 7.7 illustrates the modelled substrate values relative to the measured values for substrate.

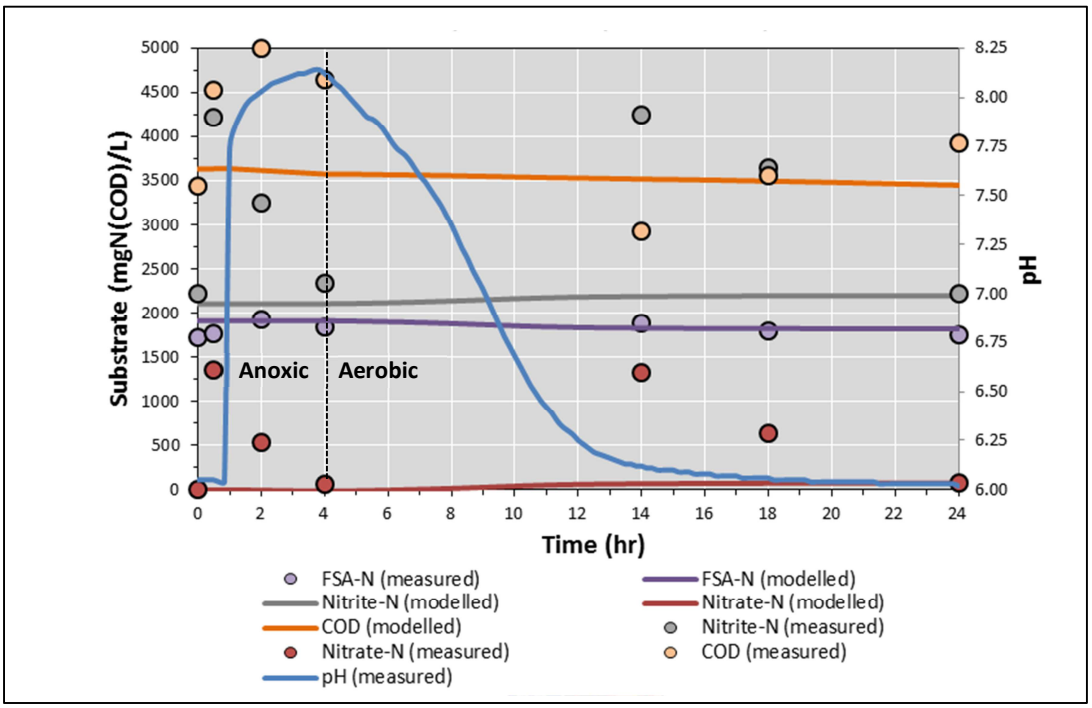


Figure 7.7: Modelled results compared to measured results for FSA-N, nitrite-N, nitrate-N and COD

The measured and modelled FSA-N values correlate well. However the values for nitrite-N and nitrate-N are not easily correlated due to the high degree of variance in the measured values. The same problem is relevant to measured COD values. This problem is ascribed to the problems experienced with the analytical methods.

The modelled changes in nitrite-N and Nitrate-N during the anoxic phase are insignificant which possibly indicate a shortcoming of the model. There is however a notable decrease of modelled COD concentration which reflect the utilisation of organic carbon substrates during denitrification.

During the aerobic phase, changes in substrate concentrations are replicated well. Figure 7.8 shows the pH factor calculated from the measured pH using the derived pH equation. The rates

of change in FSA-N, Nitrite-N and Nitrate-N correlate to the pH profile as the greatest change in the nitrogen substrates occur during the more optimal pH range. The changes in modelled substrate concentrations are however small relative to the background concentrations, as experienced in the experimental study. The model therefore reflects experimental observations.

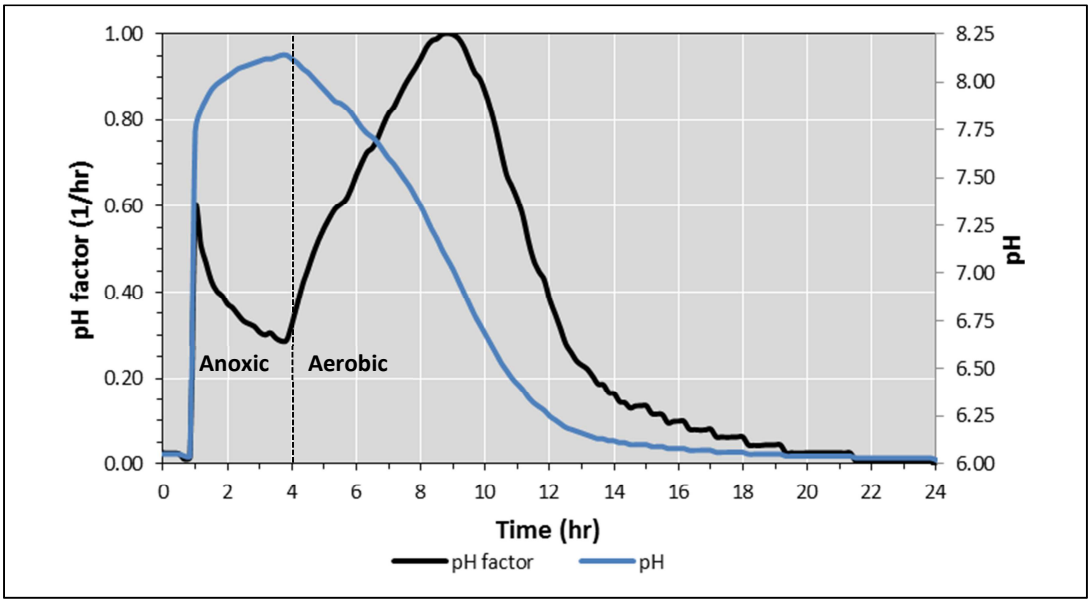


Figure 7.8: Calculated pH factor relative to measured pH.

7.8.2 Biomass

The modelled biomass groups, its various substrates and products are displayed in Figures 7.9, 7.10 and 7.11. The initial biomass concentrations are based on measured values and divided into the various organism groups for modelling purposes. The fractionation of biomass for the model as determined from trial and error is 40% heterotrophic biomass, 30% AAO biomass and 30% ANO biomass.

The changes in modelled AAO biomass results (Figure 7.9) show a decline in the active biomass during the anoxic phase as no nitrification can take place. This results in the decay of this group of organisms during the anoxic phase. The change in this biomass is very small as the autotrophic organisms' rate of decay is slow. During the aerobic phase however the change in AAO biomass reflects the changes in FSA-N initially. There is an increase in active biomass as growth occurs resulting in a decrease of FSA-N. The greatest growth occurs during the time

period of optimal pH. As the cycle nears its end the biomass stops increasing as biomass decay starts exceeding growth due to suboptimal pH. During this period the change in FSA-N concentration is very little to none.

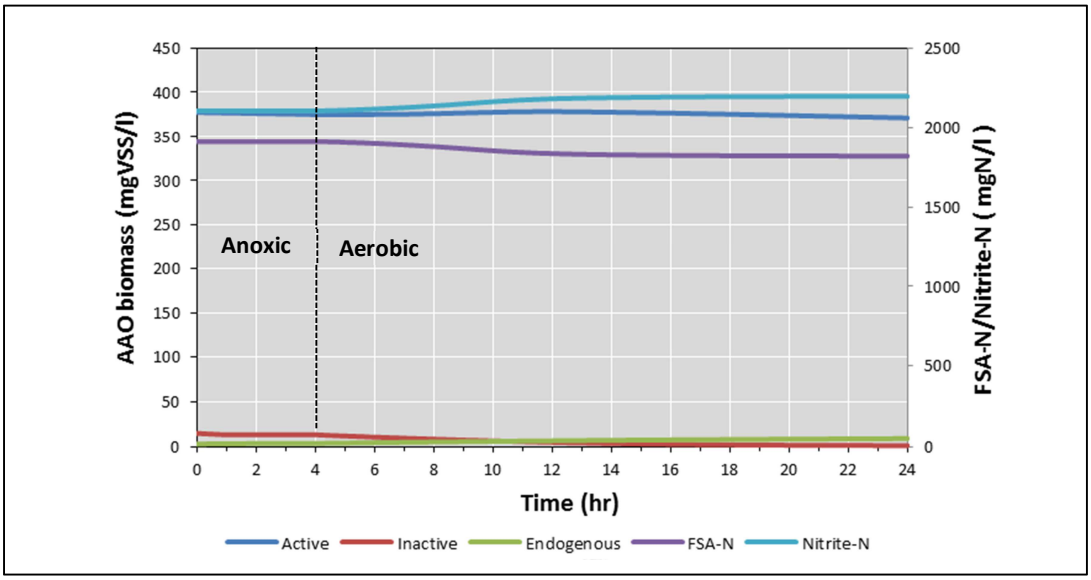


Figure 7.9: Modelled ammonia oxidising biomass, FSA-N and Nitrite-N.

The modelled ANO biomass (Figure 7.10) follows a similar trend to that of the AAOs. During the Anoxic phase there is a decrease biomass concentration followed by a growth period during the aerobic phase. The main difference however is that ANO substrate (nitrite-N) does not decrease but increases as the organisms cannot utilise the substance as quickly as it is produced due to inhibition.

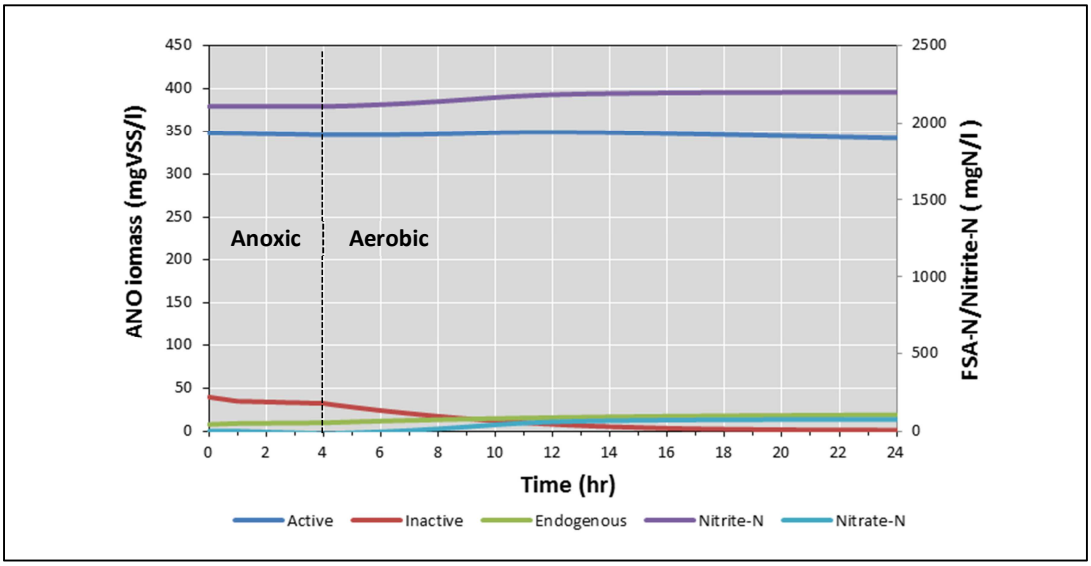


Figure 7.10: Modelled nitrite oxidising biomass, nitrite-N and nitrate-N concentrations.

The modelled heterotrophic biomass (Figure 7.11) shows growth throughout the anoxic and aerobic phase of the cycle. From the model it appears if the growth of this group of organisms, and subsequent decrease of substrate, occurs at a greater rate during the anoxic phase

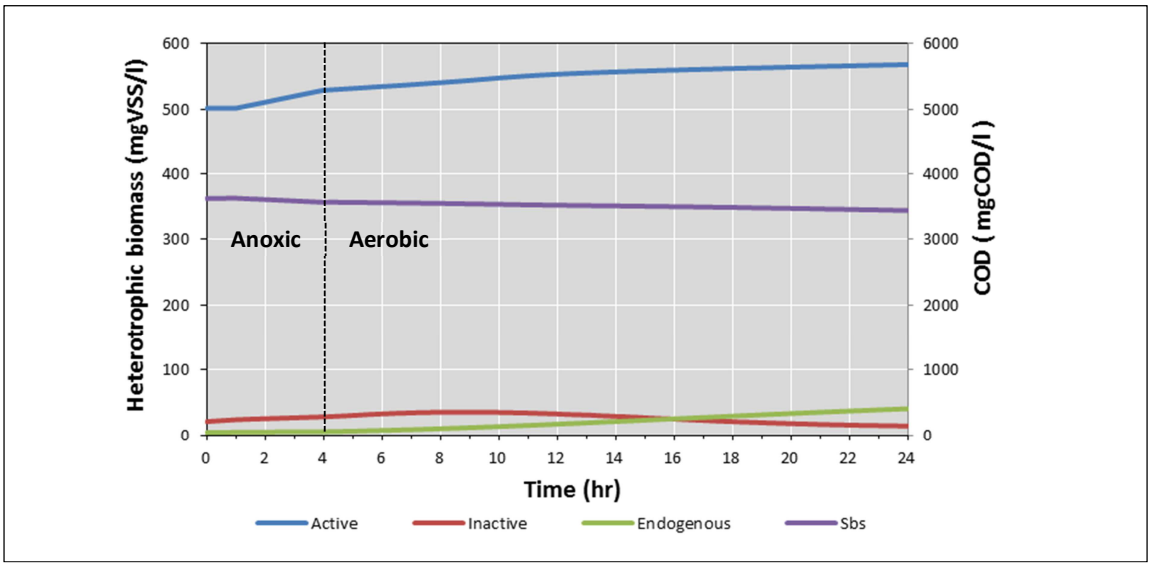


Figure 7.11: Modelled heterotrophic biomass and biodegradable soluble COD.

7.8.3 Oxygen utilisation rate (OUR)

The modelled and measured OUR results for 21-06-2010 are shown in Figure 7.12. Based on the modelled OUR, the majority of the oxygen in the system is consumed by the autotrophic nitrifying organisms. The oxygen consumption by the heterotrophs is small. This suggests that the activity of the heterotrophic organism is very low which might imply that they are also severely inhibited and perhaps even more so than the nitrifying organisms.

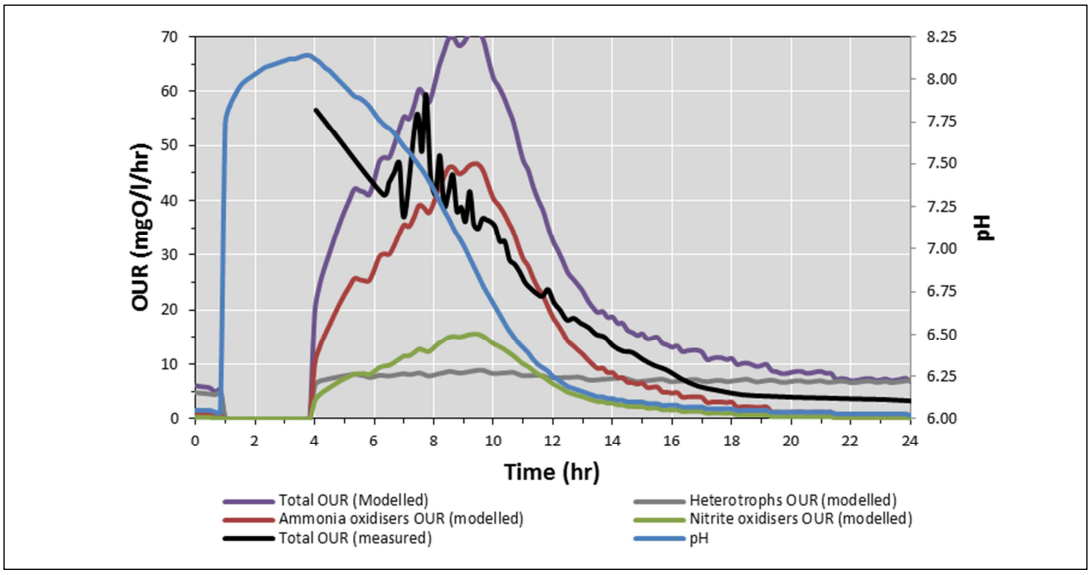


Figure 7.12: Modelled and measured OUR for 21-06-2010.

The peak modelled OUR has a offset from the peak measured OUR. The majority of oxygen is utilised by AAO and the peak activity of these organisms is dictated by pH. This implies that the derived pH function is marginally inaccurate at predicting the optimal pH range resulting in the OUR offset.

7.9 Model Limitations

The functionality of the model and results are limited to substrate utilisation and organism growth calculations. The overall results from the model compared to actual measured results show that there are various discrepancies which indicate that the model has some imperfections. More work will be required to improve the model. Such work should include estimating the true sludge fractions of the various groups of organisms. The inhibitions effects of the system environment on the organisms should also be better quantified.

Chapter 8

Conclusions and Recommendations

8.1 CONCLUSIONS

8.1.1 Experimental Unit

Operation of the sequencing batch reactor was a relatively simple process and could easily be automated in future. It is simple to alter the anoxic and aerobic processes by changing the duration of cycles and so manipulate the anoxic and aerobic mass fractions. The duration of cycles can also be adjusted to either increase or decrease the end of cycle pH levels and so control the pH range in which the process operates. Furthermore, sludge age and hydraulic retention time can also be separated, if required by introducing separate decanting and sludge wasting phases. This makes it possible to operate the system at higher or lower sludge ages independent of the exchange volume. Adjustments to the processes could therefore be achieved without changing the physical configuration of the setup, thus showing how versatile a batch reactor can be. Another advantage of the batch reactor is the simplicity of the setup which makes fault finding and maintenance simpler.

8.1.2 Online Monitoring

Continuous monitoring of the system by means of pH and ORP provided valuable information on the system performance. Progress of nitrification and denitrification processes can be evaluated instantaneously by measuring the pH and ORP. Therefore pH and ORP monitoring is very useful in the physical control of the system and can be used as a tool for automation.

8.1.3 pH Control

Control of pH by influent urine limited exchange volumes per cycle to 5% of the system volume. This was due to the high pH of urine which would increase the pH of the system beyond 8 at the start of a new cycle. If too much urine was added to the system the pH would increase to a level beyond the capable range for nitrification and the process would cease completely. Furthermore the pH at the start of a cycle (and therefore the exchange volume) had to be limited to a certain point to allow a pH buffer as a further pH increase would occur during denitrification over the anoxic phase.

The duration of anoxic phases had to be limited to 17% (4 hours) of the cycle duration (24 hours) to prevent overly high pH at the start of aerobic phases and ensure sufficient time for nitrification. Nitrification had to reduce pH sufficiently to allow for the pH increase after volume exchanges. If pH was not sufficiently low, the volume exchange and denitrification would increase the pH beyond the capable range for nitrification. Therefore there has to be a balance between exchange volumes and the duration of the aerobic phase.

8.1.4 Treatment Efficiency and Effluent Quality

Based on the chemical analyses of urine and the effluent it was determined that on average the system is capable of converting 66% of FSA-N to nitrate-N/nitrite-N. Of the 66% converted to nitrate-N/nitrite-N a further approximately 44% was converted to nitrogen gas. The system was therefore capable of achieving approximately 30% nitrogen removal. The system was also capable of achieving on average 48% COD removal.

Effluent from the system still however contains relatively high levels of ammonia and COD and is by no means sufficiently treated. The effluent does however have a unique characteristic in that the FSA-N: Nitrite-N ratio is approximately 1:1 thereby making it ideal for further treatment in an Anammox system.

Based on the treatment efficiency and the effluent quality it is concluded that a sequence batch reactor on its own may not be the best treatment option for undiluted urine. It can however serve as a pre-treatment unit for alternative systems.

8.1.5 Nitrification

It was confirmed that the optimal pH for nitrification in the system is between 7 and 8 which corresponds to literature. Nitrification could still occur at pH greater than 8 and lower than 7 but the rate decreased dramatically the further pH veered for the optimal range. When pH increased beyond 9 or decreased below 6, nitrification appeared to stop completely.

Full nitrification in the system was not achieved and conversions by nitrifying organisms were severely limited. This is mainly attributed to the inhibition of nitrifying organisms by:

- High substrate concentration
- High salinity
- Temperature fluctuation
- Sub-optimal pH ranges

It was determined from batch experiments that both ammonia oxidisers and nitrite oxidisers are inhibited but that nitrite oxidisers are generally affected worse by the conditions in the system. It is believed that in addition to its own substrate, nitrite oxidisers are also inhibited by the substrate of ammonia oxidisers.

8.1.6 Denitrification

Denitrification was likely hindered by the relative short anoxic phases. In addition to this, denitrifying organisms were exposed to pH levels that are beyond the typical optimal range of the organisms. It is also not clear exactly what the effect of the high ammonia- and salinity levels were on the organisms but is may be possible that these substances also affected the organisms adversely.

8.1.7 Modelling

The model still has various imperfections that will require further work.

These imperfections include the kinetic constants for the model which were selected from literature. Literature generally gives ranges of values for a given kinetic constant as typically observed in conventional activated sludge systems. Therefore these kinetic constants may not be best suited for this model and only serve as a starting point. It is also believed that the inhibition of the organism is not quantified and more research will have to be conducted on this area.

8.1.7 Design parameters

The design parameters for treating undiluted urine in a SBR based on this study is summarised in Table 8.1.

Table 8.1: Design parameters for a SBR treating source separated urine

Parameter	Unit	Value
Minimum sludge age	d	20
Minimum temperature	°C	20
Maximum ammonia loading rate	mgN/l	250
Maximum anoxic mass fraction	-	.167
pH upper limit	-	8.25
pH lower limit	-	6.5

8.2 RECOMMENDATIONS

8.2.1 Smaller volume exchanges and shorter cycles

Decreasing the volume exchanges will prevent the extreme pH changes which will ensure that nitrifying organisms can function within more optimal pH ranges. This may improve the overall efficiency of nitrification which will shorten the aerobic phases providing more time for the anoxic phases. Furthermore the number of cycled per 24hour period can also be decreased if nitrification is enhanced and thus compensate for the lower volume exchanges.

8.2.2 Alkalinity addition

The addition of alkalinity to the system during the aerobic phase to prevent the pH from declining to 7 will ensure that longer periods of the aerobic phase are within the optimal range. This would likely improve the overall performance of nitrification.

8.2.3 Sludge Concentration

The mass of sludge in the reactor was relatively low in comparison to conventional activated sludge systems which may be a contributing factor to the poor performance of the system. It is therefore proposed that sludge mass is increased to ensure that higher concentrations of especially nitrifying organism are maintained. This can be achieved by increasing the sludge age so as to facilitate less sludge wasting and allow the increase in population of slow growing nitrifying organisms. Alternatively the system can be changed from a suspended sludge system to an attached growth system by incorporating growth media for organisms to attach. This will prevent active organisms from washing out of the system during volume exchanges.

References

Akın, B. S., Ugurlu, A. (2005). Monitoring and control of biological nutrient removal in a sequencing batch reactor. *Process Biochemistry*, 40, 2873–2878.

Al-Rekabi, W. S., Qiang, H., Qiang, W. W. (2007). Review on Sequencing Batch Reactors. *Pakistan Journal of Nutrition*, 6 (1), 11-19.

Artan, N., Wilderer, P., Orhon, D., Morgenroth, E., Özgür, N. (2001). The mechanism and design of sequencing batch reactor systems for nutrient removal - the state of the art. *Water Science & Technology,* 43(3), 53–60.

Anthonisen, A. C., Loehr R. C., Prakasam, R. B. S., Srinath, E. G. (1976). Inhibition of nitrification by ammonia and nitrous acid. *Water Pollution Control Federation*, 48(5), 835-852.

Anderson, C. (2009). Investigating the chemical composition of urine and urea hydrolysis of stored urine (Presentation). Urine separation workshop, CSIR, Stellenbosh, South Africa.

American Public Health Association (2005). Standard Methods for the Examination of Water and Wastewater, 21st ed.

Ashton, P.C., Chutter, F. M., Cochrane, K. L., de Moor, F. C., Hely-Hutchinson, J. R., Jarvis, A. C., Robarts, A. D., Scott, W. E., Thornton, J. A., Twinch, A. J., Zohary , T. (1985). The Limnology of Hartbeespoort Dam. South African National Scientific Programmes Unit: CSIR, SANSP Report 110.

Bitton, G. (2005). Wastewater Microbiology, 3rd ed., John Wiley and Sons Inc., Hoboken, New Jersey, USA.

Canter, L. W., Knox, R. C. and Fairchild, D. M. (1988). Groundwater Quality Protection. Chelsea, MI: Lewis Publishers.

Carrera, J., Baeza, J. A., Vicint, J., Lafuente, J. (2003). Biological nitrogen removal of high-strength ammonium industrial wastewater with two-sludge system.*Water Research*, 37, 4211 – 4221.

Ciba Geigy. (1977). WissenschaftlicheTabellenGeigy, TeilbandKorperflussigkeiten, 8 ed., Basel.

Cordell, D., Drangert, J., White, S. (2008). The story of phosphorus: Global food security and food for thought. Global Environmental Change, 19, 292-305.

Davis, L. M., Masten, S. J. (2004). Principles of Environmental Engineering and Science. McGraw-Hill Inc., New York, USA.

Department of Water Affairs and Forestry (DWAF).Water Quality Management Programme. http://www.dwaf.gov.za/iwqs/eutrophication/NEMP/TrofieseStatus2003.pdf (Accessed 24 July 2014).

Ekama, G., Marais, G., (1984). Theory, design and operation of nutrient removal activated sludge processes.*WRC*, Report TT 16/84.

EPA - United States Environmental Protection Agency. (1999). Wastewater Technology Fact Sheet Sequencing Batch Reactors. EPA, 832-F-99-073.

Feng, D., Wu, Z., Xu, S. (2007). Nitrification of human urine for its stabilisation and nutrient recycling. *Bioresource Technology*, 99, 6299-6304.

Fux, C., Boehlr, M., Huber, P., Brunner., I. Siegrist, H. (2002). Biological treatment of ammonia-rich wastewater by partial nitritation and subsequent ammonium oxidation (anammox) in a pilot plant.*Journal of Biotechnology*, 99, 295-306.

Gali, A., Dosta, J., López-Palau, S., Mata-Alvarez, (2008). SBR technology for high ammonium loading rates.*Water Science and Technolgy*, 58.2, 467-472

Galloway, J.N., Cowling, E. B. (2002). Reactive nitrogen and the world: 200 years of change. *Ambio*, 31(2), 64-71.

Henze, M., Harremoës, P., la Cour Jansen, J., Arvin, E. (1997). Wastewater Treatment, 2nd ed., Springer-Verlag, Berlin, Germany.

Henze, M., van Loosdrecht, M. C. M., Ekama, G. A., Brdjanovic, D. (2008). Biological Wastewater Treatment, IWA Publishing, London, UK.

Irvine, R. L., Davis, W. B. (1971). Use of sequencing batch reactor for wastewater treatment. CPC International, Corpus Christi, TX. Presented at the 26th Annual Industrial Waste Conference, Purdue, University, West Lafayette, IN.

Kargi, F., Uygur, A. (2002). Nutrient removal performance of a sequencing batch reactor as a function of the sludge age. *Enzyme and Microbial Technology,* 31, 842–847.

Kirchmann, H., Pettersson, S. (1995). Human urine - Chemical composition and fertilizer use efficiency. *Fertilizer Research*, 40, 149-154.

Knowles, R. (1982). Denitrification.*Microbial Reviews*, 46(1), 43-70.

Kvarnström, E., Emilsson, K., Richert Stintzing, A., Johansson, M., Jönsson, H., af Petersens, E., Schönning, C., Christensen, J., Hellström, D., Qvarnström, L., Ridderstolpe, P., Drangert, J. (2006). Urine Diversion: One Step Towards Sustainable Sanitation. *EcoSanRes Publication Series*, 2006-1.

Larsen, T.A., Gujer, W. (1996). Separate management of anthropogenic nutrient solutions (human urine). *Water Science and Technology*, 34(3-4), 87-94.

Lee, G. Fred, Jones, A. R. (1991). Landfills and Groundwater Quality. *Groundwater,* 29, 482–486.

Larsen, T. A., Peters, I., Alder, A., Eggen, R., Maurer, M., Muncke, J. (2001).Re-engineering the toilet for sustainable wastewater management.*Environmental Science and Technology*, 35(9), 193A-197A.

Lower, S.K. Redox equilibria in natural waters.Reference text, Simon Fraser University.

Marais, G., Ekama, G.A. (1976) The activated sludge process Part 1 - Steady state behaviour. *Water SA,* 2(4), 163-200.

Maurer, M., Schwegler, P., Larsen, T.A. (2003). Nutrients in urine: energetic aspects of removal and recovery. *Water Science and Technology*, 48(1), 37-46.

Maurer, M., Pronk, W., Larsen, T.A. (2006). Treatment processes for source separated urine. *Water Research*, 40, 3151-3166.

McGinley, P. M., Kmet. P. (1984). Formation, Characteristics, Treatment and Disposal of Leachate from Municipal Solid Waste Landfills. Wisconsin Department of Natural Resources Special Report.

Midgley, D.C., W.V. Pitman , B.J. Middleton (1994)**.** Surface Water Resources of South Africa 1990*. Water Research Commission,* Report No: 298/1/94.

Monod, J. (1949). The growth of bacterial cultures. *Annual Review of Microbiology*, 3, 371-394.

Moussa,M.S., Hooijmansa, C.M., Lubberdinga,H.J., Gijzena,H.J., van Loosdrecht, M.C.M. (2005). Modelling nitrification, heterotrophic growth and predation in activated sludge. WaterResearch, 39 (2005), 5080–5098.

North West Provincial Government. (2005). Dam Remediation: Hartebeespoort Dam, North West Environmental Management Series 5.

Rostron, W. M., Stuckey, D. C., Young, A. A. (2001). Nitrification of high strength ammonia wastewaters: comparative study of immobilisation media. *Water Research*, 35(5), 1169-1178.

Ruiz, A., Jeison, D., Chamy, R. (2003). Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration.*Water Research*, 37, 1371-1377.

SAICE. (2006). The SAICE Infrastructure Report Card for South Africa. South African Institute of Civil Engineering, Midrand, South Africa.

Swedish Environmental Council (2007). Sweden's environmental objectives. Swedish Government)

Udert, K. M., Fux, C., Munster, M., Larsen, T.A., Siegrist, H., Gujer, W. (2003a). Nitrification an autotrophic denitrification of source separated urine. *Water Science and Technology*, 48(1), 119-130.

Udert, K. M., Larsen, T.A., Biebow, M., Gujer, W. (2003b).Urea Hydrolysis and precipitation dynamics in a urine collecting system.*Water Research*, 37, 2571-2582.

Udert, K. M., Larsen, T.A., Gujer, W. (2003c). Estimating the precipitation potential in urine collecting systems. *Water Research*, 37, 2667-2677.

Udert, K.M., Larsen T.A., Gujer, W. (2003d). Biologically induced precipitation in urine-collecting systems.*Water Science and Technolgy*, 3(3), 71-78.

Udert, K. M., Larsen, T.A., Gujer, W. (2006). Fate of major compounds in source separated urine. W*aterScience& Technology, 54(11/12)*, 413-420.

Van Dongen, U., Jetten, M.S.M., Van Loosdrecht, M.C.M. (2001). The SHARON®-Anammox® process for treatment of ammonium rich wastewater. *Water Science and Technology*, 44(1), 153-160.

Van Haandel, A., Van der Lubbe, J. (2007). Handbook of biological wastewater treatment: design and optimisation of activated sludge systems. Quist Publishing, Netherlands.

Werner, C. (2006). Ecosan project at the GTZ Headquarters, main office building, Germany – Presentation. 4th World Water Forum, Mexico City, March 16-22. http://www.worldwaterforum4.org.mx/sessions/FT3_24/Ecosan%20project%20at%20the%20GGT%20headquarters.pdf (Accessed 25 July 2014).

Wastewater Operator Certification Training, Module 1: Introduction to Wastewater Treatment. Pennsylvania Department of Environmental Protection. https://www.portal.state.pa.us/portal/server.pt/document/1411019/ww01_intro_to_ww_treatment_wb_pdf./ww01_intro_to_ww_treatment_wb_pdf. (Acessed 03 November 2014).

Winblad, U., Simpon-Herbert, M. (2004). Ecological Sanitation, 2nd Ed., Stockholm Environmental Institute, Stockholm, Sweden.

Wilsenach, J.A. (2006). Treatment of source separated urine and its effects on wastewater systems. PhD Thesis.

Stockholm International Water Institute. (2004). Securing Sanitation – A Compelling Case to Address the Crisis. Report commissioned by the Government of Norway as input to the Commission on Sustainable Development and its 2004-2005 focus on water, sanitation and related issues.

Suresh, S., Tripathi, R. K., Gernal Rana, M. N. (2011). Review on treatment of industrial wastewater using sequential batch reactor. *International Journal of Science Technology & Management*, 2(1), 64-84.

APPENDIX A

pH, ROP, Temperature and OUR Profiles for Chemically Analysed 24 Hour Sample Sets

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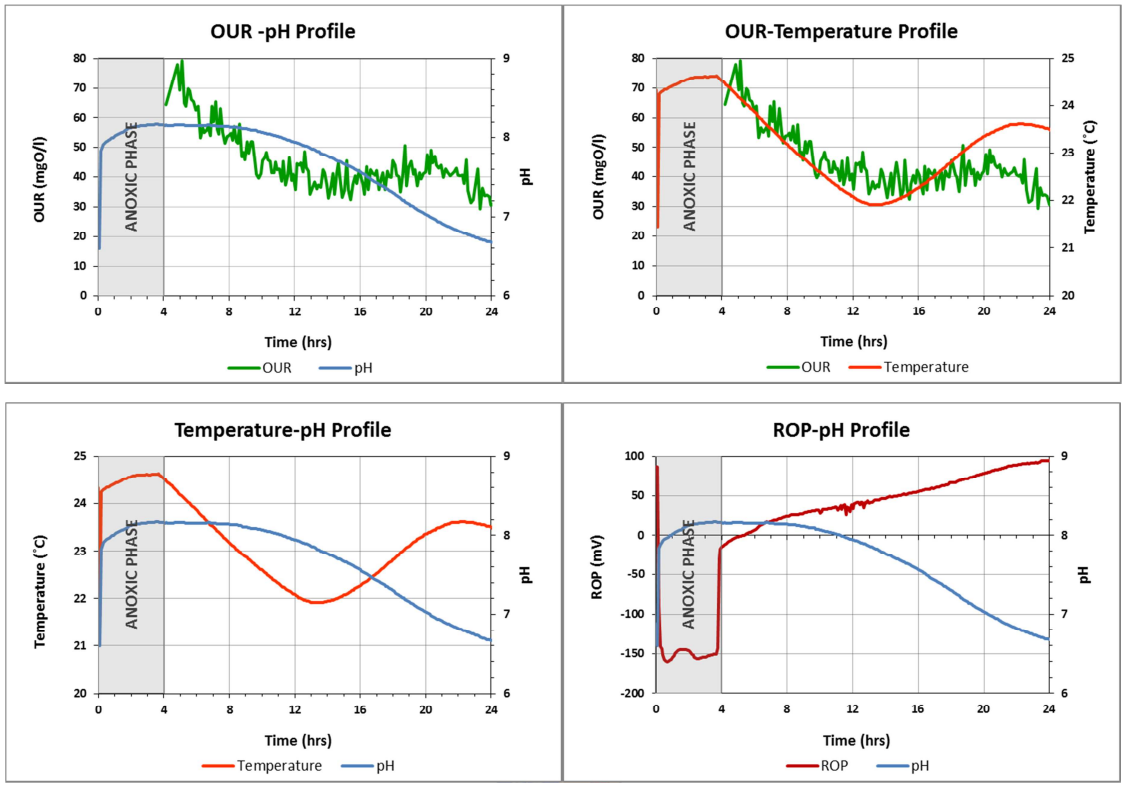

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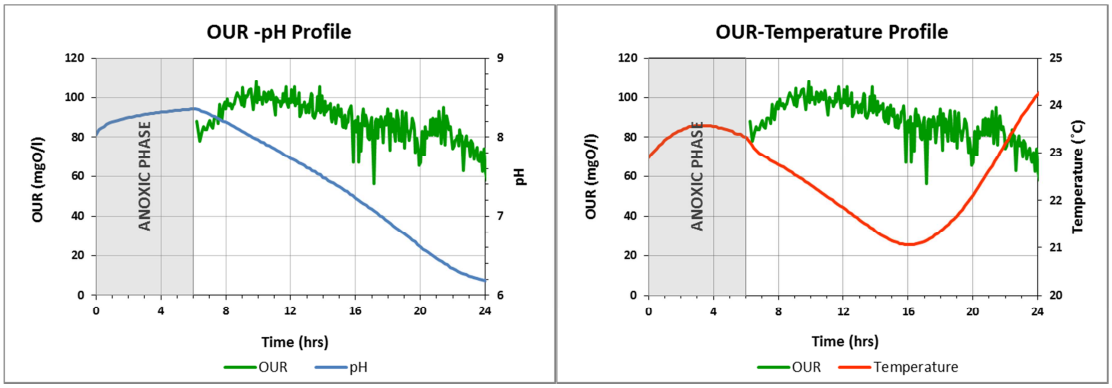

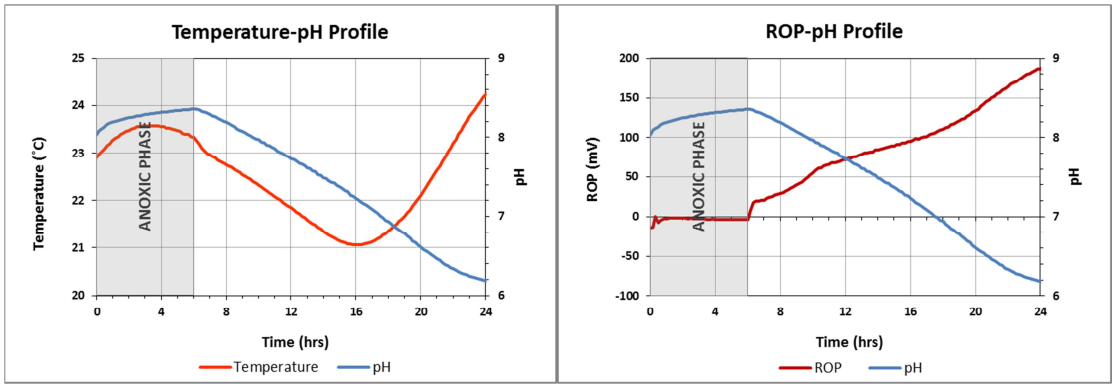

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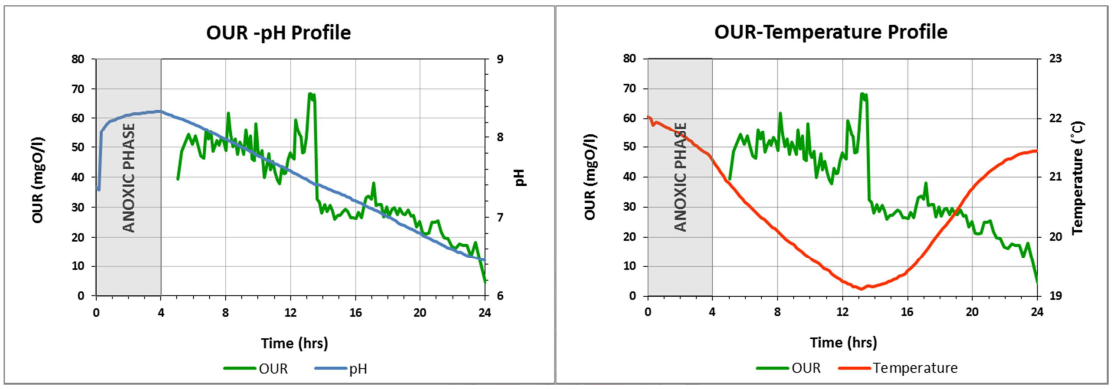

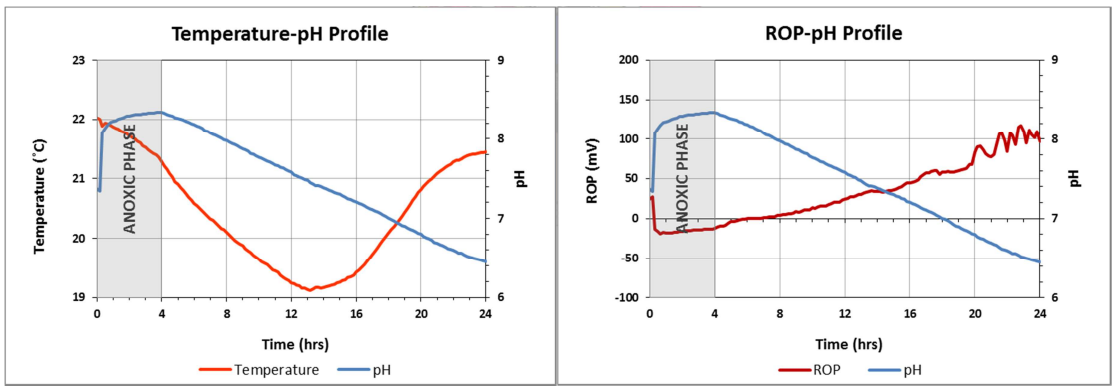

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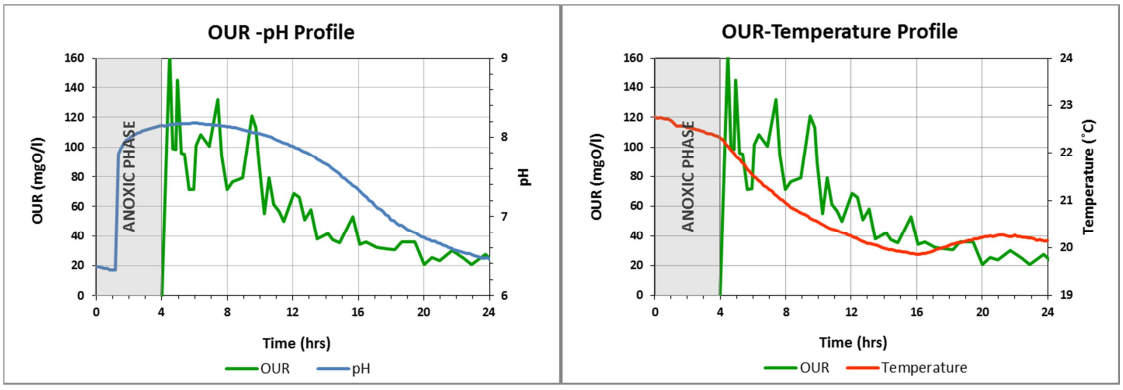

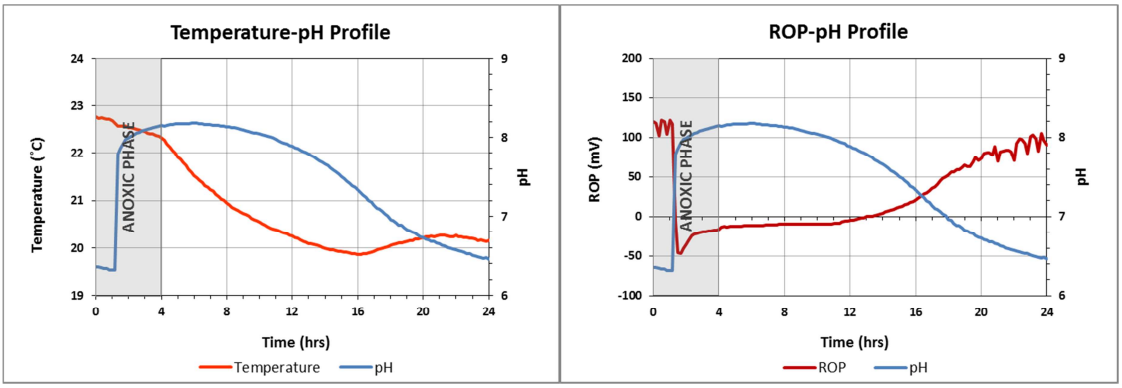

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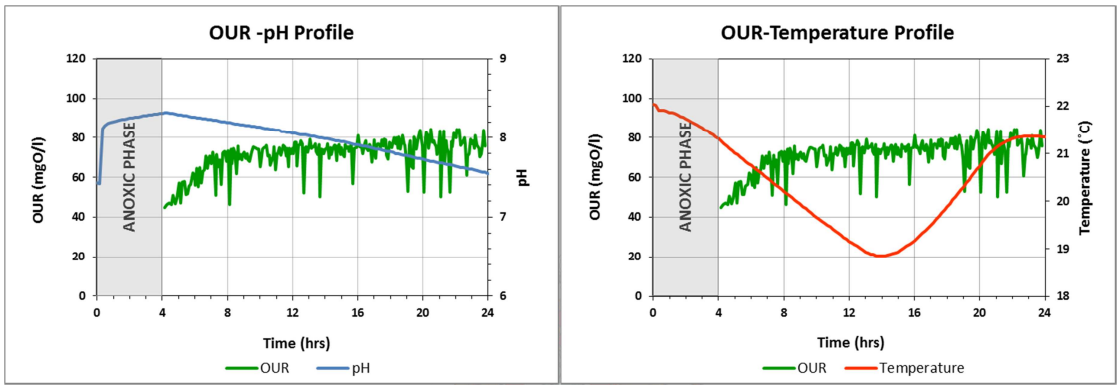

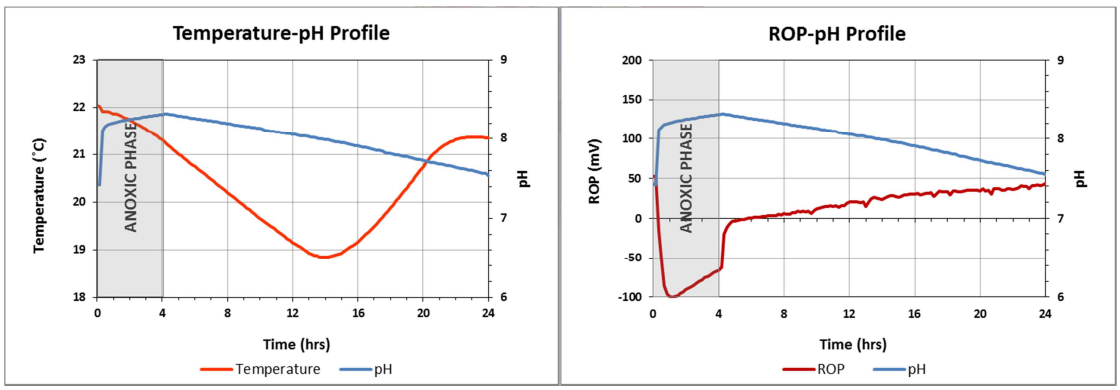

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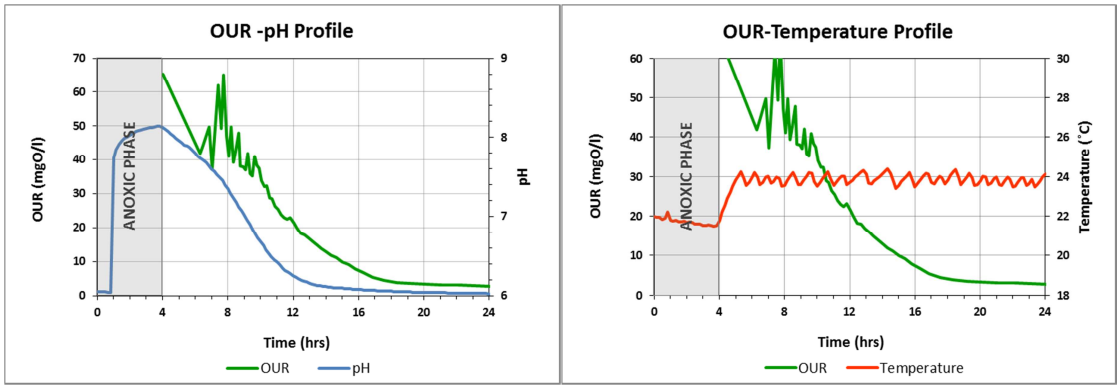

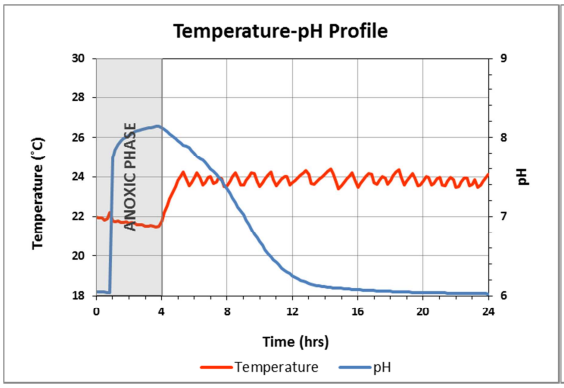

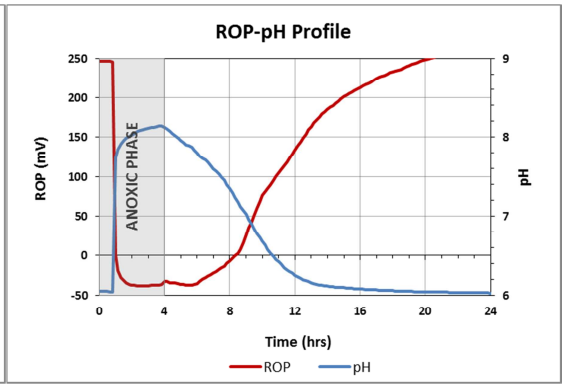

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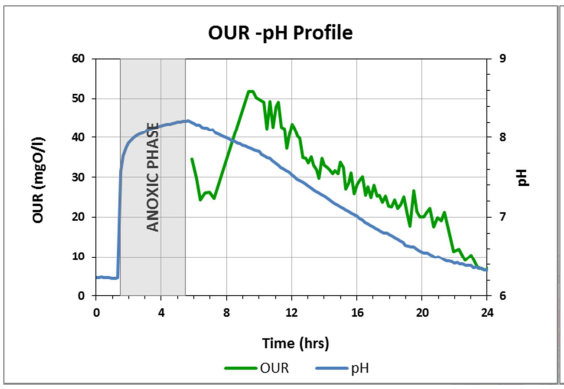

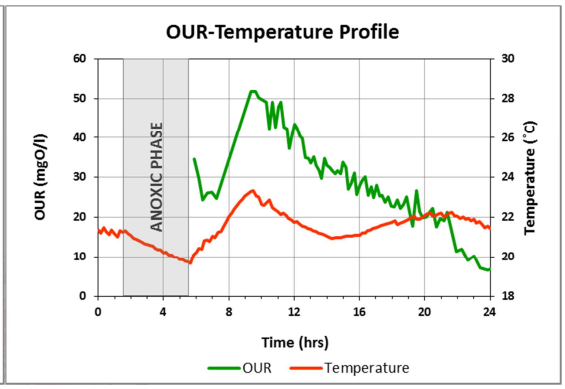

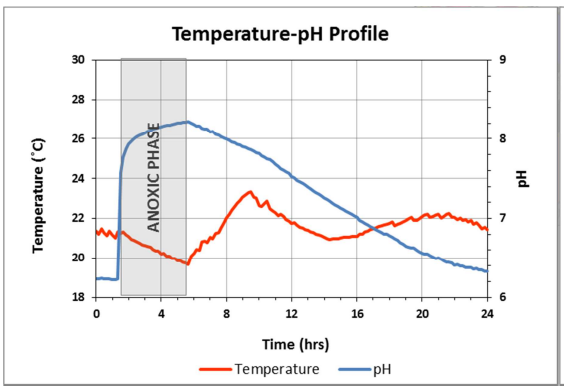

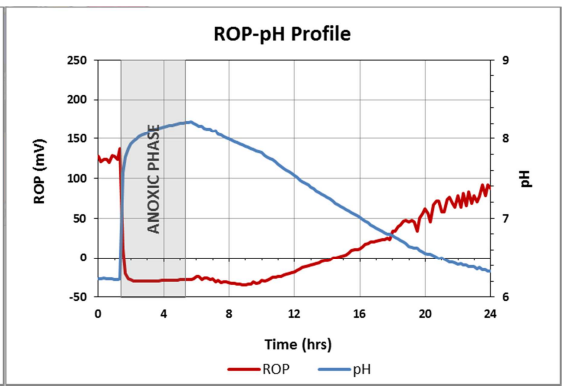

APPENDIX B

Chemical Analyses Data for 24Hour Sample Sets

1/12/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)
	1	0.75	Aerobic	6.83	150	26.5	2436	96	2420	2632	3914	#
Exchange volume effluent	2	1.75	Aerobic	6.76	156	27	2380	112	2580	2618	1030	#
1.0 l feed	3	2.25	Anoxic	8.08	-52	27	2814	184	2420	2758	3090	#
	4	3	Anoxic	8.13	-110	28	2807	152	2452	2744	3914	#
End anoxic phase	5	4	Anoxic	8.21	-120	28.5	2835	96	2420	2926	4738	1129.4
	6	7	Aerobic	8.23	-6	29.5	2807	64	2452	2842	3914	#
	7	10	Aerobic	8.16	26	29.5	2786	96	2420	2618	0	#
	8	13	Aerobic	8.02	52	28	2667	0	2428	2534	7828	#
	9	16	Aerobic	7.67	76	27	2576	48	2644	2716	3502	#
	10	19	Aerobic	7.28	116	27	2828	88	2516	2758	2472	#
	11	22	Aerobic	6.93	144	26.8	2814	168	2612	2618	4944	#
End of cycle	12	25	Aerobic	6.75	160	28	2730	248	2708	2716	824	0

1/25/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)
	1	0	Aerobic	7.12	128	26	2128	234	2310	2478	7000	#
Exchange volume effluent	2	3	Aerobic	6.91	140	25.5	2310	694	2422	2646	11400	#
	3	3.5	Anoxic	7.95	-6	25.5	2310	396	2324	2478	7000	#
	4	4	Anoxic	8.08	-74	25.5	2366	220	2324	2604	5800	#
	5	5	Anoxic	8.15	-104	25.5	2450	400	2408	2884	5800	1512.4
End anoxic phase	6	6	Anoxic	8.19	-124	25	2450	400	2408	2884	5800	#
	7	9	Aerobic	8.38	2	25	2464	384	2380	2744	11000	#
	8	12	Aerobic	8.34	28	25.5	2996	294	2338	2646	5000	#
	9	15	Aerobic	8.27	40	26.5	2450	558	2338	2856	11000	#
	10	18	Aerobic	8.13	50	26	2380	308	2324	2730	10200	#
	11	21	Aerobic	7.93	62	27	2520	682	2478	2856	13000	#
	12	30	Aerobic	7.2	114	25	2450	284	2436	2646	8200	313.1
End of cycle	13	33	Aerobic	7.04	128	25	2450	644	2604	2870	7000	#
Urine	#	#	#	9	#	#	5390	0	0	5950	7000	#

2/2/2010												
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)
Exchange volume effluent	1	0	Aerobic	7.04	150	24.5	2506	356.4	2701.6	2590	7000	#
	2	0.5	Anoxic	8.1	-50	24.5	2646	456	2602	2786	8600	#
	3	1	Anoxic	8.15	-80	24.5	2674	78.4	2535.6	2800	6600	#
	4	2	Anoxic	8.25	-110	25	2730	487.8	2718.2	2926	6200	#
End anoxic phase	5	3	Anoxic	8.28	-134	25	2450	437	2436	2912	6200	1454.6
	6	8	Aerobic	8.52	42	22.5	2744	111.6	2502.4	2814	6600	#
	7	12	Aerobic	8.44	59	22	2716	52.8	2635.2	2814	8200	#
	8	16	Aerobic	8.28	70	22	2730	187.6	3166.4	3010	10200	#
	9	20	Aerobic	7.99	86	24	2590	304.2	2568.8	2870	12200	#
	10	24	Aerobic	7.58	112	24.5	#	31	2768	2660	8600	#
	11	25	Aerobic	7.42	126	24	2632	134.4	2701.6	2828	9800	#
	12	28	Aerobic	7.27	136	23	2548	134.4	2701.6	2786	12200	#
End of cycle	13	30	Aerobic	7.18	142	22	2590	190.4	2867.6	2660	3400	363.3
	Urine	#	#	9.1	#	#	5572	0	0	5768	11000	0

2/9/2010												
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**
0	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)
Exchange volume effluent	1	0	Aerobic	7.04	146	25	2310	-74	2680.4	2548	6024	#
	2	0.5	Anoxic	7.96	-80	25.5	2520	-92.6	2517	2730	5622.4	#
	3	1	Anoxic	8.02	-114	26	2842	-146.2	2534.2	2702	5622.4	#
	4	2	Anoxic	8.1	-144	27	2737	21.6	2603	2772	5220.8	#
End anoxic phase	5	3	Anoxic	8.12	-150	27.5	2744	-105.2	2456.8	2688	2811.2	1467.3
	6	6	Aerobic	8.29	20	28	2576	-93.2	2663.2	2912	6024	#
	7	9	Aerobic	8.26	54	28.5	2744	-126.6	2714.8	2856	6024	#
	8	12	Aerobic	8.15	66	29	2730	-122.6	2783.6	2814	401.6	#
	9	15	Aerobic	8.01	80	28.5	2744	-86.4	3093.2	2772	4819.2	#
	10	18	Aerobic	7.78	96	27.5	2674	327.2	3007.2	2772	4016	#
	11	21	Aerobic	7.54	114	27	2646	24	2800.8	2800	2008	#
	12	24	Aerobic	7.33	130	26	2730	-140.8	2783.6	2730	401.6	#
	13	27	Aerobic	7.14	138	26	2688	108.8	3007.2	2618	6024	#
End of cycle	14	29	Aerobic	7.03	146	27	2520	-191	3015.8	2590	4417.6	326.5
	Urine	#	#	9	#	#	5516	0	0	5922	4016	#

2/23/2010												
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)
Exchange volume effluent	1	0	Aerobic	6.86	160	25.5	2660	438	2267.2	2730	4919.04	#
	2	0.25	Anoxic	8.07	-4	25.5	2758	342	2181.2	2842	3306.24	#
	3	1	Anoxic	8.16	-88	26	2828	372.4	2078	2856	3729.6	#
End anoxic phase	4	2	Anoxic	8.23	-124	26.2	2730	381.04	2007.48	2856	4455.36	1391.6
	5	6	Aerobic	8.41	56	25.5	2716	301.6	2112.4	2968	5342.4	#
	6	10	Aerobic	8.05	62	25	2688	286.4	2164	2898	5745.6	#
	7	14	Aerobic	7.95	74	25.5	2744	252	2198.4	2590	6148.8	#
	8	18	Aerobic	7.63	92	26	2730	250	2164	2576	5947.2	#
	9	22	Aerobic	7.08	126	25.5	2660	324.8	2198.4	2590	6148.8	#
End of cycle	10	26	Aerobic	6.76	144	25.5	2520	598.8	2215.6	2660	6552	245.5
	Urine	#	#	8.9	#	#	6090	0	0	6790	6955.2	#

3/10/2010																	
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**	**TSS**	**ISS**	**VSS**	**COD**	**TKN**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.32	160	28.5	2177	512.112	2367.888	2310	10684.8	#	3294	1842	1452	er	308
	2	0.25	Anoxic	8.18	-4	28.5	2639	506.576	2333.424	2821	7660.8	#	-	-	-	-	-
	3	2	Anoxic	8.32	-88	29.5	2618	164.432	2195.568	2716	9878.4	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.39	-124	29.5	2583	227.824	2092.176	2744	10281.6	1368.3	-	-	-	-	-
	5	10	Anoxic	8.35	56	28.5	2499	262.288	2057.712	2513	5644.8	#	-	-	-	-	-
	6	14	Aerobic	7.6	62	27.5	2352	455.504	2264.496	2429	7056	#	-	-	-	-	-
End of cycle	7	22	Aerobic	6.5	74	26	2121	203.184	2436.816	2191	10684.8	105.9	3118	1528	1590	er	224
	Urine	#	#	8.9	#	#	6188	0	0	6888	8265.6	12024.7	-	-	-	-	-

3/17/2010																	
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**	**TSS**	**ISS**	**VSS**	**COD**	**TKN**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.85	150	24.8	2142	784.4	2098.4	2065	7286.4	#	826	244	582	607.2	336
	2	0.25	Anoxic	8.42	-219	24	2016	644.4	2418.4	2408	7286.4	#	-	-	-	-	-
	3	2	Anoxic	8.41	-237	25.35	1890	210.4	1682.4	2254	6274.4	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.46	-242	26.2	1988	210.4	1682.4	2170	6679.2	1349.2	-	-	-	-	-
	5	10	Anoxic	8.45	10	26.8	2156	332.4	1650.4	2436	6072	#	-	-	-	-	-
	6	16	Aerobic	8.42	32	25.3	1988	274.4	1618.4	2009	7084	#	-	-	-	-	-
	7	22	Aerobic	8.28	45	24.32	1848	320.4	1842.4	2142	4452.8	#	-	-	-	-	-
	8	28	Aerobic	7.97	58	24.8	1834	397.4	1810.4	2051	4655.2	#	-	-	-	-	-
	9	34	Aerobic	7.11	100	27.5	1890	443.4	2034.4	2058	4857.6	#	-	-	-	-	-
End of cycle	10	38	Aerobic	6.67	149	27.2	1820	282.4	1970.4	2072	4452.8	211.1	1776	522	1254	3036	98
	Urine	#	#	8.49	#	#	5348	0	0	5628	5869.6	10108	-	-	-	-	-

3/24/2010																	
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**	**TSS**	**ISS**	**VSS**	**COD**	**TKN**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.94	100	28.66	1771	-122.8	1488.8	1960	3521.76	#	1398	523	875	242.88	252
	2	0.5	Anoxic	7.91	-177	28.5	1953	-100.6	1596.8	2079	3116.96	#	-	-	-	-	-
	3	2	Anoxic	8.1	-200	28.5	1953	-195.8	1344.8	2002	2955.04	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.19	-202	28.4	1995	4.2	1578.8	2338	2914.56	1245.4	-	-	-	-	-
	5	10	Aerobic	8.02	14	27	1799	-218	1236.8	1904	2833.6	#	-	-	-	-	-
	6	14	Aerobic	7.81	28	26.27	1722	-101.6	1380.8	1960	2955.04	#	-	-	-	-	-
	7	19	Aerobic	7.39	47	26.9	1680	-158.8	1524.8	1869	2914.56	#	-	-	-	-	-
End of cycle	8	24	Aerobic	6.83	81	27.33	1617	-137.6	1416.8	1827	2793.12	673.4	1298	532	766	1133.44	420
	Urine	#	#	8.9	#	#	5264	0	0	5663	3926.56	11450	-	-	-	-	-

4/6/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity	TSS	ISS	VSS	COD	TKN
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.67	94	23.5	1708	-109.4	1470.8	1974	3427.2	#	1639	446	1193	766.08	49
	2	0.5	Anoxic	8	-148	23.46	1764	-11.4	1372.8	2023	3709.44	#	-	-	-	-	-
	3	2	Anoxic	8.21	-149	23.56	1792	-149.8	1372.8	2009	3628.8	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.28	-158	23.71	1799	-135.8	1358.8	1939	3870.72	1154.3	-	-	-	-	-
	5	10	Aerobic	8.15	26	21.85	1799	-129.2	1386.8	1820	3265.92	#	-	-	-	-	-
	6	16	Aerobic	7.46	51	23.22	1827	-158	1484.8	1841	3346.56	#	-	-	-	-	-
End of cycle	7	24	Aerobic	6.61	85	24.49	1729	-96.2	1526.8	1813	3830.4	894	1866	645	1221	766.08	84
	Urine	#	#	9.0	#	#	5474	0	0	5852	5523.84	12888	-	-	-	-	-

4/13/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity	TSS	ISS	VSS	COD	TKN
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mgN/l)	(mgN/l)	(mgN/l)	(mgN/l)	(mgO/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.45	102	22	1694	119	1717	1806	2863	#	1230	286	944	1491.84	273
	2	1	Anoxic	8.35	-32	21	2072	44	1682	2107	2943	#	-	-	-	-	-
	3	2	Anoxic	8.57	-40	22	2051	75	1542	2170	3064	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.60	-39	22	2121	0	1472	1988	3105	1343	-	-	-	-	-
	5	10	Anoxic	8.32	-39	21	1764	119	1717	1988	3266	#	-	-	-	-	-
	6	16	Aerobic	8.04	-16	21	1764	119	1717	1904	2742	#	-	-	-	-	-
End of cycle	7	24	Aerobic	7.60	5	3	1813	84	1752	1841	2379	750	1096	223	873	1935.36	217
	Urine	#	#	8.9	#	#	4480	-464	0	5768	5080	8851	-	-	-	-	-

4/21/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity	TSS	ISS	VSS	COD	TKN
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.45	102	21.45	1708	324.5	1526	1729	2560	#	1807	747	1060	1080	252
	2	0.5	Anoxic	8.35	-32	21.06	1925	212.5	1382	1946	2480	#	-	-	-	-	-
	3	2	Anoxic	8.57	-40	21.7	1953	120.5	1346	1967	3000	#	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.6	-39	21.88	1932	228.5	1238	2023	2360	1882.3	-	-	-	-	-
	5	10	Anoxic	8.32	-39	20.87	1883	212.5	1382	1841	1720	#	-	-	-	-	-
	6	16	Aerobic	8.04	-16	21.25	1778	304.5	1418	1792	2080	#	-	-	-	-	-
End of cycle	7	24	Aerobic	6.7	5	21.85	1806	416.5	1562	1813	2120	732.3	2036	873	1163	800	147
	Urine	#	#	9.1	#	#	5635	-158	158	5852	6960	14296.7	-	-	-	-	-

5/5/2010

Stage Description	Sample no	Time step	Phase	pH	ROP	T	FSA	Nitrate	Nitrite	TKN	COD	Alkalinity	TSS	ISS	VSS	COD	TKN
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.31	122	19.95	1778	555	1802	1848	3560	#	1588	643	945	320	252
	2	0.25	Anoxic	7.78	-11	19.75	1960	924.5	2297	2170	2560	#	-	-	-	-	-
End anoxic phase	3	4	Anoxic	8.57	-13	19.71	1918	415.5	1571	2198	3600	#	-	-	-	-	-
	4	8	Aerobic	8.31	-14	19.66	1988	358	1505	2170	3080	961.3	-	-	-	-	-
	5	14	Aerobic	8.08	-2	19.85	1960	769	1835	1974	3120	#	-	-	-	-	-
	6	20	Aerobic	7.38	25	19.85	1932	826.5	1901	1960	3680	#	-	-	-	-	-
End of cycle	7	24	Aerobic	6.87	32	19.78	1750	473	1637	1932	3240	357.9	1108	434	674	1360	168
	Urine	#	#	9	#	#	5530	0	0	5670	7520	12501	-	-	-	-	-

5/20/2010																	
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**	**TSS**	**ISS**	**VSS**	**COD**	**TKN**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Anoxic starts at hr 00	1	0	Aerobic	7.54	40	21.34	1694	108	1520.5	1750	2480	857.9	1365	931	434	720	140
	2	0.5	Anoxic	8.27	-40	21.13	1848	147.75	1382.5	2002	3000	1438.4	-	-	-	-	-
	3	2	Anoxic	8.35	-109	21.21	1890	118.5	1313.5	2030	3080	1294.7	-	-	-	-	-
End anoxic phase	4	4	Anoxic	8.42	-79	20.96	1974	0	1348	2030	3080	1338.6	-	-	-	-	-
	5	14	Aerobic	8.17	9	19	1890	147.75	1382.5	1918	3000	905.4	-	-	-	-	-
	6	18	Aerobic	8.05	23	20.05	1806	78.75	1451.5	1932	2480	976.7	-	-	-	-	-
End of cycle	7	24	Aerobic	7.69	44	20.95	1750	177	1451.5	1820	2160	858.6	1701	1201	500	1320	126
	Urine	#	#	9	#	#	4382	0	0	4648	6720	13747.1	-	-	-	-	-

6/21/2010																	
Stage Description	**Sample no**	**Time step**	**Phase**	**pH**	**ROP**	**T**	**FSA**	**Nitrate**	**Nitrite**	**TKN**	**COD**	**Alkalinity**	**TSS**	**ISS**	**VSS**	**COD**	**TKN**
	(-)	(hrs)	(-)	(-)	(mV)	(°C)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(as CaCO3)	(mg/l)	(mg/l)	(mg/l)	(mgO/l)	(mgN/l)
Exchange volume effluent	1	0	Aerobic	6.03	265	23.91	1715	0	2217.5	1743	3440	384.3	1589	410	1179	1880	119
	2	0.5	Anoxic	7.73	31	23	1771	1357	4212.5	1946	4520	1028	-	-	-	-	-
	3	2	Anoxic	8.12	-39	21.69	1925	539.5	3243.5	1960	5000	1359.6	-	-	-	-	-
Anoxic ends at hr 4.00	4	4	Anoxic	8.2	-35	21.14	1834	62	2331.5	1960	4640	1033.7	-	-	-	-	-
	5	14	Aerobic	6.34	107	21.71	1876	1328.5	4241	1820	2920	864.4	-	-	-	-	-
	6	18	Aerobic	6.11	199	21.94	1792	636.75	3642.5	1778	3560	511.1	-	-	-	-	-
End of cycle	7	24	Aerobic	6.07	243	21.62	1750	76.75	2217.5	1813	3920	451.6	1642	201	1441	960	21
	Urine	#	#	9.1	#	#	5628	0	0	5782	7280	13897	-	-	-	-	-